Water Electrolysis for Hydrogen Production in Brazilian Perspective

Adonis Marcelo SALIBA-SILVA[1], Fátima M. S. CARVALHO[1], Vanderlei Sérgio BERGAMASCHI[1], Marcelo LINARDI[1]

[1] CCCH – IPEN/CNEN – Fuel Cell and Hydrogen Center of Nuclear and Energy Research Institute Av. Prof. Lineu Prestes, 2242 – CEP 05508-000 São Paulo (SP) Brasil – email: saliba@ipen.br

Abstract **– Hydrogen is a promising energy carrier, which potentially could replace the fossil fuels used in the transportation and distributed energy sector of Brazilian economy. Fossil fuels are polluting by carbogenic emissions from their combustion, being so co-responsible for present global warming. However, no large scale, cost-effective, environmentally non-carbogenic hydrogen production process is currently available for commercialization. There are feasible possibilities to use electrolysis as one of the main sources of hydrogen, especially thinking on combination with renewable sources of energy, mainly eolic and solar. In this work some perspectives for Brazilian energy context is presented, where electrolysis combined with renewable power source and fuel cell power generation would be a good basis to improve the distributed energy supply for remote areas, where the electricity grid is not present or is deficient.**

Index Terms – hydrogen, fuel cells, alkaline electrolysis, PEM electrolysis, hydrogen economy, distributed energy

I. INTRODUCTION

Nowadays, the primary sources of Brazilian energy are mainly fossil carbon and hydrocarbon, hydroelectricity, biomass, nuclear power and, less importantly, some other (biomassa tbem é) renewable forms, such as solar and eolic. The energy is normally transported as electricity or by means of chemical substances, normally hydrocarbon or carbon. The total domestic energy supply in Brazil reached 218.6 Mtoe in 2005. From this total, 97.7 Mtoe (44.7%) are related to renewable energy supply. This share is among the highest in the world, which significantly contrasts with the global average of 13.3%, and with the 6% average observed in OECD countries (1). However, the usage of fossil energy is economically convenient, but the environment has suffered since Brazil is still contributing to discharge great quantity of CO_2, causing the greenhouse effect with consequences to the global warming. So, the *Hydrogen Economy* (2; 3; 4; 5) is envisaged to be established for next decades in order to slow down the carbogenic impacts.

To set up this economy, hydrogen should be produced massively. The use of this gas has a series of advantages: it can be produced from and converted into electricity with high efficiency; the most available raw material for hydrogen production is water, in this case, hydrogen is a completely renewable fuel, since the product of hydrogen utilization (either through combustion or through electrochemical conversion) is pure water or water vapor; hydrogen can be stored as liquid, gas, or solid (metal hydrides); it can be transported over large distances using pipelines, tankers, or rail trucks; the H_2 gas can be converted into other forms of energy in more ways and more efficiently than any other fuel, either by flame combustion or by fuel cell; this gas produces small amounts of NO_x even if it is burned with air at high temperatures (6). Nevertheless, many efforts should be made to produce hydrogen in a non-carbogenic route. In this way, by principle, as no fossil hydrocarbon should be used, then the only possibility is to split water in its gas constituents, H_2 and O_2, by means of electricity. There are various possibilities to do so, from bacterial route to thermal splitting, but one of the technologies, already fully implanted, for almost a century, is the production of H_2 by electrolysis. Electrolysis could be made either by the traditional alkaline electrolysis or by Protonic Exchange Membrane Electrolysis Cell (PEM EC). The PEM electrolysis unit is the newest of the electrolysis technologies.

This paper presents the possibilities to use electrolysis as one of the main sources of hydrogen, especially thinking on combination with renewable sources of energy, mainly eolic and solar (6; 7). For Brazilian situation, electrolysis combined with renewable power source and fuel cell power generation would be a good basis to improve the distributed energy supply for remote areas, where the electricity network is not present or is deficient.

II. HYDROGEN PRODUCTION

As analyzed by Newborough (8), electrolyzers, which are the most viable technological process to produce non-carbogenic hydrogen, compete in a ground where H_2 is usually produced by large process plant, based on low-cost reforms of hydrocarbons to hydrogen (e.g. by steam reformation of methane).

The electrolyzer role in the future markets for this gas, relative to the conventional production methods, is a strong function of electrolyzer and electricity cost. The carbon emissions implications of the produced gases are particularly important to the future scenario of electrolyzer technology, because electrolyzers may use renewable and 'low-carbon' electricity for generating hydrogen to be used in fuel cells, hydrogen engines, combustors and other industrial applications. When

Financial support should be acknowledged to IPEN/CNEN-SP for supplying the necessary conditions to carry out this work and analysis.

compared with usual methods of generating hydrogen, the low carbon implications of using electrolytic hydrogen will be very advantageous. However, relative to prices practiced today, large decreases in unit costs will be important if electrolyzer technology aims at this potential massive generation. Crabtree et al (4) presents a good diagnostics, in figure 1, of hydrogen production and its future necessities in a scenario for 2030, supposing that the world will be making it path towards the *Hydrogen Economy*.

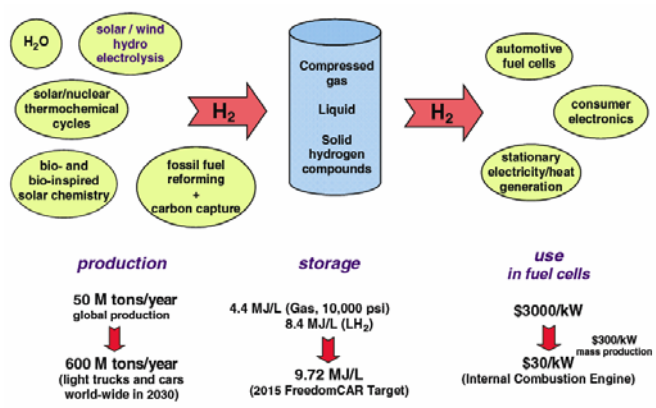

Figure 1: World needs for Hydrogen Production. In the picture it is presented three links of the hydrogen energy chain: production, storage, and use in fuel cells. Each link must connect seamlessly with the others to create an effective infrastructure, and each link has fundamental challenges that must be solved, as indicated. (4)

As electrolysis nowadays is responsible for just 4% of this 50 millon tons/year , it is evident, the great request to increase the presence of the set "Solar/Wind/Hydroelectricity Electrolysis" to assist the improvement of non-carbogenic aims.

III. Electrolysis Possibilities

Electrolysis generally consumes considerably more energy per unit of hydrogen produced than does making hydrogen from hydrocarbons. However, electrolysis is a potential source of hydrogen energy for several (5):

1. Water (and the hydrogen it contains) is more abundant than hydrocarbons are. Depletion and geopolitical concerns for water are in general far less serious than are those for hydrocarbons. Further, there are geographical regions in the nation and around the world where hydrocarbons (especially natural gas, the predominant source of hydrogen reformation) are simply not available; hydrogen from water may be the only practical means of providing hydrogen in such settings.
2. The net energy costs of making hydrogen through electrolysis must be viewed in a comprehensive economic context. Electrolysis can be a means of converting low-cost energy (e.g., coal) into much-higher-value heat if the result is to replace gasoline or other transport fuels, considering sequestration of carbonaceous subproducts.
3. Electrolysis is seen as a potentially cost-effective means of producing hydrogen on a distributed scale and at appropriate costs to meet the challenges of supplying the hydrogen needs of the early generations of fuel cell vehicles. Electrolyzers are compact and can realistically be situated at existing fueling stations.
4. Electrolysis presents a path to hydrogen production from renewably generated electrical power. From an energy perspective, electrolysis is literally a way to transform electricity into fuel. Electrolysis is thus the means of linking renewably generated power to transport fuels markets. Currently, renewable solar, wind, and hydro power, by themselves, produce only electricity.
5. Electrolyzers operating in tandem with power-generating devices (including fuel cells) present a new architecture for markets related to distributed energy storage. Various electrolyzer makers are developing products that can make hydrogen when primary electricity is available, and then store and use that hydrogen for subsequent regeneration into electricity as needed. This same concept is being applied directly to renewable sources, creating the means to produce power-on-demand from inherently intermittent renewables.

IV. Technology of Electrolysis

The chemistry to produce hydrogen by electrolysis is very simple and known technologically since the beginning of last century. Hydrogen is produced via electrolysis by passing electricity through two electrodes in water. The water molecule is split and produces oxygen at the anode and hydrogen at the cathode.
Ivy (9) summarizes the electrolyzer types into three possibilities of industrial electrolysis units, which have been produced today. Two of them involve an aqueous solution of potassium hydroxide (KOH), which is used because of its high conductivity and are referred to as alkaline electrolyzers. These units can be either unipolar or bipolar. The unipolar electrolyzer resembles a tank and has electrodes connected in parallel. A membrane is placed between the cathode and anode, which separate the hydrogen and oxygen as the gasses are produced, but allows the transfer of ions. The bipolar design resembles a filter press. Electrolysis cells are connected in series, and hydrogen is produced on one side of the cell, oxygen on the other. Again, a membrane separates the electrodes.

The third type of electrolysis unit is a Solid Polymer Electrolyte (SPE) electrolyzer. These systems are also referred to as PEM or Proton Exchange Membrane electrolyzers. In this unit the electrolyte is a solid ion conducting membrane as opposed to the aqueous solution in the alkaline electrolyzers. The membrane allows the H^+ ion to transfer from the anode side of the membrane to the cathode side, where it forms hydrogen. The SPE membrane also serves to separate the hydrogen and oxygen gasses, as oxygen is produced (+ SOEC?).

Regardless of the technology, the overall electrolysis reaction is the same:

$$H_2O \rightarrow ½\, O_2 + H_2 \qquad E^o = -1{,}23V$$

However, reaction at each electrode differs between PEM and alkaline systems. In a PEM system (acid media) the reactions at the electrodes are:

PEM: H_2 production (cathode):

$$2\,H^+ + 2e^- \rightarrow H_2 \qquad E^o = -0{,}00\ V$$

PEM: O_2 production (anode):

$$H_2O \rightarrow ½\, O_2 + 2\,H^+ + 2e^- \qquad E^o = -1{,}23\ V$$

In an alkaline system, the reaction at each electrode are:

Alkaline H_2 production (cathode):

$$2\,H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^o = -0{,}83\ V$$

Alkaline O_2 production (anode):

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad E^o = -0{,}40\ V$$

V. Available electrolyzers

Table I presents the data collect in 2004 by Ivy (9) summarizes some of the main electrolyzers being produced and their energy data. From this data, it is possible to infer that Norsk Hydro is the biggest electrolyzer producing around 380,000 kg H_2/year.

TABLE I: ELECTROLYZER EQUIPMENTS AND THEIR ENERGY AND PRODUCTION DATA (9)

	Energy Required: System		Energy Required: Electrolyzer	Hydrogen Production	System Power Requirement
Manufacturer Model	kWh/Nm3	kWh/kg	kWh/Nm3	Nm3/hr	kW
Stuart: IMET 1000	4.8	53.4	4.2	60	288
Teledyne: EC-750	5.6	62.3	-	42	235.2
Proton: HOGEN 380	6.3	70.1	-	10	63
Norsk Hydro: Atmospheric Type No.5040 (5150 Amp DC)	4.8	53.5	4.3	485	2330
Avalence: Hydrofiller 175	5.4	60.5	-	4.6	25

Obs: Stuart, Teledyne and Norsk are bipolar and Avalence are alkaline electrolyzer, Proton-Hogen is PEM electrolyzer.

According to Ivy (9), if the system were to be used for fueling, it will supply approximately only 1,900 cars, requiring 2.3 MW of electricity. This electricity demand would likely prevent the purchase of cheaper industrial electricity in this scenario, thus raising the price of hydrogen. If the system were to be used in a large hydrogen generation plant, the limited hydrogen production capacity means that a significant number of electrolyzer units would be required. Considering the needs for 500,000 kg H_2/day hydrogen generation plant using nuclear power and electrolysis, it would require 500 of the largest electrolyzer units available in the market. In these circumstances, electrolyzers 10 to 100 times the size of today's units should be developed. In the same study, the energy efficiency ranges were calculated giving results in the range of 56-73% and PEM electrolyzer had the worst result (56%). Nevertheless, the PEM theoretical laboratorial tests indicate the inverse of this tendency. Doucet et al. (10), working with a 1 kW PEM electrolyzer, indicated that this level of efficiency in PEMEC, with many researching being carried out, could reach values of 75%. Sheriff et al (6) account that typical industrial electrolyzers have electricity consumption between 4.5 and 6.0 kWh/Nm^3, corresponding to the efficiency of 65–80%, and advanced electrolyzers have been reported to develop an efficiency of 90%.

VI. Linking Electrolyzer and Renewable Energy

Supposing if there is a direct coupling electrolyzer with a wind turbine or solar panel, there would be an intermittent operation, implying in highly variable power output. Sheriff et al (6) attempts to fact that with alkaline electrolyzers at very low energy loads the rate at which hydrogen and oxygen are produced, which is proportional to current density, may be lower than the rate at which these gases permeate through the electrolyte, and mix with each other. This may create hazardous conditions inside the electrolyzer. Hydrogen flammability limits in oxygen are between 4.6% and 93.9%, but the alarms and automatic shutdown of the electrolyzer are set at much safer concentrations. This is more pronounced in the alkaline than in PEM electrolyzers. Hydrogen permeation rate at 80ºC through Nafion 117, typically used in PEM electrolyzers, should be less than 1.25.10^{-4} cm^3/s/cm^2 at atmospheric pressure, corresponding to a current density of 0.002 A/cm^2 (Kocha et al., 2002 in (6)), which is rather negligible compared to 1 A/cm^2, which is a typical current density in PEM electrolyzers at full power. Oxygen permeation rate through hydrated Nafion membrane is considerably lower (Sakai et al., 1986 in (6)). Another problem related to operation with a highly variable power source is thermal management. The electrolyzer takes time to reach its normal operating temperature, but due to intermittent operation it may operate most of the time at a temperature below nominal, which results in a lower efficiency. So, necessarily, a DC/DC conditioning should be set to link solar/wind energy to the electrolyzer.

On the other hand, the efficiency of an electrolyzer is inversely proportional to the cell potential, which in turn is determined by the current density, and that in turn directly corresponds to the rate of hydrogen production per unit of electrode active area. A higher voltage would result in more hydrogen production, but at a lower efficiency.

Usually, cell voltage is selected at about 2 V, but a lower nominal voltage (as low as 1.6 V) may be selected, if the efficiency is more important than size (and capital cost) of the electrolyzer. In addition, there are power losses in voltage regulation and some power is needed for the auxiliary equipment (pumps, fans, solenoid valves, instrumentation and controls).

For all these above quoted implications, coupling of a source such as a wind turbine and solar panels with an electrolyzer may result in a somewhat lower efficiency, due to the losses related to power/voltage matching. Voltage regulation, either

AC/DC or DC/DC would consume some power. These devices may be designed to operate with efficiency as high as 93–95%, but this high efficiency may be achieved only in a very narrow power range. In a highly variable mode of operation such as with the input from the wind turbine, this efficiency may be considerably lower. Batteries buffer is thought to be used in the power conditioning.

Based on the suggested configurations of Barbir (7) and Sheriff (6), a possible integrated system arrangement functional in Brazilian context for remote areas to produce hydrogen and power is presented in figure 2.

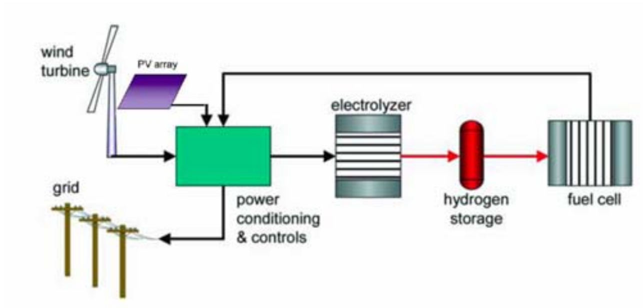

Figure 2: Schematic diagram of integrated wind/solar and hydrogen utility energy system.

Following this combination of grid and renewable energy, it is possible to keep the electrolyzer working with virtually no interruptions and, so, producing hydrogen continuously for storage and use in fuel cells.

VII. Brazilian Possibilities in Electrolysis

Considering the solar and wind energy as the renewables sources for remote areas, it is possible to have a rough idea of the available potential in Brazil.

A. Brazilian resources and distributed power

According to ANEEL information (11), Brazil reached the level of 100,000 MW of installed power in 2007, where hydroelectricity contributes with 74.7%. Nevertheless, the electricity grid covers the country unevenly; so many areas have a lack of energy, as could be seen in figure 3. It could be noticed that the remote areas without grid power concentrate in northeast and northern parts of the country, where many villages and cities in rain forest, including Manaus, uses ironically fossil energy to produce electricity. The *Agreste* region of semi-arid northeast is in the same situation. From the point of view of future *Hydrogen Economy* a renewable source of energy should be offered to those regions.

B. Solar and wind energy potential

As could be seen in figure 4, the solar irradiation map of Brazil (1; 11), it is noticeable that many regions in the country are feasible for continuous use of solar energy, which could be easily linked to a modular electrolysis system, as shown schematically in figure 2. Almost in the whole country there are spots as good candidates to be part of electrolysis module installations, based on solar energy. Nevertheless, in northeast region of Brazil, mainly inland, there are very adequate conditions to get a continuous solar capture and to use solar power supply for many hours a day more than in the southern region, since the insolation, due to the semi-arid climate and nearness to the equator, helps to enhance the solar power per square meter, as indicated in the map by less reddish colors. The less coverage of power grid in this region must be added to fact.

Figure 3 – Electrical energy grid in Brazil (11)

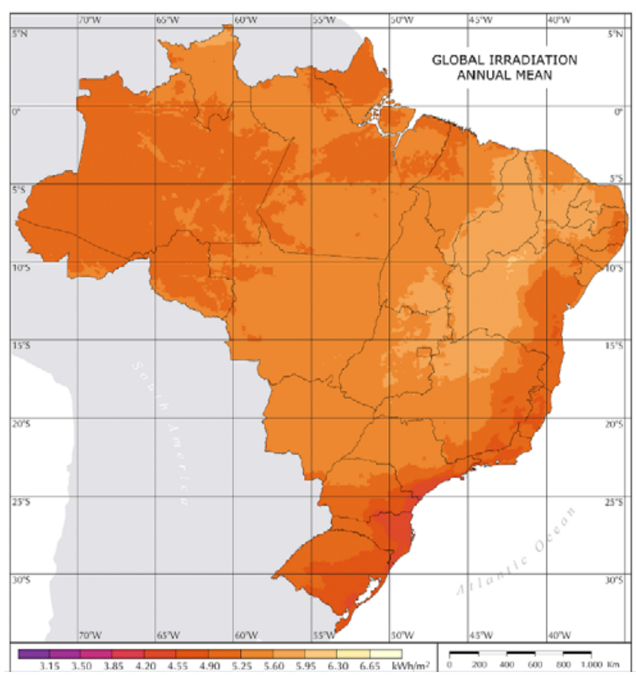

Figure 4: Brazilian map for daily irradiation – annual mean in kW/m^2 (1)

The wind energy in Brazil presents also a good possibility of producing energy in many areas, as shown in figure 5.

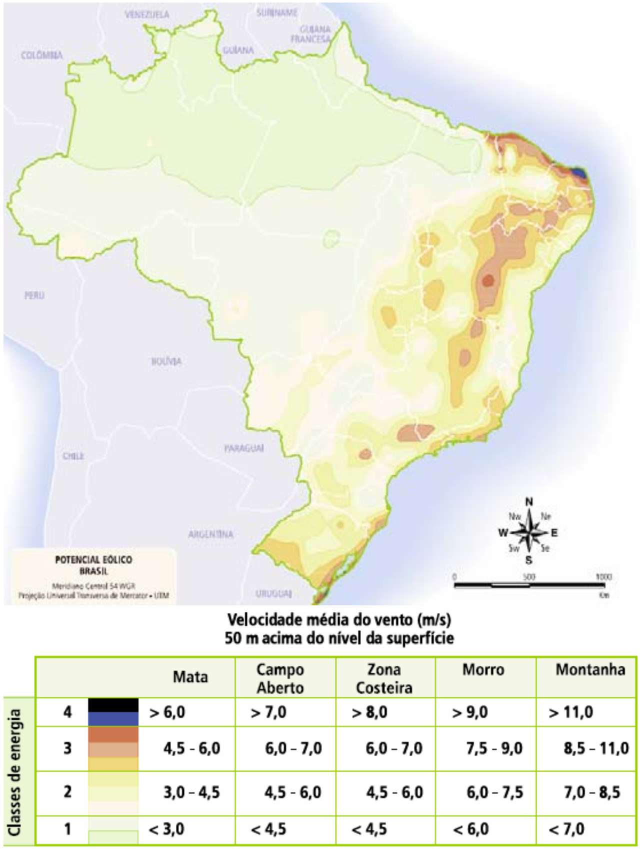

Figure 5: Eolic Potential in Brazil

Both sources, either solar or wind, depending on the area, could supply sufficient energy, for small electrolyzer modules, in a lower cost basis, depending on the evolving technology, The technology and intensive research are presently lowering the prices of small equipment and installation for small and private modules, following the steps of installation of big equipments (12), (13).

C. Electrolysis as a potential solution for remote areas

The hydrogen production by the combination of electrolysis, using either PEM electrolyzer or alkaline one, becomes feasible in remote areas not well covered by the grid. A suggested solution, mainly for remote areas of rain forest, would be the usage of solar energy to produce hydrogen by an electrolyzer inside a barge with solar panels and small wind turbines, floating in the rivers of the rain forest producing hydrogen, during the day by solar/wind and by night using only wind. The H_2 could be pressurized and stored in tanks located bellow the barges in contact with river water. The barges could also distribute the gas to the villages in the route travel. The barge being in the middle of the rivers would avoid the shade of trees crowns and also eventual animals which would tread over the solar panels, if they were on the ground. The supplied hydrogen would be employed to get power using fuel cells. In this way, this schema would be complete, extracting energy from the nature and giving the required electricity to remote areas without producing harmful impact in the nature.

In general, it can be concluded that an area of around 100 m^2 of photovoltaic panel over a barge, could supply roughly around 15.0 kg of H_2/day by electrolyzers (either by membrane or alkaline type), consuming an average of 5-6 kWh to produce 1.0 Nm^3 H_2, according to table I. The energy contained in 15.0 kg of H_2 converted by fuel cell, would give around 250 kWh/day of electric energy ready to be used by any remote village (200 houses, with average consumption of 40 kWh/day).

As normal barges may reach easier big dimensions such as having horizontal area of 4000 m^2 or more, the photovoltaic system could get 40-50 times more energy from proportionally installed solar panels. Nevertheless, this solution could be much better, depending on the new upcoming technologie, promising great increase in solar energy capture (12). Barges could be planned as *The Science Barge* developed by Groundwork Hudson Valley in New York (14) having small solar panels and eolic turbines, as suggested in the figure 6, using the system proposed in figure 2 to produce H_2.

General view of The Science Burge

Detailed view of The Science Barge, showing the solar panels and small eolic turbines.

Figure 6: The Science Barge is a project of Groundwork Hudson Valley in NY (14)

VIII. Conclusions

Renewable energy sources are available and abundant in Brazil, mainly in regions without a proper power grid. These regions still use carbogenic means to produce power. It is proposed a hydrogen energy system based on a non-stop module, using renewable energy capture (solar/wind) to produce hydrogen by an electrolyzer, either alkaline or PEM. This module could be assembled in a barge, having hydrogen tanks to store the gases. The barge would hover in rivers of remote areas and simultaneously distribute the hydrogen to small villages. Those villages could then produce cost effective and environmental friendly electrical energy by fuel cell modules and distributing locally the power.

IX. Acknowledgements

Thanks are due to Fuel Cell and Hydrogen Center of IPEN/CNEN/MCT for providing conditions to study and plan new renewable energy uses, in order to help the Brazilian society to enter in Hydrogen Economy, with more equity.

X. References

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