PHYSICOCHEMICAL, EXERGETIC AND ECONOMICAL ANALYSIS OF BIOGAS REFORMING: HYDROGEN PRODUCTION

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Abstract. *The utilization of biogas for production of hydrogen-rich syngas through thermochemical processes such as steam reforming and dry reforming is suggested in this study. Ultimately, these gases could be utilized by fuel cells to generate electricity and heat. The composition of biogas depends strongly on conditions where this gas is produced (thermodynamic conditions such as temperature and pressure where biogas' feedstocks are utilized, beyond composition of own feedstock and utilized technology for biogas processing). Physicochemical analysis was performed with objective to evaluate the composition of syngas generated through reforming process, making a special attention to the content of hydrogen in the cited syngas. The adopted biogas in this study was based on the biogas generated in a small wastewater treatment system installed in São Paulo State University (UNESP) at Guaratinguetá. The volume of constituents was 61.8%* CH_4 *and 34.4%* CO_2 *after purification. Some traces of* O_2 *and* N_2 *were encountered. The suggested thermodynamic conditions detected in physical-chemical and exergetic analysis was in a range of 600-900°C and 1 atm. This pressure was adopted since in this way, an equipment of pressurization and depressurization is not necessary, diminishing the costs of installation and utilization of energy. Basing on this temperature, the generation of hydrogen-rich biogas is devoted with low utilization of energy which in this case is necessary as heat source. The exergetic analysis has as objective to determinate the most convenient thermodynamic conditions for studied hydrogen production process. Calculations concerning rational and exergetic efficiencies were developed. Basing on this analysis, the suggested conditions were 1 atm and maximum 700°C. Ultimately, an economic analysis was performed to evaluate the cost of produced hydrogen depending on of imposed conditions such as cost of installation of studied reformer system, operation, maintenance, and cost of biogas and carbon credits. This hydrogen production process is an efficient mean of production since their costs are near those encountered in some economic analyses available on the literature. The possibility to insert carbon credits was cited, since this biohydrogen production process contributes to diminish environmental impact.*

Keywords: *Hydrogen production, biogas, physicochemical analysis, exergetic analysis, economic analysis.*

1. INTRODUCTION

The utilization of enormous amount of natural resources and its unavoidable effect on local and global environment have contributed to the need to diminish environmental impact caused, as an example, by energy generation systems.

The adequate disposal and (or) treatment of residues contribute not only to the maintenance of well-being of population but also could contribute to generate additional resources such as biogas by wastewater treatment systems. As an example, a small and low-cost wastewater treatment system with biogas production installed in a campus of São Paulo State University, campus of Guaratinguetá (Brazil), and composition of produced biogas was cited in this work. This system is able to receive and to treat part of the wastewater produced in this campus, diminishing costs. Previously, the overall volume of this residue has been piped by state-owned company of Guaratinguetá, which disposes part of his wastewater inadequately in Paraiba River.

Beyond treating wastewater, an attention concerning the water produced during this treatment (reclaimed water) and the produced biogas must taking into account. This type of water (which contains nutrients for the plants) could be used in the gardens. The biogas could be used for energy purposes in own campus.

The utilization of biogas as a feedstock for biohydrogen production has be widely researched due to its low environmental impact and due to its availability, since this fuel could be produced utilizing various feedstocks through various technologies and processes.

In a project recently approved by FAPESP, a state-owned company responsible by financial support of projects performed in the Brazilian state of São Paulo, theoretical analysis was developed to evaluate the content of hydrogen to be produced through steam reforming. The choice of this technology of hydrogen production is due to the large experience devoted by Energy Systems Optimization Group maintained in this campus, and by higher efficiency of production. Another motive to choose this technology is the ease of project and development and its low cost of installation. Other measurements such as exergy efficiencies and irreversibilities have contributed to determine the steam reforming process if compared with other processes such as partial oxidation and autothermal reforming. However, due to the high amount of carbon dioxide (CO_2) in the produced biogas, and due to the high cost necessary to extract it, steam reforming process associated with dry reforming (where the own CO_2 is utilized to react with methane gas (CH_4), the principal constituent of biogas) is suggested. Both reforming processes are accepted and no more additional process is necessary since the volume of CO_2 contained into the biogas is smaller if compared with CH_4.

In this work a physical-chemical, exergetic and economic were developed as mean to determine the more optimized conditions for hydrogen production. The steam reforming and dry reforming are endothermic processes. Due to this, high temperatures of hydrogen production are foreseen and hence a major amount of fuel as heat source is necessary.

Connected with both analyses, an economic analysis was developed to evaluate its viability. Some findings were considered such the possibility to utilize electricity and the own biogas as heat source to perform the reactions. The introduction of emission trading schemes such as carbon credits have become possible the introduction of environmentally-friendly technologies, in special for technologies which allow the capture of greenhouse gases such as biogas. The evaluation of the produced biogas volume and the amount of greenhouse gases emitted by hydrogen production process allow to determine the value of carbon credit, which could be utilized to the infra-structure, diminishing the costs of produced hydrogen and hence, becoming this technology more-competitive.

2. PHYSICOCHEMICAL ANALYSIS

This analysis has as objective to evaluate the composition of syngas generated through reforming process, especially content of hydrogen in this syngas. The contents of constituents of cited biogas (which is near a typical biogas from wastewater treatment systems) was 54% CH_4 and 40% CO_2 before H_2S purification, and 61.8% CH_4 and 34.4% CO_2 after purification. Some traces of O_2 and N_2 were encountered in the biogas in both cases however these small amounts are negligible and no problems during hydrogen production are foreseen. The amount of encountered H_2S was 2.8% before purification and 1.2% after purification process. This process is performed through low-cost devices which utilize small pieces of iron extracted from machining processes (Silveira et al., 2008).

The equilibrium constant associated with steam and dry reforming of methane and the formula which determines molar fractions of reactants and products of reaction could be cited as indicated by Van Wylen et al. (1998):

$$\ln K = -\frac{\Delta G^0}{\bar{R}T} \quad (1)$$

$$\ln\left[\frac{y^{nc}.y^{nd}}{y^{na}.y^{nb}}.\left(\frac{P}{P^0}\right)^{nc+nd-na-nb}\right] = -\frac{\Delta G^0}{\bar{R}T} \quad (2)$$

$$y_i = \frac{n_i}{n_{TOT}} \quad (3)$$

Where: P is overall pressure, and y_i are molar fractions of gaseous components. After obtaining the values of conversion (also known as advance degree) of global reactions of steam and dry reforming, fractions (χi) of each component in equilibrium could be calculated (Silveira et al., 2003).

$$Keq = Keq_p = \frac{P(H_2)^6.P(CO_2)^2}{P(EtOH)^1.P(H_2O)^3} \quad \text{(steam reforming)} \quad (4)$$

$$Keq = Keq_p = \frac{P(H_2)^6.P(CO_2)^2}{P(EtOH)^1.P(H_2O)^3} \quad \text{(dry reforming)} \quad (5)$$

As steam reforming as dry reforming of methane are foreseen in this evaluation. Both reactions are described below:

$CH_4 + 2(H_2O) \Rightarrow CO_2 + 4(H_2)$	Δh_f^0 = 165 kJ/mol	$CH_4 + CO_2 \Rightarrow 2(CO) + 2(H_2)$	Δh_f^0 = 247 kJ/mol

However, other reactions can occur in parallel. These reactions must being avoided introducing adequate catalysts and thermodynamic conditions:

$CO_2 + H_2 \Rightarrow CO + H_2O$	Δh_f^0 = 41 kJ/mol	$CO + 3\ H_2 \Rightarrow CH_4 + H_2O$	Δh_f^0 = -206,1 kJ/mol
$2\ CO \rightarrow CO_2 + C_{(s)}$	Δh_f^0 = -172,46 kJ/mol		

The conversions of each reaction (steam and dry reforming of methane) are depicted below:

	CH_4	**+**	**$2(H_2O)$**	$\leftrightarrow$	**CO_2**	**+**	**$4(H_2)$**
nº moles:	n. (1-α)		2.n. (1-α)		n. α		4.n. α
	CH_4	**+**	**CO_2**	$\leftrightarrow$	**$2(CO)$**	**+**	**$2(H_2)$**
nº moles:	n. (1-α)		n. (1-α)		2.n. α		2.n. α

Finalizing, basing on composition of biogas cited above, the behaviour of conversion of biogas is depicted in the Fig. 1:

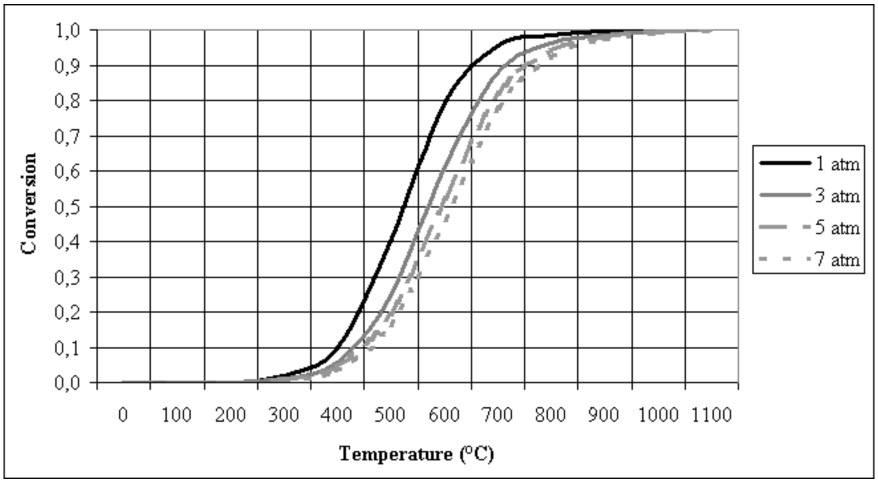

Fig.1: Conversion of studied biogas depending on temperature and pressure.

As cited in Fig. 1, the conversion increases as temperature also increases, in contrary to pressure, since conversion of biogas decreases as pressure increases.

For a biogas production of 9 Nm^3 per day (that is the capacity of production of biogas in the wastewater treatment system as cited Silveira et al., 2008), the reforming process in the best conditions could produce about 1,3 kg H_2 per day, which could generate about 15-20 kWh electricity if a PEMFC (Proton Exchange Membrane Fuel Cell) is considered. A performance of 100% for hydrogen production process was adopted, and following some recent works, the electric efficiency of a PEMFC could attain 40-50% (Souza, 2005).

3. EXERGETIC ANALYSIS

Associated with physicochemical analysis, the exergetic analysis has also as objective to evaluate the most adequate conditions to perform the hydrogen production, in this case, temperature and pressure where the highest efficiencies of production could be encountered. To determine them, calculations of irreversibilities of studied process, and its exergetic and rational efficiencies are suggested.

Firstly, some formulas were utilized as cited above (Silveira et al., 2003):

$ex_{SPECIE} = ex_{TD} + ex_{CH} + ex_{H}$ (general) (6)	$ex_{TD} = (h_i - h_0) - T_0(si - s_0)$ (thermodynamic) (7)
$ex_{CH} = ex_Q + RT_0 \ln(\frac{P_i}{P_0})$ (chemical) (8)	

Energy flow, irreversibility, and exergetic and rational efficiencies are calculated utilizing the following equations (Silveira et al., 2003):

$Ex = (m_{SPECIE})(ex_{SPECIE})$ (9)	$I = \sum_{i=1}^{N} \dot{Ex}_{INPUT} - \sum_{i=1}^{N} \dot{Ex}_{OUTPUT} \geq 0$ (irreversibility) (10)
$\frac{\sum_{i=1}^{N} Ex_{OUTPUT}}{\sum_{i=1}^{N} Ex_{INPUT}} .100 = \psi$ (rational efficiency)(11)	$\eta_{EX} = \frac{Ex_{H2}}{\sum Ex_{INPUT} - \sum Ex_{CO2}} .100$ (exergetic efficiency) (12)

Subsequently, results were plotted to obtain conclusions concerning this exergetic analysis, depending on temperature and pressure of reactions. Figures 3, 4 and 5 depict performances of irreversibility rates, exergetic efficiencies and rational efficiencies, respectively.

For this analysis, an amount of hydrogen was fixed (0,085 kg/h). As conversion of reactants increases, a minor amount of reactants is necessary. Due to this fact, lower irreversibilities were detected at higher temperatures and lower pressures. However, at temperatures greater than 800°C, an increase of irreversibilities is detected. The lowest rational efficiencies were detected at 1 atm and at higher temperatures due to lower amount of methane in these cases. Methane has high value of chemical exergy, which contribute to define enormously the results. The highest exergetic efficiencies were detected at 1 atm and higher temperatures.

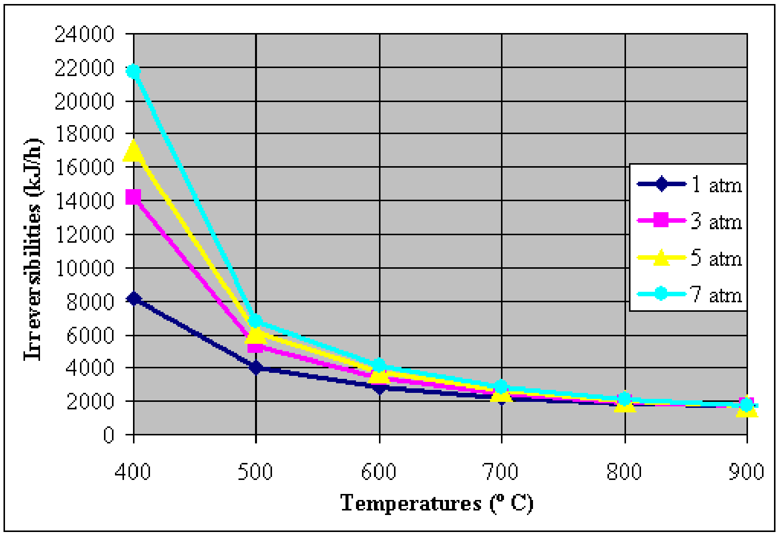

Figure 2: Behaviour of irreversibility rates.

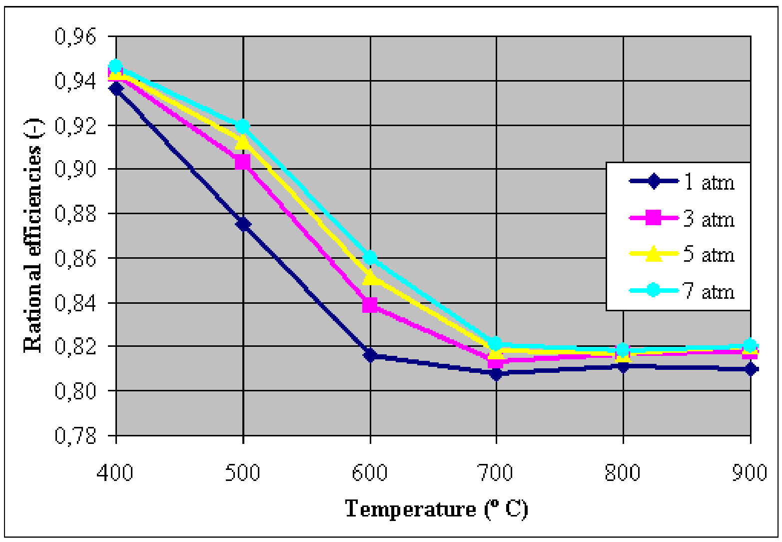

Figure 3: Behaviour of rational efficiencies.

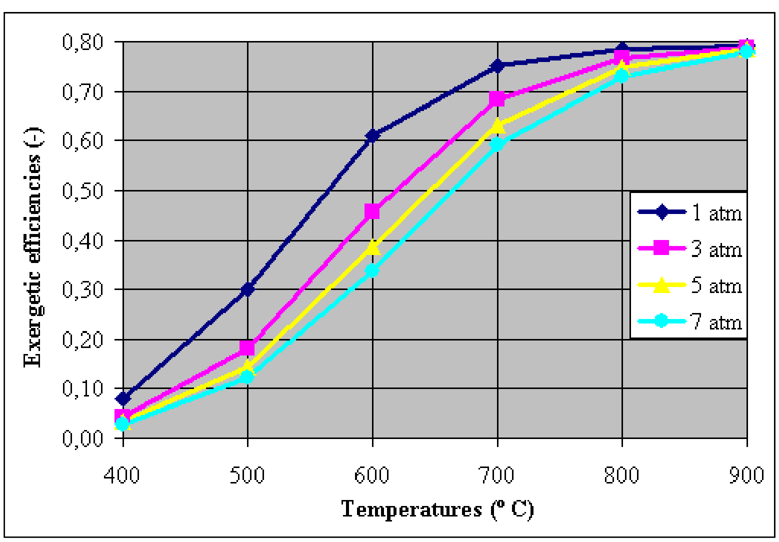

Figure 4: Behaviour of exergetic efficiencies.

4. ECONOMIC ANALYSIS

An economic analysis is an important way to determine the economic viability of hydrogen production system utilizing small volumes of biogas. As biogas has a high content of energy and high potential of greenhouse effect, carbon credits credit could be obtained.

To determine an economic analysis, some findings were considered such the possibility to utilize electricity and own biogas as heat source to perform the reactions, annual period of utilization of hydrogen production system of 5000 to 7000 hours, maximum interest rate of 20% per annum (considering the Brazilian conditions), and maximum payback of 20 years. In this analysis, the adopted cost for biogas is 0,004 US$/kWh.

The calculation process to be developed in this analysis is cited below (Souza, 2005):

$C_{H_2} = \frac{Inv_{REF} * f}{H * E_{H_2}} + C_{OP} + C_{MAN}$ (cost of hydrogen) (13)	$E_{H2} = m_{H2} \times PCI_{H2}$ (energy flow of hydrogen)(14)
$E_{COMB} = m_{COMB} \times PCI_{COMB}$ (energy flow of fuel) (15)	$C_{OP} = \frac{E_{COMB} * P_{COMB}}{E_{H_2}}$ (operation cost) (16)
$C_{OP} = \frac{E_{ELET} * P_{ELET}}{E_{H_2}}$ (maintenance cost) (17)	

Where:

$f = \frac{q^k * (q-1)}{q^k - 1}$ (18)	$q = 1 + \frac{r}{100}$ (19)

The results were in Figs 5 and 6:

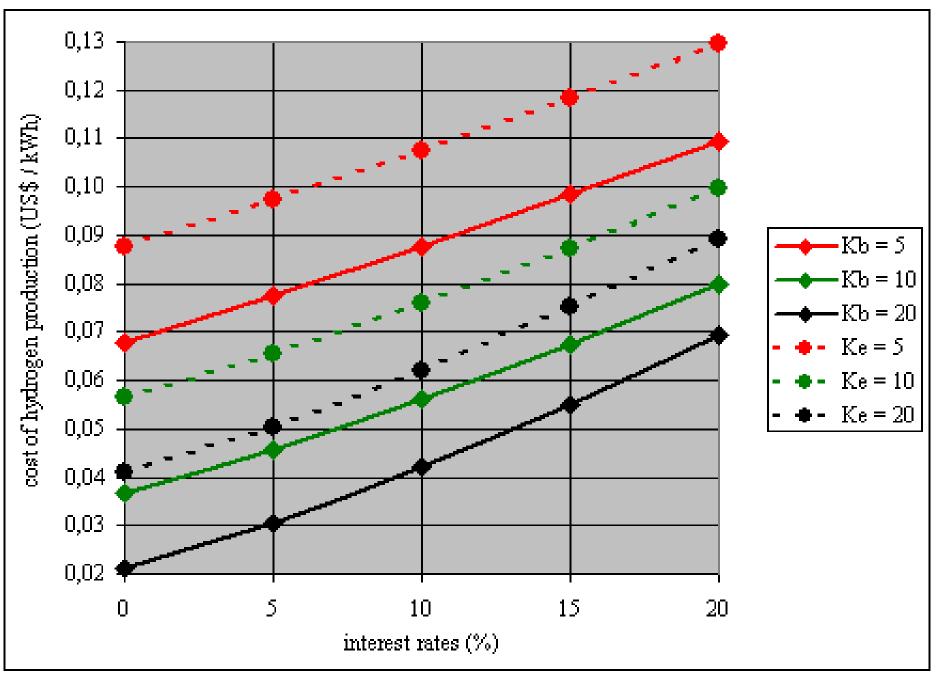

Figure 5: Cost of hydrogen production depending on interest rates and pay-backs (Kb = pay-back utilizing biogas - Ke = pay-back utilizing electricity). Annual period of operation: 5000 h.

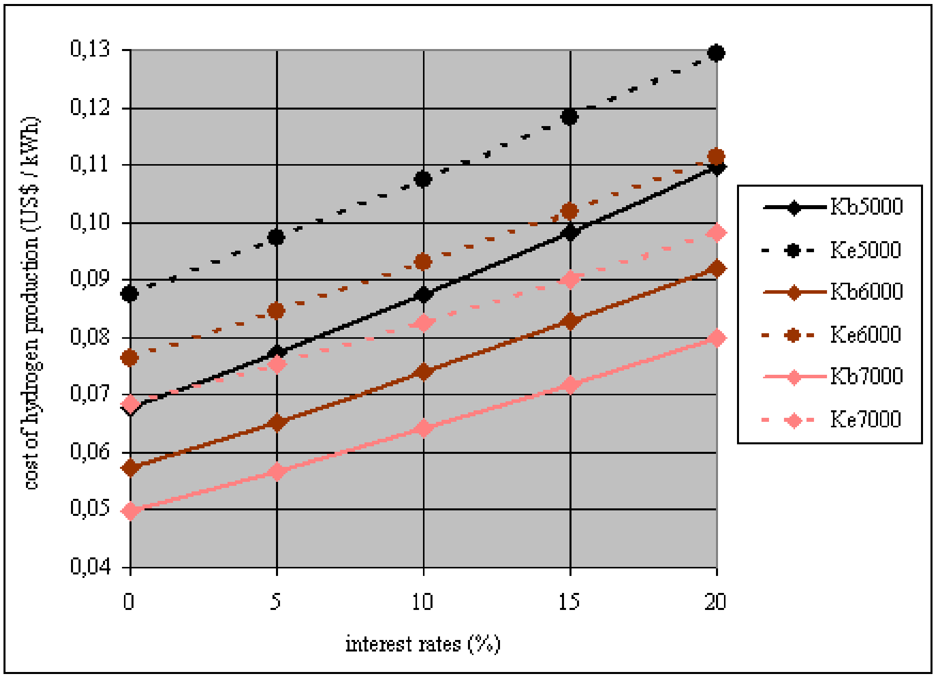

Figure 6: Cost of hydrogen production depending on interest rates and annual period of operation (Kb = annual period of operation utilizing biogas - Ke = annual period of operation utilizing electricity). Pay-back: 5 years.

Figures 7 and 9 depict the behaviour of hydrogen production cost with cost of biogas, whereas Figs. 8 and 10 depict the behaviour of hydrogen production cost with cost of carbon credits:

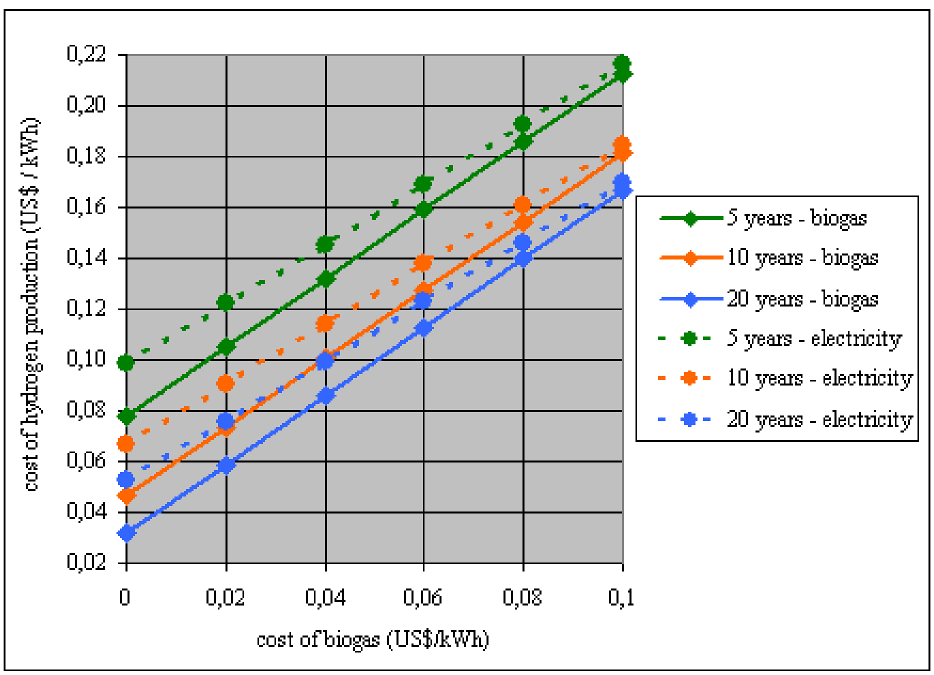

Figure 7: Cost of hydrogen production depending on cost of biogas and pay-backs. Annual period of operation: 5000 h. Interest rates: 8% per annum.

The lowest cost detected of hydrogen produced was 0.03029 and 0.01114 US$/kWh whether electricity and biogas as heat sources are utilized, respectively. In the last case, an additional cost associated with biogas was not considered. This cost should be added in some cases due to the utilization of equipments (such as H_2S purification system) to maintain biogas production only although this cost is low and do not become the process prohibitive.

Inserting gains concerning carbon credits, the installation of a low-cost hydrogen production system is possible.

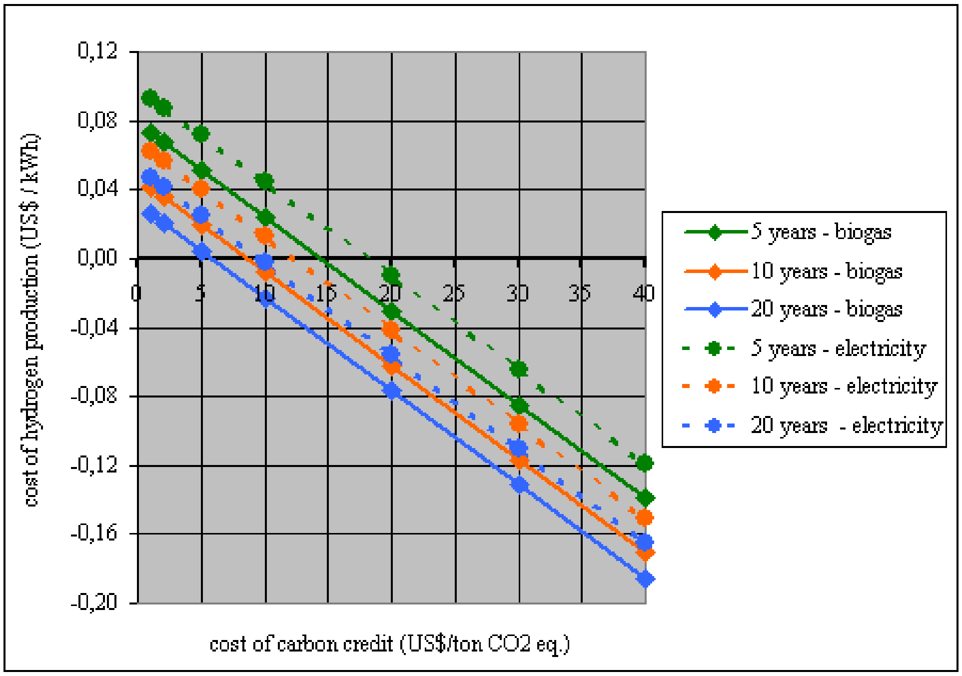

Figure 8: Cost of hydrogen production depending on cost of carbon credit and pay-backs. Annual period of operation: 5000 h. Interest rates: 8% per annum.

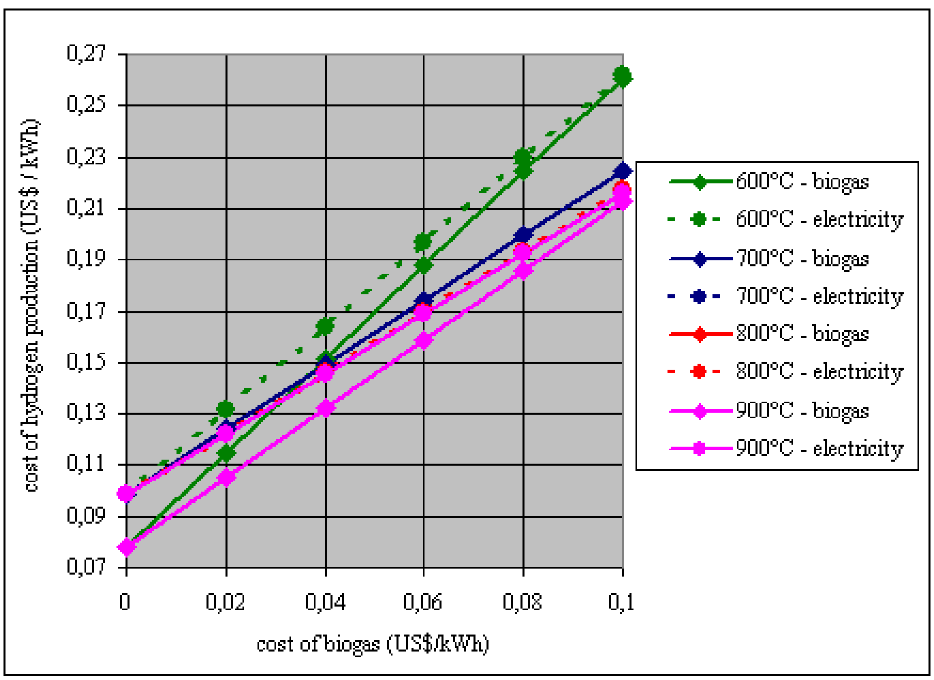

Figure 9: Cost of hydrogen production depending on cost of biogas and temperature of operation of reformer. Annual period of operation: 5000 h. Interest rates: 8% per annum. Pay-back: 5 years.

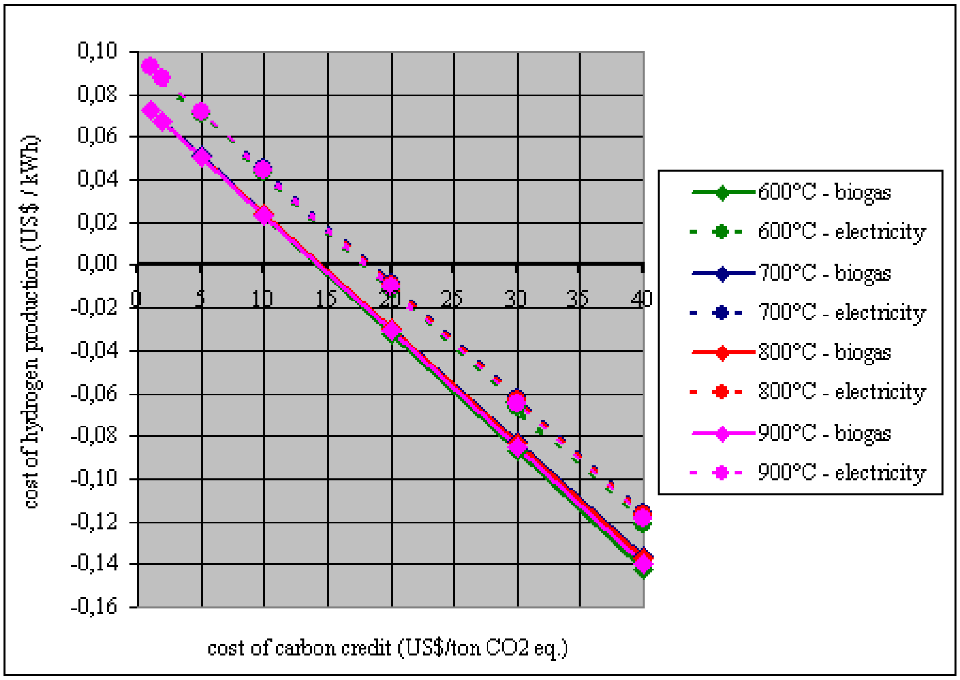

Figure 10: Cost of hydrogen production depending on cost of carbon credit and temperature of operation of reformer. Annual period of operation: 5000 h. Interest rates: 8% per annum. Pay-back: 5 years.

5. CONCLUSIONS

Through this work, the feasibility of hydrogen production utilizing biogas from a wastewater treatment system was possible to put in evidence. To subsidize this affirmation, some analyses were developed. Firstly, a physicochemical analysis was developed with objective to evaluate optimal conditions of biohydrogen production. In this way, it was possible to observe that the higher the temperature of operation the higher is conversion of biogas, as the lower its pressure the higher is its conversion. The increase of selectivity of hydrogen was also observed as soon as conversion of biogas was observed. As physicochemical as exergetic analyses concluded that the optimal conditions of studied way of hydrogen production were at 600°C and higher and at 1 atm. Processes at slightly-lowest temperatures could be also developed, however the biogas conversion and selectivity of hydrogen would be much lower, contributing to increase the final cost of hydrogen.

Ultimately an economic analysis was developed. Some conditions were suggested such as annual period of operation of 5000 hours, pay-back equal to 5 years and interest rates equal to 8% per annum. These conditions are near Brazilian conditions. Without carbon credits, the suggested temperature was 700-900°C. However, the differences among costs of hydrogen production are minimal at low cost of carbon credits. As cost of carbon credits increase, the cost of hydrogen production with reforming at 600°C becomes lower.

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