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PROCESSES OF HYDROGEN PRODUCTION: MAIN REACTIONS AND THEIR PROBLEMS

It is essential, especially for the long term, to have inexhaustible energy sources that create minimal damage to the natural environment. Many of the renewable sources are linked directly or indirectly to the Sun. Instead, H_2 is a very important element; with regard to renewable energies it is an energy carrier that can in the future replace fossil fuels. For this reason, in this study the role of the H_2 and the main technologies of its production, as an important step towards the future energy choices, are discussed.

Energy quality in different area

Quality is the contrast between different forms of energy, the different tropic levels in ecological systems and the propensity of energy to convert from one form to another.

The concept refers to our empirical experience of the characteristics of different energy forms as they flow and transform. It appeals to our common perception of the heat value, versatility, and environmental performance of different energy forms and the way in which a small increment in energy flow can sometimes produce a large transformation effect on both energy physical state and energy. For example the transition from a solid state to liquid may only involve a very small addition of energy. Methods of evaluating energy quality are concerned to

develop a system of ranking energy qualities in hierarchic way.

Since ancient times there has been deep philosophical, aesthetic and scientific interest in contrast of quality with quantity. In some respects the history of modern and postmodern thought can be characterized by the phenomenological approach to these two concepts. A central question has been whether the many different qualitative aspects of the world can be understood in terms of rational quantities, or whether the qualitative and quantitative are irreconcilable: that is, there is no "rational quality". Many scientists and analytic philosophers say they are not, and therefore consider some qualitative phenomena like, for instance, spirituality, and astrology to be unquantifiable, unanalysable by scientific methods, and therefore ungrounded in physical reality.

The notion of energy quality therefore has a tendency to be linked with phenomena that many scientists consider unquantifiable, or at least incommunicable, and are subsequently dismissed out of hand.

The ranking and scientific analysis of energy quality was first proposed in 1851 by William Thomson under the concept of “availability”. This concept was continued in Germany under the title “die Exergie” (the exergy) and standardised in Japan. Exergy analysis now forms a common part of many industrial and ecological energy analyses. In an ecological context exergy is used as a goal function in ecological models, and expresses energy “with a built-in measure of quality like energy” (S.E. Jorgensen, G. Bendoricchio, 2001, p. 392).

Energy quality evaluation methods

It appears to be two main kinds of methodology used for the calculation of energy quality. These can be classified as either receiver or donor methods. One of the main differences that distinguishes these classes is the assumption of whether energy quality can be upgraded in an energy transformation process.

Receiver methods: view energy quality as a measure and indicator of the relative ease with which energy converts from one form to another. That is, how much energy is received from a transformation or transfer process. For example, two types of indicators of energetic quality are: the hydrogen/carbon (H/C) ratio, and its inverse, the carbon intensity of energy. The latter is an indicator of relative environmental quality. However in multistage industrial conversion systems, such as a hydrogen production system using solar energy, the energy quality is not upgraded.

Donor methods: view energy quality as a measure of the amount of energy used in an energy transformation, and that goes into sustaining a product or service. That is how much energy is donated to an energy transformation process. These methods are used in ecological physical chemistry, and ecosystem evaluation. From this view, the energy quality is upgraded in the multistage tropic conversions of ecological systems. Donor methods attempt to understand the usefulness of an energetic process by quantifying the extent to which higher quality energy controls lower quality energy.

Energy quality in physical -chemical science (direct energy transformations)

Constant energy form but variable energy flow

The concept of energy quality may be more intuitive if one considers examples where the form of energy remains constant but the amount of energy flowing, or transferred is varied. For instance if we consider only the inertial form of energy, then the energy quality of a moving body is higher when it moves with a greater velocity. If we consider only the heat form of energy, then a higher temperature has higher quality. And if we consider only the light form of energy then light with higher frequency has greater quality. All these differences in energy quality are therefore easily measured with the appropriate scientific instrument.

Variable energy form, but constant energy flow

The situation becomes more complex when the form of energy does not remain constant. In this context it is possible to formulate the question of energy quality in terms of conversion of one form of energy into another, that is transformation of energy. Here, energy quality is defined by the relative ease with which the energy transforms. If energy A is relatively easier to convert to energy B but energy B is relatively harder to convert to energy A, then the quality of energy A is defined as being higher than that of B. The ranking of energy quality is also defined in a similar way.

Energy quality in ecological physical chemistry (direct and indirect energy transformations)

Ecological physical chemistry is concerned with energy conversions where energy forms and flows are not held constant, and how for example the form changes toward successive indirect transformation steps in an ecological food chain. However in developing an accounting system for these energy conversions, theorists found that they needed a reference point where the energy form and the average flow is held constant.

Constant energy form and constant energy flow

In order to try and make things more easily understood a method is used that is the inverse of approach mentioned above.

That is, the energy quality is determined with reference to a base constant energy form and flow. This base is then contrasted against varying energy forms and flows. This method was employed in the discipline known as systems ecology, where the base reference with an averaged constant flow is the solar energy form.

This was referred to as the “solar energy transformation ratio”. With the subsequent development of the energy nomenclature the phrase, “solar energy transformation ratio” was shortened to the term “solar transformity”, where “transformity” simply means, “energy transformation ratio”.



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Variable energy form, and variable energy flow

Energy quality is related to the understanding that different energy forms have different amounts of energy available and can vary and amplify the flows of other energy forms in ways that encourage the further transformation of lower quality energy forms.

From this view, the actual flow of calories or joules can decrease as energy is used and dispersed throughout the world. The result of such energy transformation processes can be products, informations, services or commodities that are understood to be of higher 'quality' than the original energy forms. Although the base reference energy form flow is held constant all others are allowed to vary.

Energy quality in this sense means that, "the flows become either very concentrated in information content, either capable of controlling, amplifying and causing work that would not be otherwise possible". The generic term "energy transformation ratio", or "transformity" refers to the energy quality "factor". This ratio compares two energy forms that are varied during the flow of a transformation process.

Energy quality in biophysical economics (indirect energy transformations)

The notion of energy quality was also recognised in the economic sciences. In the context of biophysical economics energy quality was measured by the amount of economic output generated per unit of energy input (C.J. Cleveland, 2000, p. 1). The estimation of energy quality in an economic context is also associated with embodied energy methodologies. Another example of the economic relevance of the energy quality concept is given by "Energy Profit Ratio" (EPR), measure of energy quality and a pivotal index for assessing the economic performance of fuels. Both the direct and indirect energy inputs embodied in goods and services must be included in the denominator of the fraction expressing energy quality in economic sciences.

Lowest quality

Energy is a quantifiable state function of every physical system. Energy allows one to predict how much work a physical system could make, or how much heat it can exchange. In general, energy is inferred whenever there is a change in the properties of an object or system. This is where the early exploration of the nature of energy began. As our understanding of the nature of energy progressed, scientists found it to exist in many forms not readily observable by the average unaided observer. In fact, in some cases the presence of particular types of energy prevents changes from being easily observed in a particular object or system. Empirical observations have shown that the total quantity of energy is conserved. This makes the concept of energy very important in physics.

Energy is identified into different categories and concerns:

- [A] Alternative energy
- [B] Energy conversion
- [C] Energy development
- [D] Electric power
- [E] Electricity
- [F] Energy by country
- [H] Energy economics
- [G] Energy policy
- [I] Energy portal
- [M] Free energy
- [N] Fuels
- [K] Heat
- [L] Home appliances
- [O] Low-carbon economy
- [P] Nuclear fusion.

It is essential, in particular in the long term, to have access to inexhaustible energy sources that produce minimal damage to the natural

environment - renewable energy sources. In order to negate effects on the environment, it is necessary to learn to use sustainable energy in satisfactory mode. The simplest way to use the Sun is to capture its heat using a sheet of glass that lets light pass through it but retains the heat. It is not so easy to use the Sun for heating in winter as it is an abundant source in the summer months but not in winter, when it is necessary to store the summer heat and use it in winter. This is possible but expensive. The availability of energy is an essential component of development. The ways in which energy is produced and used in the world has both positive and negative effects on the environment (human activities, atmospheric pollution, acid rain), greenhouse gas and CO₂ emissions have increased, and all these factors consequently have an effect also on climate stability. Much needs to be done to save energy. The services provided by energy, such as heating, illumination, transport and telecommunications, may be obtained at the same time consuming much less.

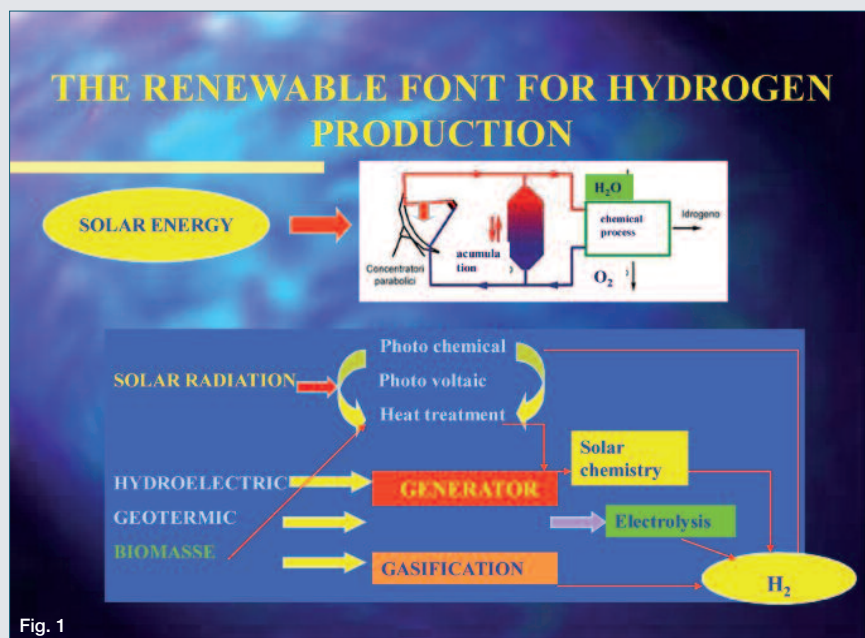


Fig. 1

In such a situation it is advisable to favor transition towards an energy system with a low environmental impact, that is more sustainable and cleaner than the existing one - a solution that could be based on hydrogen. Hydrogen does not produce CO_2 or other pollutants when used. It can be produced in such a way that this gas is not released at all, or so as to ensure CO_2 is easily "sequestered". It can make an important contribution to strategies aimed at stabilizing greenhouse gas concentration in the atmosphere. It can be obtained from several different sources, in particular, from renewable sources, using different processes (biomass gasification or pyrolysis); thermal dissociation of water using solar energy; electrolysis of water using hydroelectric, photovoltaic or wind energy; by biological or photoelectrochemical processes.

Hydrogen from renewable sources

Production of H_2 from renewable sources includes 6 important ways different from each other (Fig. 1).

Carbon sources containing (hydrogen from biomass)

The photosynthesis of plant material is a renewable source of substances used to provide energy. The only amount of such material that is discarded annually worldwide has been estimated at 150 Gtons and is therefore of clear interest in a recovery of energy contained.

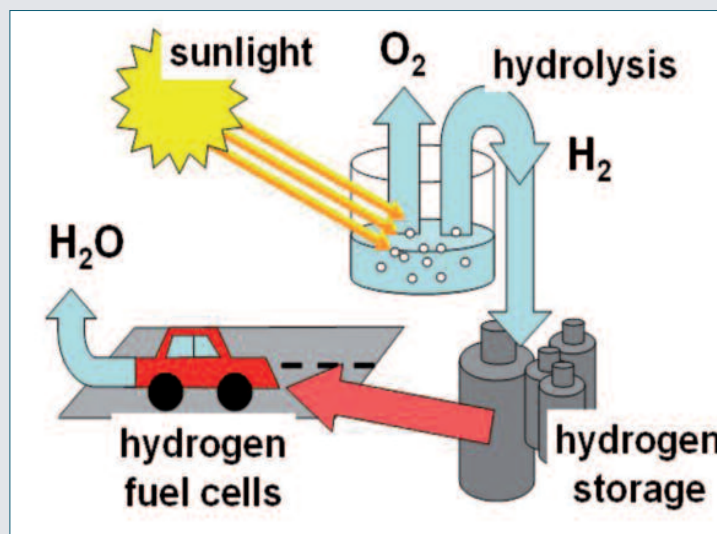
The methods proposed (and largely used) to recover energy from biomass are numerous, ranging from simple direct combustion to anaerobic digestion with biogas production, the production of alcohol by fermentation, with the production of thermo-chemical pyrolysis of hydrocarbon mixtures. With some of these methods mixtures of gases such as hydrogen-rich are obtained and different methods to increase and recover this amount have been proposed. Our use of biomass as fuel to generate electricity is, and it will still be relatively long, the type of use more convenient

Direct thermal decomposition

It was noted that at sufficiently high temperatures the water decomposition reaction are spontaneous. Thermodynamic calculations that take into account the dependence of enthalpy and entropy on T show that only 2000 K above the steam is sufficiently dissociated with the formation of quantity "interesting" of hydrogen.

The problem therefore presents significant technological difficulties. It must be able to concentrate solar energy (or heat from other sources) at temperatures above 2000 K, to build a reactor capable of working at these temperatures, to separate the hydrogen produced by steam and other unreacted species (not just oxygen). Dissociation reaction produced in the potential of these types of processes, however, has encouraged research and many proposals have been put forward for each of the points presented above.

To reach a temperature of 2500 K at which the vapor is dissociated by 25% requires a concentration of solar radiation in the order of 10000. The reactor must withstand the temperatures reached and



should not react with the products of decomposition, so the choice is restricted to zirconia (2715 °C), MgO (2800 °C), thorium oxide (3050 °C), materials having sufficient thermal and mechanical stability and good thermal shock resistance. The most complex aspect is, however, the separation of the hydrogen produced.

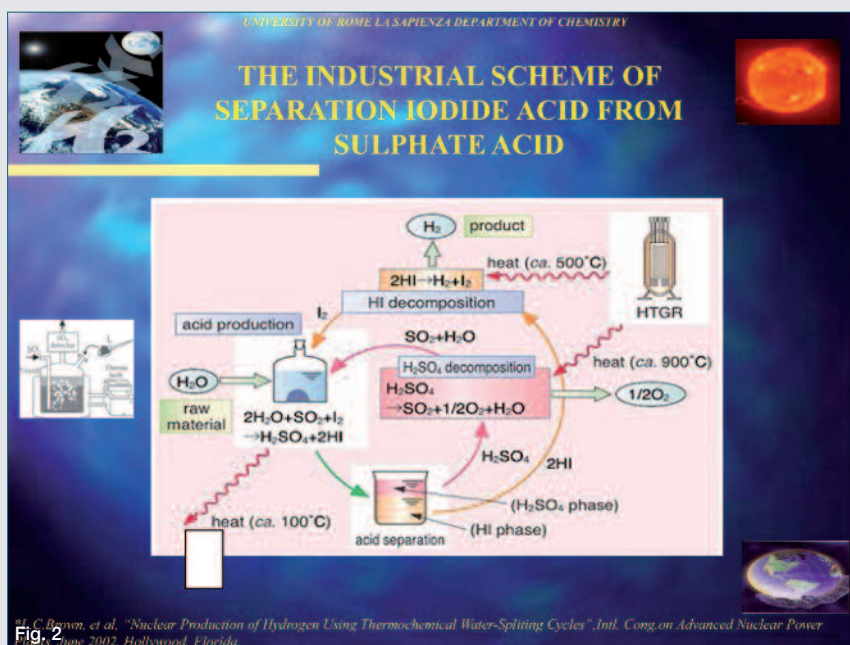
Different methods are proposed for the separation at low temperature, at which the recombination is kinetically hindered, but the waste of heat energy due to the excess steam and cooling of secondary products is energetically untenable. Today, most researcher uses porous membranes to obtain a partial separation of hydrogen by effusion in a fluidynamic system called Knudsen flow. Zirconia crucibles with a porosity of 20-30% and an average size of pores of 5 microns were studied. To obtain an efficient separation of gas, it is necessary to operate in a particular hydrodynamic system (Knudsen flow), which, under the given conditions requires that the pressure in the reactor does not exceed 50 mbar.

Thermochemical process

The technological difficulties of the thermal decomposition of water conducted (especially in the Seventies and Eighties years) researches for an alternative process which, while always starting from water and heat, allows to obtain hydrogen in a technically more accessible way. In the Seventies thermal energy was assumed to be nuclear energy and this explains why these researches have been developed particularly in Euratom (Ispra), but of course the results can be used with thermal energy from any source. The objective of this research is to find a cycle:

- $\text{H}_2\text{O} + \text{X} = \text{H}_2 + \text{XO}$
- $\text{XO} = \text{X} + 0.5\text{O}_2$
- $\text{H}_2\text{O} = \text{H}_2 + 0.5\text{O}_2$

the sum of which shall take place in accessible technology way. Thermodynamic studies have failed to find X, but they allowed us to

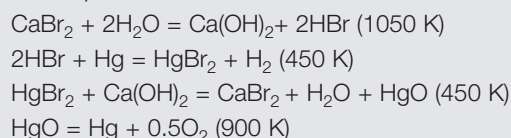


hypothesize a number of more complex cycles (3-5 reactions) that can obtain the required result, i.e. the decomposition of water into hydrogen and oxygen (produced separately). These cycles were evaluated with a set of parameters:

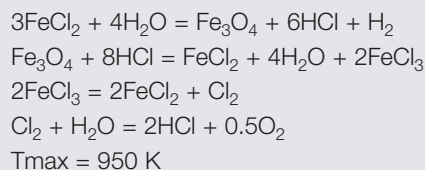
- a) thermal efficiency and heat transfer,
- b) conversion of chemical reactions,
- c) side reactions,
- d) toxicity of the products involved,
- e) availability and cost of these products,
- f) materials and their corrosion problems,
- g) maximum temperature process.

The thermodynamic and kinetic data of literature have been well integrated with experimental evaluations and a number of cycles has been demonstrated as feasible in a pilot plant scale:

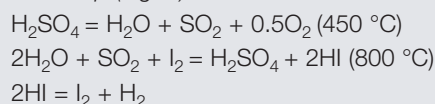
first step



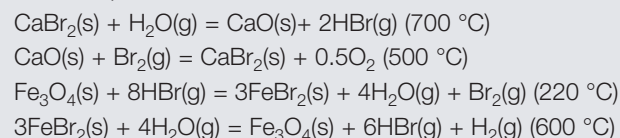
second step



third step (Fig. 2)




fourth step

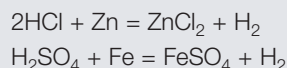


This cycle is studied at the University of Tokyo and in 1984 at the Fifth International Conference a demonstration tank that produced 3 (three!) liters/hour of hydrogen was presented by Atomic Japan Agency (JARY). The decline of the nuclear hypothesis has slowed; however, these studies seem to show signs of revival in the event of direct use of solar energy.

Photorelectrolysis



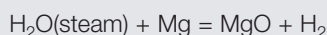
a) The active metals like potassium, sodium and calcium react readily with water at room temperature, forming hydrogen gas and the corresponding hydroxides. Some metals, such as gold and platinum, not only do not react with water but are very inactive with many other substances. In the form of nuggets, in which they may be found, or in jewellery, they remain untarnished even after years of exposure. All metals can be arranged in an order of decreasing activity. In Tab. 1 there is a portion of such a list and includes several common metals. This table is sufficient for understanding the involved principles. Potassium, the most active metal, is at the top; gold, the least active metal, is at the bottom. The activity of the metals reflects their tendency to lose electrons, thereby becoming positively charged. Potassium metal readily loses electrons, whereas gold holds electrons tenaciously. Any metal is able to displace from solution the ions of any metal below it in the series. Since zinc is above copper, we know that if zinc metal is placed in a solution of copper ions, the copper will be displaced as metal. The metals above hydrogen in the series can be used to displace hydrogen from an acid. Again this process results from a transfer of electrons. The metals give off electrons to become an ion, while the H^+ accepts an electron to become a neutral H atom, a usual. $2H$ atoms pair to become an H_2 molecule:



The most active metals readily liberate hydrogen from cold water. The less active metals, magnesium through iron, when heated will react with steam forming oxides and liberating hydrogen. The reaction of magnesium with steam is violent:

Tab. 1 - Activity series of metals

K, Ca, Na	React readily with cold water $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + 1/2\text{H}_2$
Mg, Al, Zn, Cr, Fe, Cd, Co, Ni	Heated metals react with steam $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2$ $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
Sn, Pb	React very slowly with acids
Cu, Hg, Ag, Pt, Au	Will not liberate hydrogen from acids



For this reason water cannot be successfully used in controlling aircraft fires where magnesium alloys are present. The oxides of the less active metals, those below chromium, can be reduced by hydrogen. An understanding of basic chemistry should not require memorization of the exact order of metals in the activity series, but the table should be studied carefully so that the relative activity of the more familiar metals can be recalled.

b) The accidental observation of oxygen evolution from powders of TiO_2 in 1972 brought Fujishima and Honda to build the first electrochemical device. Irradiated TiO_2 acts as an anode (a photon of energy equal to or greater than the energy gap of the semiconductor creates a hole in the valence band, which recombines with an electron provided by the species present in solution). A standard cathode platinum closes the circuit (H_2) since the energy gap of TiO_2 is 3.1 eV, the energy is more than enough to be the decomposition of water with good speed. Solar radiation in only a few photons has energy equal to or greater than this value and that is why the total efficiency is very low. More extensive research has been developed in the following directions:

- i) study of the influence of surface structure on the photoelectrochemical reactions;
- ii) using photocathodes (p-type semiconductor on which the incident photons let free electrons in the valence band, allowing the development of hydrogen) and photoanode TiO_2 (n-type semiconductor with energy gap lower). In some cases it is necessary to use an inert and transparent protective layer to prevent the decomposition once in contact with the solution, while using the same device for a photoanode and a photocathode.

The deposition of small isles on photoelectrode metal with catalytic activity (electrocatalysis), a device that has shown some very interesting possibilities for development was proposed in 1987 by Kainthla and Khan. A p-InP photocathode made by electrocatalytic platinum is coupled to a n-GaAs photoanode electrochemical oxidation protected with a film of MnO_2 in a concentrated KOH solution.

Subsequent improvements allowed to arrive on a laboratory scale to a conversion of 16% of incident solar energy.

Research on photoelectrolysis also develops two additional lines: improving the efficiency of TiO_2 , the cost is very attractive relative to other semiconductors, and the use of reduction of devices in which a photocathode hydrogen is produced by reduction coupled to the oxidation of some waste, that is competitive with respect to the decomposition of water (egg H_2S , alcohol).

The biological methods

The biological hydrogen production processes have been classified as follows:

1. Biophotolysis water using algae and cyanobacteria,
2. Photolysis of organic compounds by photosynthetic bacteria,
3. Hydrogen production by fermentation of organic compounds,

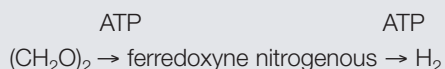
4. Hybrid systems using photosynthetic bacteria and promoters of fermentation.

1. *Biophotolysis water using algae and cyanobacteria* - The method uses the same processes used for the photosynthesis of vegetable matter, but adapts them to the production of hydrogen. In photosynthesis, light absorption is due to two different photosynthetic processes operating in series, one leads to the decomposition of water with evolution of oxygen, the other one reduces CO_2 .

To replace this second process with the formation of hydrogen hydrogenase enzyme must be present in eukaryotic microalgae (green algae) and prokaryotes (cyanobacteria or blue-green algae). One of the biggest obstacles to the photoproduction of hydrogen is the deactivation of the system that produces hydrogen from the oxygen photogeneration. Cyanobacteria, however, are also able to fix nitrogen via the nitrogenous enzyme.

2. *Photolysis of organic compounds by photosynthetic bacteria* - The phototropic bacteria are considered in the literature the most promising microbial system for the biological production of hydrogen as:

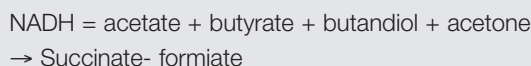
- a) have high yields of conversion (theoretical),
- b) do not produce oxygen and therefore have no problems from oxygen to the other systems,
- c) can use a broad spectrum of light,
- d) can use organic matter from waste (including waste water). A general scheme for these processes can be represented as follows:



3. *Hydrogen production by fermentation of organic compounds* - Hydrogen production by fermentation has many advantages from the point of view of possible industrial production, in fact: the bacteria that cause fermentation have high speed development of hydrogen evolution; the production of hydrogen from organic substrates is continuous (day and night); the growth rate can be obtained by providing by suitable microorganisms to the production system.

The production can be enhanced by the effective coupling of the following factors:

- a. an efficient source of electrons
- b. an active hydrogenase



NADH is produced by glycolysis of glucose to pyruvate, in the presence of succinate and CO_2 from formate consuming NADH is consumed but a budget for the remaining NADH can be the above reactions. It follows from all this the need to remove the CO_2 from the liquid culture.

Scheme 1 - Scheme of hybrid systems

a) Glucose \rightarrow Formiate \rightarrow H ₂ + CO ₂ ADP (Fd-ox)
b) Glucose \rightarrow Acetate (+H ₂) \rightarrow H ₂ + CO ₂ $\uparrow \downarrow$ hv ATP (Fd-red)
c) Glucose \rightarrow Succinate (+H ₂) \rightarrow H ₂ + CO ₂ hydrogenate nitrogenous

through the formation of organic acids, which turn the product of departure for the photosynthetic bacteria in the production of hydrogen. Anaerobic bacteria are not able to break down the sugars decomposing them to hydrogen and CO₂, but they decompose the carbohydrates with the formation of organic acids, that are unable to give hydrogen. With the combination of the two types of bacteria not only the demand for light energy is reduced, but also the production of hydrogen is increased (Scheme 1).

H₂ production from fossil fuels

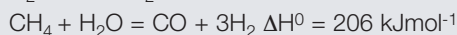
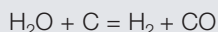
The methods for producing hydrogen from fossil fuels can be so classified as follows:

1. steam reforming;
2. partial oxidation;
3. coal gasification.

Reforming natural gas

The process can be divided into four steps and commercial preparation depends of the a and b reactions. The "water gas method" utilizes steam which is passed over white-hot carbon:

a. Reaction of steam reforming (SR)



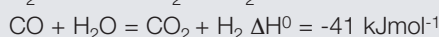
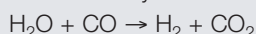
The experimental conditions used in the SR reaction are: temperature between 850 and 900 °C, bar pressure between 15 and 20, ratio steam/C between 3 and 3.5, Ni-based catalyst supported on α -alumina. The reactor is made up of tubes filled with catalyst in a combustion chamber where fuel is injected (often natural gas) that provides the heat necessary in order that the reaction occurs.

The carbon dioxide can easily be removed leaving pure hydrogen.

b. Water shift reaction (WS)

Carbon monoxide and hydrogen both burn readily in air so this method has been used extensively for the manufacture of a gaseous fuel. Carbon monoxide and water are heated to 500 °C in the presence of a catalyst hydrogen and carbon dioxide:

catalyst



4. Hybrid systems using photosynthetic bacteria and promoters of the fermentation - Hybrid systems consist of nonphotosynthetic bacteria and photosynthetic bacteria. For example, *Clostridium* is used to produce hydrogen

The complete reaction is: $2\text{H}_2\text{O} + \text{C} \rightarrow \text{CO}_2 + 2\text{H}_2$

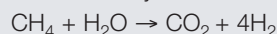
The WS reaction occurs in two steps with a gradual decrease in temperature: first step between 500 and 300 °C on catalysts consisting of mixed oxides of Fe, Cr and Mg; second step around 200 °C on catalysts based on oxides of Cu and Zn. On leaving the second step gases contain about 20% of CO₂ and 0.2-0.3% CO, at a temperature close to 300 °C and a pressure between 10 and 20 bar.

c. Removal of carbon dioxide (chemical or physical absorption); the final purification.

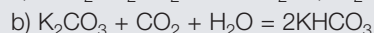
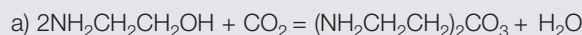
The greatest amount of hydrogen obtained by heating cracking hydrocarbons



catalyst



The methods used consist in absorption with solutions of weak bases (ethanolamine, and carbonates):



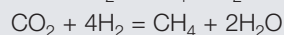
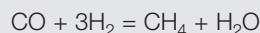
both reactions are exothermic and occur in packed columns (the filler material must be sized according to the temperature of the column). The absorption solution bottom must be periodically regenerated. The regeneration takes place in a desorption column after depressurization. Carbon dioxide is recovered and sent to use (for example, urea production) or is eliminated. At the same time other impurities (methane, carbon monoxide) need to be removed and molecular sieves diffusion through membranes is very useful to this aim:

a. The molecular sieves are compounds, which form porosity resort for cavity size comparable to that of controlled substances to be retained, while hydrogen flows freely.

b. Hydrogen has a diffusion coefficient through polymeric and metallic membranes, six times greater than that of impurities, in particular with membranes constituted by Pd-Ag alloys a hydrogen content of impurities less than 0.5 ppm can be obtained.

d. Final purification

The final purification is performed by a wash with cryogenic liquid nitrogen or by the reaction of methanation, the former when hydrogen is used for the synthesis of ammonia, in other cases using the methanation reaction:



They are exothermic and occur at relatively low temperatures (about 300 °C) in the presence of nickel-based catalysts. The method has the

disadvantage of consuming hydrogen and produce methane, which in turn can cause problems when present in hydrogen matrix.

Partial oxidation

In this process steam and power along with an oxygen defect are introduced into a combustion chamber in which occur:

1. Oxidation (exothermic)
2. Cracking reactions (endothermic)
3. The reaction of water gas (endothermic) $C + H_2O = CO + H_2$ occurs in addition to the already considered SR (endothermic) and WAS (exothermic).

The interest of the method is that liquid hydrocarbons can be used. Eventual sulfur impurities complicate the first two reactions producing H_2S .

Below is an example of operating conditions and results:

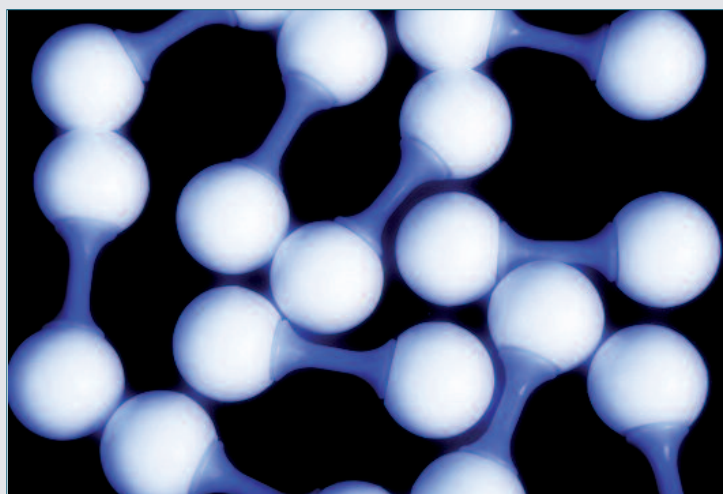
- a. Heavy fuel oil supply (2% sulfur),
- b. Report vapor/C 0.5; oxygen $0.26 \text{ m}^3 \text{ per m}^3 \text{ of gas}$,
- c. Injection temperature/oil mixture 350°C steam,
- d. Oxygen injection temperature 150°C ,
- e. Pressure 35 bar.

In the reactor the temperature rises up to $1300\text{--}1400^\circ\text{C}$ and this explains why catalysts are not necessary. The composition of the gas produced is: a) 46% H_2 ; b) CO 47%; c) 5% CO_2 ; d) H_2 1%; e) 0.3% CH_4 .

Coal gasification

Coal gasification is the oldest method of producing hydrogen from fossil fuels using coal, leading to a high temperature coal bed through controlled combustion (reaction gas air).

A subsequent steam injection allows the aforementioned reaction water gas, which leads to a roughly equimolar mixture of CO and H_2 . Given the greater availability of coal compared to oil and gas using coal to produce hydrogen can be especially attractive in those countries (China) where it is very available. The methods used today are in fact partial oxidation of carbonaceous material with new devices, fluidized bed and the treatment of polluting gases.



Hydrogen from fossil fuels to power fuel cells

The methods described above have been studied for plants that produce large quantities of chemicals (for example, even more than 1,000 tons per day of ammonia) and ill-adapted to the production of hydrogen fuel cells used for the food drive or for the combined domestic or condominium (powers between 5 and 200 kW).

There are many studies for the development of systems capable of reforming operations on board vehicles (on-board reforming) or even in small or medium stationary applications (on reforming house).

On board reforming

The topic is of great interest to car manufacturers and oil companies because they plan to use fuels such as methanol or even gasoline that can be distributed using the existing network (overcoming the problems associated with distribution and transport of hydrogen).

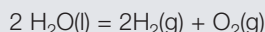
Environmentalists, however, oppose this option, because it is considered an obstacle to the emergence of a true hydrogen economy, including the claim that such a solution would drastically reduce, in addition to pollution, emissions of CO_2 is not accepted by all experts sector. In such research companies like Nuvera, Johnson Matthey, McDermott, and, in the field of cars, General Motors, Ford, Toyota are engaged.

On house reforming

For stationary installations, the matter is relatively simple because it is often possible to exploit the distribution of natural gas, the reformer, the problem remaining the a scaling-up in the opposite direction to the U.S. Traditional. The UTC Fuel Cells has installed more than 200 plants known as PC 25 PAFC Constituted by using natural gas as a fuel base, similar plants are built in Italy by Ansaldo (Museum of Science and Technology in Milan). Nuvera Fuel Cells produces a system with 5 kW PEFC also powered by natural gas.

Electrolytic production of hydrogen

The reaction of water electrolysis (WE)



at a temperature of 298 K and a pressure of a bar has the following thermodynamic data:

$$\Delta G^\circ = 474 \text{ kJmol}^{-1}$$

$$\Delta H^\circ = 571 \text{ kJmol}^{-1}$$

$$\Delta S^\circ = 325 \text{ Jmol}^{-1}\text{K}^{-1}$$

The reaction is not so spontaneous in these conditions of temperature and pressure, but because it is endothermic and occurs with an increase of entropy it can be spontaneous at temperatures high enough (see below). The WE can be performed at temperatures



close to ambient. The electrochemical reactor (electrolyzer) consists of: a) electrode (cathode) at which H_2 is formed; b) electrode (anode) at which O_2 is formed. Between these two electrodes is an electrolyte interposed containing an inert solution which must ensure the electrical transport in ionic form and ensure the correct electrode reactions take place. In most cases the contact and to prevent the recombination of the gases the two electrodes is necessary to divide the solution into two compartments separated by a suitable device (diaphragm or membrane).

1. *Surge of electrode.* The electrode reactions do not occur in the simple form with which we have summarized the thermodynamic point of view, but through a series of stages involving the absorption of the reagent on the electrode, the breakdown and subsequent formation of chemical bonds, the evolution of gas formed, determining the speed of the process, the nature of the electrode material (electro catalysis) and of the electrolyte used.

2. *Fall ohmic* depends on the composition of the solution. Normally choose or KOH to the maximum concentration or sulfuric acid at 30% are used and working at the highest temperature compatible with these solutions. The presence of a diaphragm and/or a membrane doubles ohmic loss, while irrelevant is the contribution of the conductors of the first kind.

3. *Electrolyzers of industrial interest.* The first electrolysis was carried out by Nicholson and Carlisle in 1800 using a device similar to the Volta cell, whose invention is of the same years. However, it was only at the beginning of last century, with the availability of electrical power generators of great power that the electrolysis of water became the method of producing the hydrogen needed for the synthesis of ammonia (Novara, Fauser) and other industrial processes. The first electrolyzers operated with carbon steel cathodes, anodes of Ni and an asbestos diaphragm separating two compartments of solution consisting of KOH concentration between 20 and 25% by weight. Tensions were higher than 2 V for a current density around

2,500 A/m², with an energy consumption of 5104 kWh per t (4 kWh per m³) of hydrogen. The spread of the reforming of hydrocarbons has not made competitive electrolytic production of large quantities of hydrogen. Yet this method has continued throughout the last century used for the production of small quantities of hydrogen. It is required especially when high purity is needed or in particular situations in terms of strategic (India) or economic (Aswan, Norway, Canada) reasons. In the context of Hydrogen Economy (HE) the electrolysis of water is returned to be the most interesting for the production of large amounts of hydrogen and a lot of research and development effort is devoted to the improvement of alkaline electrolyzers and to develop other types of electrolyzer, even using the studies related to fuel-cells.

Advanced alkaline electrolyzers

In recent years the return of these electrolyzers has been improved by working in three directions: new electrode materials for reducing the anodic and cathodic overvoltages, using conventional electrodes covered with thin layers containing rare earth oxides of Co and Ni-Raney. The nickel oxide-diagrams based non-conductive on both sides of the electrodes which are pressed (zero-gap cell). The total ohmic resistance is further reduced by working at temperatures up to 160 °C, enabling to increase the concentration of KOH, but requires working pressures of the order of 10-20 atmosphere; so reaching well above 80% energy efficiency.

Polymer electrolyte electrolyzers

This is a type of electrolyser developed in the late seventies of last century, using as electrolyte a polymer membrane constructed from a skeleton. Made of wool perfluoroethylene and conductor of the second kind through the insertion of $-SO_3H$ groups that dissociate in presence of water, liberating H^+ ions that can move through the membrane and reach the cathode where they form hydrogen: The "solution" is therefore highly acidic and requires completely different electrode materials by alkaline electrolyzers. It takes impregnated felts carbonaceous material on which are deposited in small amounts, micro-particles of platinum (or mixtures of Pt group elements).

They produce good yields even at low temperatures, but the reduced cost structure of the electrolyzer is in contrast to the high cost of membranes and electrodes.

Electrolysis produces steam at high temperature

Another type of electrolyzator considered for the electrolysis of H_2O is a fully solid-state that works at temperatures above 1000 °C, so using steam. In this case, the solution is a solid oxide composed of ZrO_2 and Y_2O_3 , which has a grid with positions of O_2 -ion, not occupied. This oxide leads to high temperatures because of the movement of these vacancies; O_2 -ions are oxidized on an anode oxide, while the cathode is generally Ni or alloy. Under these conditions, the

reversible potential is around 0.8 V and also surges are relatively low allowing to work in the cell voltages of the order of 1.2 V, however, must provide heat both to start the cell and to maintain the temperature. This type of electrolyser is commercially available (e.g. Siemens).

We conclude about electrolysis of water, that if today the cost of electrolytic hydrogen production is still higher than that from fossil fuels, this situation can turn into a relatively short time.

Of the three types of electrolyser that we have illustrated, the alkaline electrolyser is the most advanced large-scale production (a problem the corrosive power of the solution).

The polymer membrane electrolyzer is preferable to charge less corrosive and more flexible response (problem investment costs), the electrolyser solid state then it is very interesting from the point of view of energy efficiency when you have high thermal energy, but obvious attention must be paid to the choice of the materials.

Conclusions

A hydrogen-based energy system can guarantee to the same benefits as those offered today by fossil fuels, although in full respect of the most stringent environmental constraints.

The development of hydrogen as an energy vector presupposes the existence of a wide range of integrated technologies. It also demands the gradual creation of the conditions required to overcome the barriers related to safety problems and acceptability (familiarity with the technologies, standards, regulations, etc.).

Moreover, a hydrogen based system is likely to be more expensive. Although widely used in industry, particularly in chemical and oil refining processes, its large-scale use as an energy vector would require substantial enhancements regarding yields and costs of existing technologies, as well as the development of completely new tech-

nologies to ensure its economical and reliable use in the various phases of the technological chain (production, transport, accumulation, final use). Since it consists of a clean vector but not of an energy source, the greatest obstacle standing in the way of its large-scale use is the availability, which is not guaranteed at the moment, of an inexhaustible, low-cost energy source from which to produce hydrogen in the long period in a sustainable way.

For this reason, many research initiatives are aimed at developing production systems mainly or exclusively using non polluting and acceptably cheap renewable energy sources (for instance, hydrogen from biomasses, or hydrogen obtained using solar energy or other renewable sources). With current production, storage, transport and utilization technologies it will take a few decades before hydrogen can be used as an energy vector. It will be introduced gradually and technologies and application sectors are currently being identified which offer the most interesting opportunities for pilot ventures and its initial introduction into the market.

However, margins of sustainability exist if the 'externalities' are quantified and included, that is, the costs due to damage to health and to the environment. All the primary sources of renewable energy permit to obtain hydrogen, following similar or alternative routes; in general the convenience is greater where the route has less passages.

The H₂ production from biomass can be a way to run as.

The energy consumption of the process in general is much less compared to other methods. The reality has shown (many scientific papers confirm this: a complex system for the biological physical and chemical correlations, but even if the 'best from the technological point of view; "regularity" and "interference", time and speed of reaction as well as other important parameters that play a fundamental role for the process are depending on not completely known mechanisms.

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