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AN OVERVIEW OF THE PRODUCTION OF HYDROGEN AS A FUEL IN BRAZIL

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Abstract. *The use of hydrogen as an energy carrier in Brazil is discussed. An overview is presented of how the hydrogen can be used for energy transport in the same way such as electricity and other fuels are. Hydrogen is mostly found in water, hydrocarbons, methane, alcohol and coal. The energy used to extract hydrogen from a substance is much higher than the energy contained in it. The most accepted use of hydrogen is as fuel, for fixed and mobile fuel cells.*

Nowadays there are two reasonably well established methods for hydrogen production: the Steam Methane Reforming (SMR) and electrolysis. Notice that none of these methods avoids the Carnot limit.

This work presents an analysis of the present situation of petroleum use for transportation in Brazil, and its presumed substitution by hydrogen in the Brazilian scenario. The hydrogen production using energy sources such as natural gas, ethanol and electrolysis are presented, energy balances are made and projections of actual needs are made allowing the knowledge of future engineering challenges.

Keywords. *Hydrogen, Transportation, Brazil*

1. Introduction

The term "hydrogen economy" is used to define the energy system for the production, storage, distribution and use of hydrogen as energy carrier to the end user. The replacement of petroleum fuels used in transportation vehicles such as automobiles, trucks, trains, aircrafts and ships by hydrogen is presently the main platform for those who advocate its use.

Energy from hydrogen is obtained by chemical reactions either by its oxidation in combustion engines or by an inverse electrolytic reaction in fuel cells, which generate power more efficiently and in a cleaner way. The origin of this movement dates from the early seventies when the needs for a strategically safer solution for energy supply and for environmental reasoning, gave strong incentive for the development of such an alternative.

Among the international community, the USA is the leading country in the development of the hydrogen economy. This can be seen in a April 2002 workshop organized by the American Department of Energy titled *"National Hydrogen Energy Roadmap*" (DOE, 2002), where 250 representatives from 135 organizations gathered to project the objectives and future needs to implement the hydrogen economy in the USA. Their main conclusion is that "...hydrogen has the potential to play a major rule in America's future energy system".

Following this lead and considering the peculiar characteristic of the Brazilian energy system, the Ministry of Mines and Energy organized in 2004, a group of 105 experts from different government offices, research institutions and organizations which after several meetings produced a report named: *"A Program for Structuring the Hydrogen Economy in Brazil"* (MME, 2005). Although this report is not an official national program, it indicates clearly the federal government will to develop a long-range project to implement in a broad way the hydrogen as an alternative fuel in Brazil.

Around 75% of the electricity generated in Brazil comes from hydropower plants (ANEEL, 2006) indicating that electrolysis for hydrogen production should be one of the main alternatives. Ethanol, biomass and biogas are potentially the most important long-range renewable sources of heat for hydrogen production, since Brazil has already matured the technology for their production. The use of natural gas is also proposed for the first phase of the hydrogen production since the industrial reform of natural gas is a technology which is already mature.

Twenty-five years is the time estimated in the report (MME, 2005) for the introduction of hydrogen as a fuel in the energy system. This is due to the huge technological, industrial, normative and legal challenges identified. The necessary public funds, disputed intensively with other areas of the federal budget will be also another difficulty. However, the public acceptance will probably be the final judge for the viability and the time schedule for the implementation of a hydrogen economy in Brazil.

2. The hydrogen as a fuel

Hydrogen is stable when two hydrogen atoms are combined into a single molecule (H_2), which is a gas at atmospheric pressure, and it is in this form that it can be used as a fuel. Although hydrogen is the most abundant element in the nature it is always found combined with other elements as in the water (H_2O), methane gas (CH_4) and other heavier hydrocarbon molecules such as ethanol and natural gas.

To extract hydrogen from these substances to form H_2 requires external energy sources generally in the form of heat for reforming processes or electricity used in electrolysis. These energies can come from solar energy (hydro, wind, photovoltaic and biomass), fossil fuel combustion or nuclear fission.

The energy consumed to produce H_2 is significantly larger than the energy content of the hydrogen gas itself. Therefore, H_2 is not a primary source of energy but an energy carrier in the same way as electricity is. The production of both energy carriers from thermal sources is bounded by the Carnot limit, which leads to equivalent economical and environmental impacts, differing only on the actual value of the thermal efficiency obtained in the production process. Thus, both hydrogen as well as electricity should be considered premium energy carriers.

The thermal efficiency for production of electricity using fossil or nuclear fission is 30% to 40%, reaching more than 50% for combined cicles. The energy content of hydrogen varies from 20% to 80% of the energy used to produce it (Uhrig, 2004). Since approximately 75% of the Brazilian electrical power comes from cheap hydropower and considering the still unused potential in the northern region of the country, electrolysis to produce hydrogen could be a way around. As for the future, some studies on the use of direct production of H_2 by gamma radiolysis are under way, even with some doubts from many experts.

The hydrogen is the lightest element (~0.098 kg/m^3) and for electro-chemical reaction or combustion with oxygen, its energy density per-unit-mass basis is quite high. However, its lower energy density per unit-volume basis at atmospheric pressure is one of the lowest among all fuels (~37 MJ/m^3). Clearly, this last figure brings us many engineering challenges that may be difficult to address (Uhrig, 2004).

One of them is to increase the energy density per unit volume basis in order to reduce volume capacity required in storage and volumetric flow rate in distribution of the hydrogen. Increasing hydrogen density by compressing it isothermally to high pressures (35 MPa to 70 MPa) will increase the density to about 0.70 kg/m^3 thus increasing energy density.

Another solution would be liquefying the hydrogen gas at cryogenic temperatures (20K under atmospheric pressures). Even though, in both cases the energy density is still well below the values for gasoline and diesel fuel used in transportation. The need for large pressurized tanks make the use of hydrogen for transportation vehicles very difficult and the need for large volumetric flow rates makes the distribution from one point to another also very difficult. The need of high pressures or very low temperatures added to the fact that hydrogen burns with an invisible flame requires special handling conditions and consequently a set of governmental regulations and codes for safety use of this fuel.

Public acceptance is another important issue regarding the use of hydrogen for transportation. Although, in Brazil, the experience of using natural gas and ethanol as fuels for automobiles, trucks and buses has been relatively successful, it is known that its acceptance is strongly related to price and performance as well as decisive political support.

The strongest point in using hydrogen as substitute for petroleum fuels is that fuel cells efficiency is at least twice as high when compared to combustion engines used in vehicles. It is usually advocated that the use of fuel cells would reduce pollutants and green house gases, but this should be carefully analyzed since one should consider the overall energy cycle including the hydrogen production processes.

In this present work we will focus only on the hydrogen production issue and address the Brazilian energy scenario with and without hydrogen using for transportation and discuss the most promising hydrogen production processes applicable for Brazil. Although the storage of hydrogen, distribution or transportation of hydrogen to fuel stations, dispensing the hydrogen into the vehicles and utilization of hydrogen in fuel cells for example are important issues, these will be reviewed in a later work allowing for a more comprehensive analysis.

3. The hydrogen as a fuel for transportation

World geopolitical uncertainties caused nowadays the barrel cost elevation to more than U$ 70 in the international market and the tendency is that this value will increase even more.

According to the Ministry of Mines and Energy recent note, Brazil will reach petroleum self-sufficiency producing 1.75 million barrels per day in early 2006. However, the self-sufficiency is a result of a low economical growth, with an average that is below 2.5% of the GNP per year from 2000 to 2005, rather than being a result of a higher rate of production increase. In fact, during those years, the petroleum consumption was almost constant as a result of the low economic development and the use of alternative energy sources as alcohol. Figure (1) presents the petroleum consumption and production curves in the last 10 years and their intersection in 2006, representing the self-sufficiency condition.

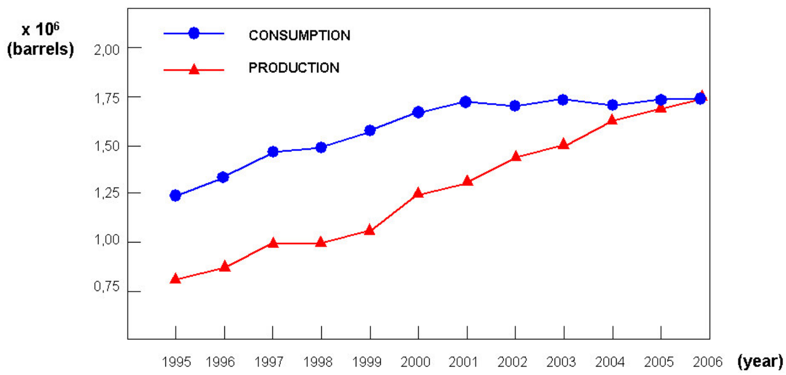

Figure 1. Yearly consumption and production of petroleum in Brazil
(MME 2006, Ministry of Mines and Energy, Informative Report)

According to Petrobras Annual Report (Petrobras, 2005), from the total petroleum used in Brazil, 17% is burn on transport in cars (gasoline), 39% in trucks, trains and ships (diesel oil) and 6% in aircrafts (kerosene), with a total of 62%. The remainder 38% of the petroleum used is spent on lubricating oils (17%), nafta (7%) and others (14%). Figure (2) shows the distribution of petroleum consumption for transportation. The aviation consumption is on the same order of railroad consumption.

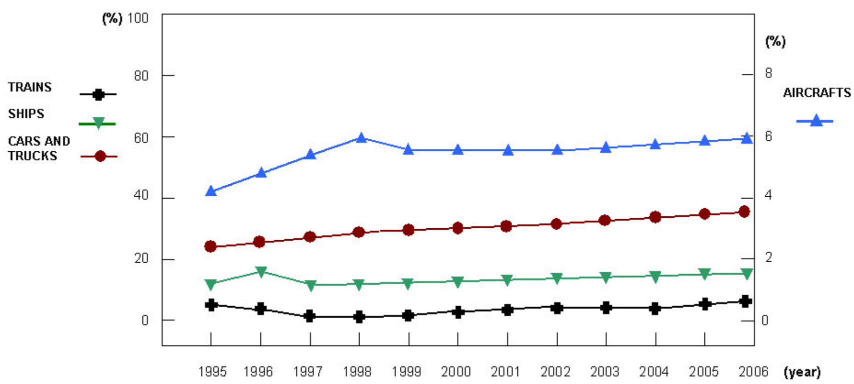

Figure 2. Consumption of petroleum for transportation
(Petrobrás, 2006, Annual Report)

Considering that each petroleum barrel contains approximately 6,120 MJ, and that 62% of the Brazilian petroleum is spent in cars, trucks, trains, ships and aircrafts, the daily consumption of energy from petroleum for transportation would be:

$$1.75 \times 10^6 \text{ (barrel / day)} \times 6{,}120 \text{ (MJ/barrel)} \times 0{,}62 = 6.64 \times 10^9 \text{ MJ/day} \quad (1)$$

Taking into account that the energy density per unit mass in hydrogen is about 120 MJ/kg, it should be necessary in a scenario where all petroleum is to be substituted by hydrogen:

$$6.64 \times 10^9 \text{ (MJ/day)} / 120 \text{ (MJ/kg)} = 55.4 \times 10^6 \text{ kg/day} \quad (2)$$

or 55,400 ton/day of hydrogen to substitute all petroleum burned in combustion engines.

Naturally, the beginning of hydrogen use as a fuel for transportation fuel will occur in internal combustion motors as it is happening currently for natural gas. Since hydrogen burning in motors is less efficient when compared with electricity conversion in fuel cells, resulting in a higher H_2 consumption, combustion engines will be gradually substituted by fuel cells, depending on the price reduction of new vehicles that will have fuel cell technology, and on the vehicle fleet renewal rate. Therefore, this substitution will have its time schedule dictated by technological and economical reasons.

If all necessary hydrogen should be totally used today for electricity conversion in fuel cells, which efficiency is approximately twice of that for combustion engines, it should be necessary around half of the above presented hydrogen quantity, or 27,700 ton of hydrogen per day or something like 10 million ton per year for transportation only.

For comparison purposes, 50 million ton per year of hydrogen is produced world-wide for industrial use. In Brazil, recent data indicates that hydrogen production as energy carrier, just for illustration, is almost despicable, around 0.5 ton per year (MME, 2005).

The most promising methods of hydrogen production in Brazil are natural gas reforming, ethanol reforming and electrolysis, which are described below.

3.1 Hydrogen production from natural gas

At present days, around half of the world hydrogen production comes from natural gas and half from electrolysis depending on which is the cheapest way of H_2 production in each country.

The supply of natural gas in Brazil has received a lot of attention due to political changes in the neighbouring country, the Bolivia. Although those political changes might be short lasting, their effects shall be long-standing because they are part of a Latin American political movement.

Actually, around 30% of the gas consumed in Brazil comes from Bolivia (ANP, 2006). It travels more than 23,000 km through a gas pipeline and it brings strong dependency and strategic uncertainty. To reduce this dependency, the Brazilian government started the development of alternatives such as the import of natural gas from Venezuela, which is also strategically complex as requires another gas pipeline, and the increase of national natural gas reserves exploration.

After 2003, due to a new exploration strategy, it has been revealed a large potential for gas production in Santos basin which can transform Brazil in a self-sufficient natural gas producer country. It is foreseen that in the next five years, Brazil dependence on Bolivian gas will be around half of the present consumption.

Nowadays, it is well known that Santos basin has big natural gas reserves in an area of 352,000 km^2. This resource has not extensively been explored until the present days because it was cheaper the import of gas from Bolivia. Due to new political changes, the effective natural gas exploration in Brazilian ocean will be a short-term reality. However, due to geological peculiarities and deep perforations, reaching to 7 km including water and under water soil, there are big engineering challenges to overcome.

According to Petrobras (Jornal E&P, 2006), Santos basin has five production poles: Merluza, Mexilhão, BS 500, Sul and Centro.

At present time, just Merluza platform produces 1.2 million m^3/day of natural gas, with a forecast production of 100% increase in two years. By constructing a second platform, the production can reach 8 million m^3/day.

The Sul pole produces at moment just petroleum and is located in São Paulo, Paraná and Santa Catarina seacoast. Studies show that in the next 8 years the petroleum production can be increased as well as 3 million m^3/day of natural gas can be produced.

The Centro pole is nowadays under exploration and has a big potential of oil and gas production.

Mexilhão has a potential of 15 million m^3/day. It is located in São Paulo and the foreseen production to 2008 is of 8 million m^3/day.

BS 500 has a very big potential of oil production and can produce 20 million m^3/day of natural gas in a medium time span.

As it can be concluded, natural gas is a energy source which is under expansion in Brazil and will belong soon to the national energetic culture.

Figure (3) presents the gas production evolution in Brazil in the last ten years (ANP, 2006).

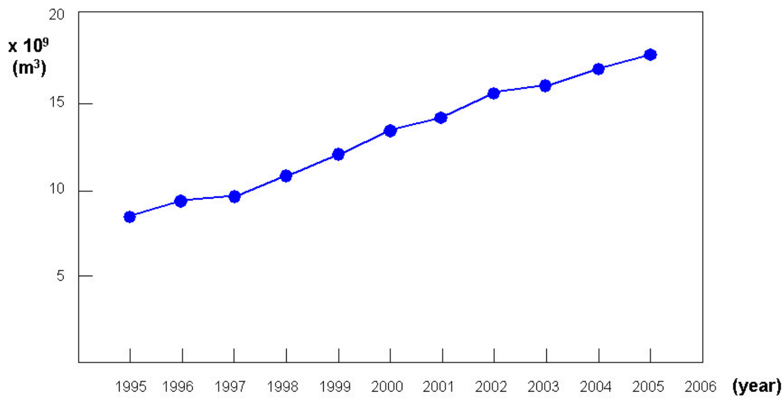

Figure 3. Production of natural gas in Brazil
(ANP, Petroleum National Agency, Natural Gas Monthly Report)

The natural gas is odourless, lighter than air, non-toxic, and is a mixture of light hydrocarbon which relative density to air is from 0.55 to 0.69. Natural gas is a source of clean energy of fossil origin, coming from organic material decomposition. When it is found in porous subsoil stones together with petroleum, it is known as associated gas. When natural gas is found with less or none petroleum, it is known as not associated gas.

A typical composition of natural gas is predominant on methane (CH_4) which percentage is more than 95% (it can be as low as 85%), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}) and other gases in little quantity. It contains low quantities of carbon dioxide (CO_2), sulfur compounds, water and contaminants as nitrogen (N_2). Its combustion is complete and, as a result, are produced the non-toxic components CO_2 and water steam.

After being used just for burning, natural gas will also be used to hydrogen production as it contains the hydrocarbon methane in its composition.

Steam Methane Reforming (SMR) is one of the more important methods of hydrogen production. This is an endothermic process which uses thermal energy and water steam to separate hydrogen atoms from the methane molecule. Natural gas reacts with steam water at moderate temperatures (up to 600°C) and moderate pressures (0.3 MPa) in catalytic surfaces. The SMR process occurs in two stages.

In the first stage, CH_4 reacts with steam of water under a temperature of around 600°C in gas furnaces, in which natural gas is burned and furnishes the necessary heat. The first reaction is:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \tag{3}$$

In the second stage, the reaction occurs at approximately 450°C, the carbon monoxide (CO) reacts with steam water resulting in carbon dioxide (CO_2) and hydrogen under the following reversible reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{4}$$

Under an environmental point of view, SMR process is a source of CO_2 and contributes for the global heating.

The typical overall efficiency of SMR in the process of H_2 production is around 80% (Uhrig, 2004). So, if we consider the prior estimated amount of energy required to substitute the petroleum spent for transportation nowadays in Brazil (6.64 x 10^9 MJ/day) and that each cubic meter of natural gas contains around 37.2 MJ, it should be necessary:

$$6.64 \times 10^9 \ (MJ/day) \ / \ 0.8 \times 37.2 \ (MJ/m^3) = 2.22 \times 10^8 \ m^3/day \quad (5)$$

or approximately 222 million m^3 of natural gas per day.

In 2005, the production of natural gas in Brazil reached 48 million m^3 per day. The total consumption was 66 million m^3 per day (IBP, 2005).

The consumption in 2005 of natural gas for transportation in Brazil was 29 million m^3/day, which represents around 44% of the total natural gas burned in Brazil. The remainder 37 million m^3 per day had industrial use.

Taking in to account the total necessity of natural gas required for hydrogen production at present days in Brazil (222 million m^3 per day) and the present production of this commodity (48 million m^3 per day), it should be necessary to multiply by 4.6 the current production of natural gas just for transportation. If all combustion motors should be substituted by fuel cell motors, the actual production of natural gas should be multiplied by 2.3.

3.2 Hydrogen production from ethanol

The sugar cane is a traditional cultivation in Brazil since the XVI century. Nowadays, Brazil is the leader in ethanol (C_2H_5OH) production from sugar cane in the world. This is due to appropriate climate conditions and the availability of big areas for planting.

According to the Agriculture Ministry, the total area dedicated to sugar cane production is 6 million hectare and the actual production is around 360 million ton per year (ALCOPAR, 2006). The amount of ethanol produced from sugar cane in Brazil in 2004/2005 was 14.9 millions cubic meter (BRASIL, 2005). Figure (4) illustrates the increase of ethanol production in Brazil in the last five years. However, the present-day production of ethanol is still smaller than the peak of 15.4 million m^3 that happened in 1997/1998.

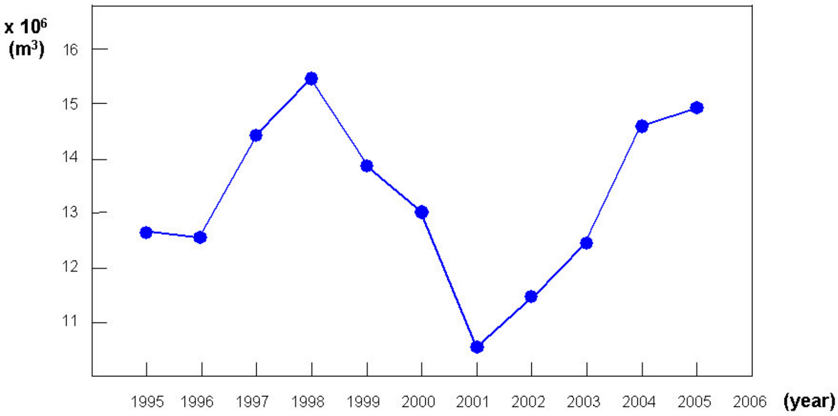

Figure 4. Ethanol production in Brazil
(BRASIL 2005, Agriculture Ministry)

The production of hydrogen from ethanol occurs in a reforming process. The Steam Ethanol Reforming (SER) is a catalytic endothermic process which has the following primary reaction and shall be made preferably at temperatures around 600°C:

$$C_2H_5OH + 3H_2O \longrightarrow 6H_2 + 2CO_2 \quad (6)$$

In the secondary reaction the hydrogen and the carbon dioxide produced react among themselves and produce methane and carbon monoxide as presented in Eq. (7) and Eq. (8), noting that the later is the same as in (4):

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad (7)$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \quad (8)$$

As a final result, is formed a gas mixture known as synthesis gas which contain hydrogen, carbon dioxide, methane and carbon monoxide. To obtain hydrogen, the gasses mixture passes through purification equipment. Special care shall be taken to CO as it is a highly toxic gas.

According to CENEH (2004), through the present ethanol production is possible generate approximately 5,000 ton of hydrogen per day. Taking into account prior estimative presented in this work, the total hydrogen necessary to substitute the petroleum burned on transportation in Brazil is 55,400 ton per day. Therefore, it should be necessary to increase 11 times the actual production of ethanol under this purpose by burning hydrogen in combustion motors. By using H_2 in fuel cells, the actual production of ethanol should be multiplied by 5.5.

Finally, it is very important to emphasize that SER process is a source of greenhouse gases (CO_2), highly toxic gases (CO) and lightly toxic gases (CH_4), which is widely believed to impact Earth climate.

3.3 Hydrogen Production by Electrolysis

Electrolysis needs water and energy in the form of electricity for water splitting in H_2 and O_2. Since the beginning of the last century, hydrogen has been used by man as a consequence of the discovery of electricity.

On October 19, 1901, Alberto Santos Dumont was the first man who made a turn around Eiffel Tower in Paris, (Hoffman, 2003). His aerostat, the blimp N^o 6, an aircraft lighter than air, used hydrogen. Today, the well-tested conventional alkaline low-pressure electrolysis of water is a well-known process used to hydrogen production.

Besides H_2 production, the electrolysis of water also produces oxygen and heavy water which have commercial value.

The electrolysis of water is a method of hydrogen production only economically feasible in countries like Brazil, where electricity is not expensive due to its predominant hydro origin instead of thermal one. So, the key to water electrolysis for economic production of hydrogen is the low cost of electricity.

According do ANEEL (2006), 75% of total electrical power generated in Brazil comes from hydroelectric power plants, 21% comes from thermoelectric power plants, 2% are produced in Almirante Alvaro Alberto (Angra) two nuclear power plants and 2% comes from other origins like small hydroelectric turbines, aeolian and solar as shown in Fig. (5).

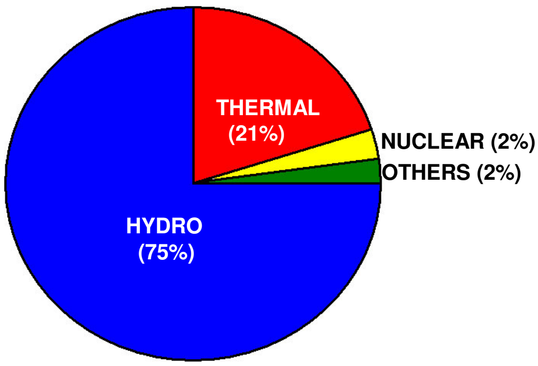

Figure 5. Brazilian source of electricity
(ANEEL 2006, Electric National Agency)

Electrolysis decomposes the water through two partial reactions that take place in two electrodes. The electrodes themselves are separated by an ion aqueous alkaline conducting electrolyte. Hydrogen is produced at the negative electrode (cathode) and oxygen at the positive electrode (anode). The necessary exchange of charge occurs through the ions flow. In order to keep the produced gasses isolated, the two reaction areas are separated by an ion conducting micro-porous diaphragm separator.

There are also two additional processes still in the development phase, namely the high pressure and the high temperature processes.

Through special material choice and optimisation, high-pressure water electrolysis allows the generation of hydrogen at pressures up to 5 MPa. The goal of this effort is to reach, along with the high output pressure, an appropriately optimised operational efficiency which is applicable for strongly varying load.

High temperature electrolysers were under discussion as an interesting alternative many years ago. The main advantage of such a process would be to obtain part of the energy required for water molecule splitting using high temperature heat and afterwards complete the electrolysis with lower electricity consumption with an overall energy saving. The discussions focussed on the use of heat from solar concentrators or waste heat from power stations. Interest in this method of electrolysis has however declined in the last few years.

The conventional production of H_2 can reach efficiencies, related to the lower heating value of hydrogen, around 65% and output pressures of 0.2 MPa to 0.5 MPa. Operating efficiencies lie in the 50 to 60% range for the smaller electrolysers and around 65 to70% for the larger plants.

Units with capacities from 1 kW_e to 125 MW_e are available in the world. Several manufacturers have also established themselves in the 1 kW_e to 100 kW_e range in Europe.

As a general value, it is necessary around 2 MW_e of electric power to produce 1 ton of hydrogen per day. As already presented, the amount of hydrogen necessary to substitute the petroleum burned in Brazil in transportation issues is around 55,400 ton per day (combustion motors) or 22,700 ton per day (fuel cell motors). Therefore, the total electrical power necessary to production of hydrogen through electrolysis at present days in Brazil is:

$$55{,}400\ ton/day\ x\ 2\ MW_e day/\ ton = 110{,}800\ MW_e \tag{9}$$

or 110.8 GW_e. By using fuel cell motors, this value is reduced to 55.4 GW_e.

According to ANEEL (2006), the total electrical power generated in Brazil is around 94.8 GW_e. Therefore it should be necessary more than the present production of electricity by considering hydrogen production necessities if it should be used in combustion motors. By using fuel cell motors, it should be necessary more than half of the present electrical power for H_2 production.

The electricity presents a price variation as a result of law of supply and demand. As an example, Fig. (6) illustrates the medium price of electric energy in Brazil during 2003 and 2004.

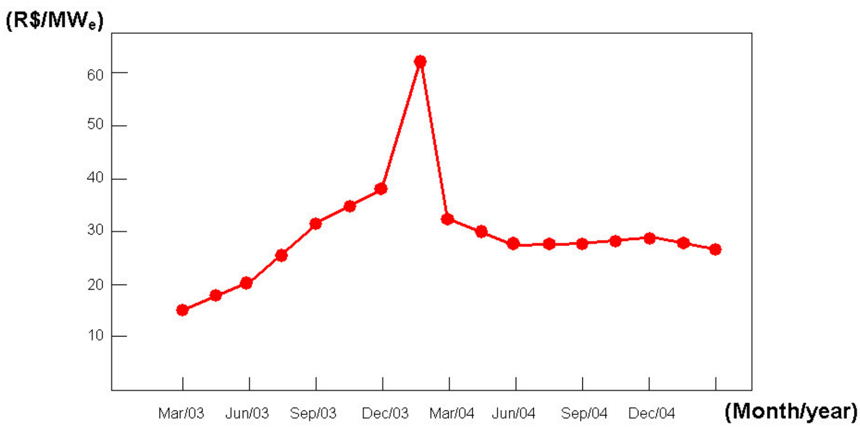

Figure 6. Fluctuations of electricity price during 2003/2004
(ANEEL 2006, Electric National Agency)

To overcome demand fluctuations, every power plant has an excess of electricity generation due to peak energy demanding as a result of network plant outages. The capital costs related to this excess of capacity are sunk costs which must be added to the cost of energy.

Figure (7) illustrates the electricity excess generation in the year of 2004, resulting a total energy of 4,307 $GW_e h$. This energy should be used to produce hydrogen.

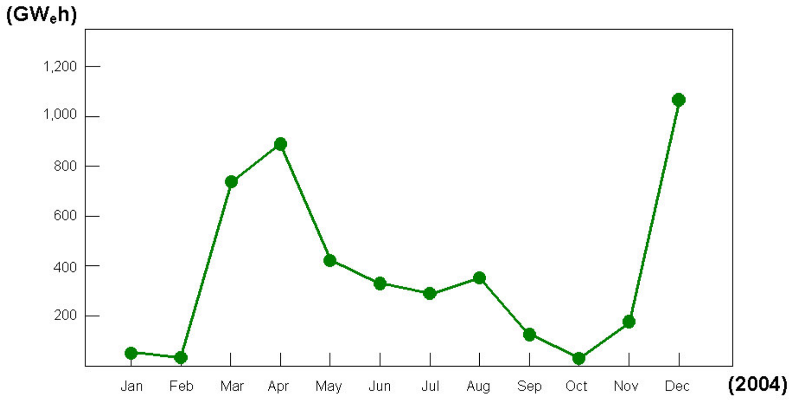

Figure 7. Excess of electricity during 2004
(ANEEL 2006, Electric National Agency)

By considering that the production of 1 ton per day of H_2 requires 2 MW_e of electrical power, it is necessary 48 $MW_e h$ of energy to produce 1 ton of hydrogen. Therefore, the total production of H_2 that should be done in the year of 2004 was:

$$\frac{4,307 \text{ x } 10^3 \; MW_e \, h}{48 \; MW_e \, h/ton} = 89,729 \; ton \qquad (10)$$

or 245 ton per day. This value is around 10% of all hydrogen required by using fuel cell motors or 5% if hydrogen is burned in combustion motors.

4. Conclusions

In this work, the hydrogen economy in Brazil was treated under a transportation energetic focus. The presented overview point out the actual possibilities and future necessities of hydrogen production through natural gas, ethanol and electrolysis as they look to be more applicable to the Brazilian scenario.

Assuming the substitution of all petroleum burned in Brazil by hydrogen, the necessary production of H_2 today should be 20 million ton per year for feeding all combustion motors. By using fuel cells and electrical motors instead of combustion motors, this value should drop to 10 million ton per year.

If the origin of the required energy should be natural gas, it should be necessary the increasing of the present production from 17.7 billion m^3 per year to 80.6 billion m^3 per year by using combustion motors and to 40.3 billion m^3 per year using fuel cell fitted electrical motors.

If the produced hydrogen should be ethanol origin, the actual production of alcohol should be multiplied by 11 (combustion motors) or by 5.5 (fuel cell motors). As a result, the sugar cane cultivation area should be 66 million hectare or 33 million hectare (around 3 or 1.5 times São Paulo State area) respectively.

By using electrolysis, more than the present Brazilian electrical power which is 94.8 GW_e should be used to hydrogen production (combustion motors) or more than a half of this value in the case of fuel cell using.

5. Acknowledgement

The authors thank to Dr. Robert E. Uhrig, who inspired this work.

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