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POTENTIAL OF BIOHYDROGEN PRODUCTION IN LANDFILLS OF THE CITY OF SÃO PAULO: ELECTROLYSIS X STEAM REFORMING

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Abstract. *In this paper are studied two processes that use biogas to obtain biohydrogen. Initially is analyzed the water electrolysis process with the use of electric energy generated in conjunction with internal combustion engine / generator (ICE) operating with landfill biogas. Subsequently is studied the steam reforming of biogas for the production of biohydrogen, which also uses this biofuel for the generation of superheated steam necessary for the reform process. The objective is to perform the energy analysis in order to determine the efficiency of the processe and the biohydrogen production potential in the sanitary landfills of the city of São Paulo. As a conclusion, one has to consider the availability of biogas in the city of São Paulo, there is a great potential for the production of biohydrogen, and that the steam reforming process of biogas presents a higher level of efficiency from a thermodynamic point of view.*

Keywords: *biodydrogen, biogas, electrolysis, steam reform*

NOMENCLATURA

$\dot{E}_{biogasICE}$: power supplied by burning of the biogas in the ICE [kW]
$E_{req.}$: electricity required in the electrolyser [kW]
LHV_{biogas}: lower heating value of biogas [kJ/kg]
LHV_{H_2}: lower heating value of hydrogen [kJ/kg]
$\dot{m}_{biogas.boiler.}$: biogas mass flow in the boiler [kg/s]
$\dot{m}_{biogasICE}$: biogas mass flow in the ICE [kg/s]
$\dot{m}_{biogas.ref.}$: biogas mass flow in the reformer [kg/s]
$\dot{m}_{H_2}$: hydrogen mass flow [kg/s]
$\dot{W}_{ICE}$: electric power produced in the ICE [kW]
$\eta_{electro.el.ICE}$: energetic efficiency of the electrolysis process [-]
$\eta_{electrolyzer}$: efficiency of the electrolyzer [-]
$\eta_{el.ICE}$: electric efficiency of the ICE [-]
$\eta_{reforma}$: energetic efficiency of the biogas steam reform process [-]

1. INTRODUCTION

The Brazilian energy matrix is very diversified, with great capacity for the production of fossil and renewable fuels. Currently, a major challenge for scientists and researchers is the development of new technologies for alternative sources of energy are explored more broadly for the benefit of the population and the environment. In this context, research related to the processes of obtaining hydrogen has become constant, since this energy vector has great capacity for energy storage, and if it is produced from renewable sources, it can be an economically and ecologically strategic fuel for Brazil to depend less oil and other fossil fuels (BRAGA et al. (2013), ACAR et al. (2013)).

The biohydrogen produced by electrolysis of water is based on the passage of an electric current through an electrolytic conductor (alkaline or polymeric), which results in the separation of the water molecule into biohydrogen (H_2) and oxygen (O_2). The biohydrogen produced by this process is of high quality, since no carbon, sulfur or nitrogen compounds are generated. The electrolysis process is free of pollution when only reactions are analyzed, but life cycle emissions are a direct function of the electricity source used in the process (LEVIN et al., 2010).

The reform process consists of two reactors (reform reactor and reactor shift). In the reform reactor catalytic reactions occur the biogas with water steam. The products of these reactions are hydrogen and carbon monoxide. In the reactor shift all CO produced in the reform reactor, react with the water steam producing hydrogen and carbon dioxide. Thus, at the end of the reform process, the main products of the reactions are hydrogen and carbon dioxide (SILVEIRA, 2017).

2. ENERGETIC ANALYSIS

In order to carry out the energy analysis of the electrolysis process, it was considered electricity generated in an internal combustion engine to biogas. And for the steam reform process the biogas was considered as fuel to be used in the reformer and in the boiler. This study is based on the biogas production of three sanitary landfills in the city of São Paulo, according to Tab. 1.

Tabela 1: Produção de biogás dos aterros sanitários da cidade de São Paulo (PAULINO, 2017)

Landfill sanitary	**Average biogas production [Nm^3/h]**
Caieiras	19000
CDR	15000
CLT	16333
Total	50333

2.1 Análise Energética do Processo de Eletrólise

For the electrolysis process it was considered an internal combustion engine for biogas generating electricity to be used in the electrolyser in order to produce biohydrogen, the inputs and process products are presented in Fig. 1.

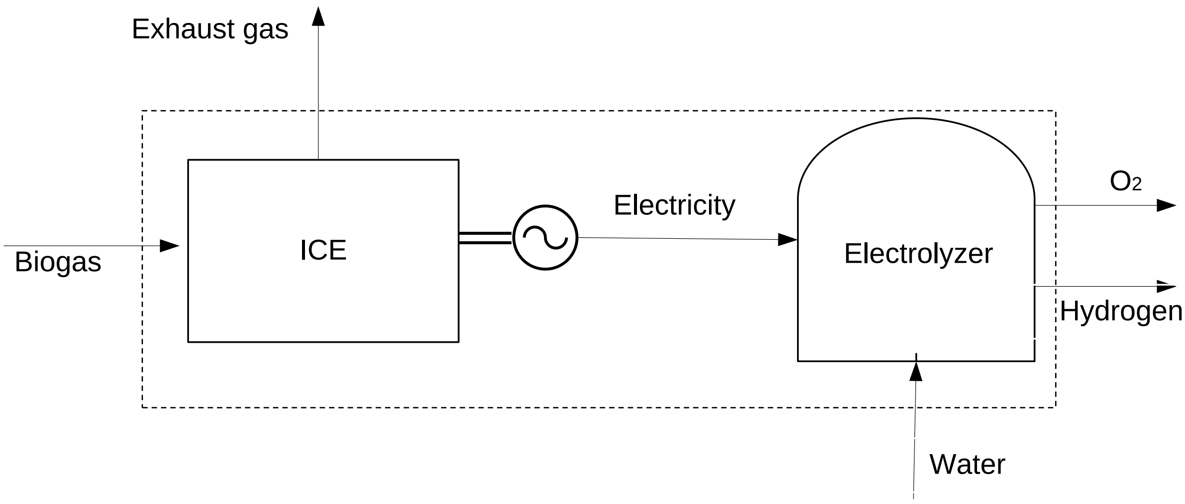

Figure 1: Flowchart of the electrolysis process (PAULINO, 2017)

The energy efficiency of the electrolysis process using the electricity produced during the biogas burning in the ICE was calculated by an adaptation of Braga et al. (2013), according to Eq. (1).

$$\eta_{electro.el.ICE} = \eta_{\text{electrolyzer}} * \eta_{el.ICE} \quad (1)$$

Where:

$\eta_{electro.el.ICE}$: energetic efficiency of the electrolysis process [-]

$\eta_{\text{electrolyzer}}$: efficiency of the electrolyzer [-]

$\eta_{el.ICE}$: electric efficiency of the ICE [-]

The energy efficiency of the electrolyzer was determined using Eq. (2) (BRAGA et al. 2013),

$$\eta_{\text{electrolyzer}} = \frac{\dot{m}_{H_2} * LHV_{H_2}}{E_{req.}} \tag{2}$$

Where:
$E_{req.}$: electricity required in the electrolyser [kW]
LHV_{H_2}: lower heating value of hydrogen[kJ/kg]
$\dot{m}_{H_2}$: hydrogen mass flow [kg/s]
$\eta_{\text{electrolyzerr}}$: efficiency of the electrolyzer [-]

The characteristics of the electrolyser selected for this study are given in table 2.

Table1: Electrolyzer characteristics (HYDROGENICS, 2016)

Capacity	600 Nm^3/h
Required electrical power	2940 kW
Water consumed	1.05 m^3/h

The Eq. (3) e (4) were utilized to determine the amount of biogas needed to produce the maximum power capacity in the ICE.

$$\eta_{el.ICE} = \frac{\dot{W}_{ICE}}{\dot{E}_{biogasICE}} \tag{3}$$

Where:

$$\dot{E}_{biogasICE} = \dot{m}_{biogasICE} * LHV_{biogas} \tag{4}$$

Where:
$\dot{E}_{biogasICE}$: power supplied by burning of the biogas in the ICE [kW]
LHV_{biogas}: lower heating value of biogas [kJ/kg]
$\dot{m}_{biogasICE}$: biogas mass flow in the ICE [kg/s]
$\dot{W}_{ICE}$: electric power produced in the ICE [kW]
$\eta_{el.ICE}$: electric efficiency of the ICE [-]

In order to find the electricity demand of the electrolyser, a biogas generator engine with 3,370kW and electrical efficiency of 42.9% (Caterpillar - model CG 260-16 (60 Hz)) was considered.

2.2 Energetic Analysis of the Steam Reform Process

According to Braga et al. (2013) the reactions indicated in Equations (5) and (6) occur in the main reformer.

$CH_4 + H_2O \rightarrow CO + 3H_2$ (steam reform of methane) (5)

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ (dry reforming of methane) (6)

According to Braga (2014), in 1 mole of biogas (0.55 mols of and 0.45 mols) all reacts in dry reforming.
Final reaction of the biogas steam reforming is shown in equation (7):

$$0.386\ steam\ reforming + 0.614\ dry\ reforming = final\ biogas\ reform \tag{7}$$

The following reactions can be used for steam reforming of biogas :

- Principal Reformer:

$$CH_4 + 0.386H_2O + 0.614CO_2 \rightarrow 1.614CO + 2.386H_2 \quad (8)$$

- Reactor shift:

$$1.614CO + 1.614H_2O \rightarrow 1.614CO_2 + 1.614H_2 \quad (9)$$

- Overall reaction with 74.4% efficiency:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (10)$$

The Figure 2 shows the flow diagram of the biogas steam reforming process used for energetic analysis.

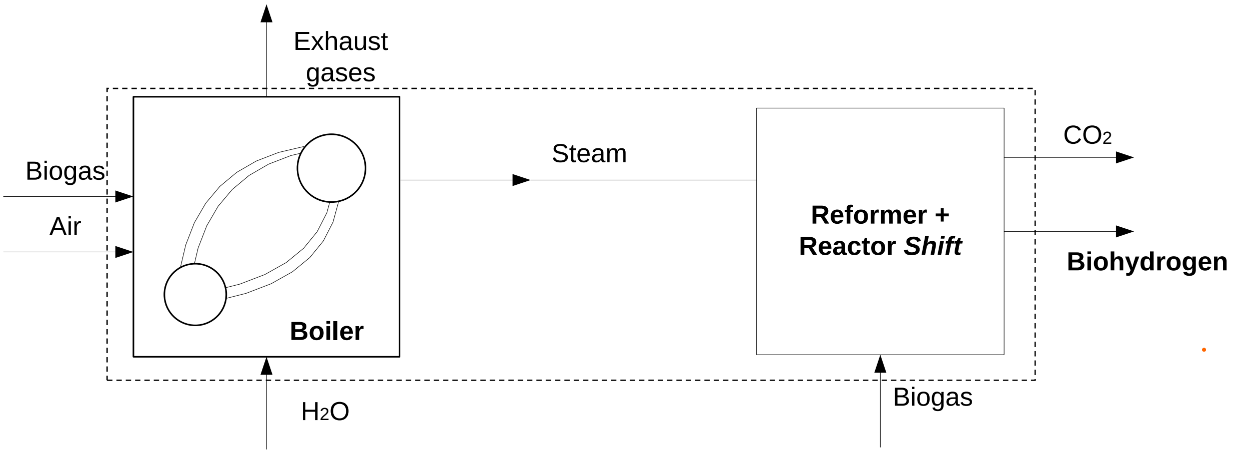

Figure 2: Flowchart of the steam reform process (PAULINO, 2017)

The energy efficiency of the biogas vapor reforming process can be calculated by equation (11), given by BRAGA (2014).

$$\eta_{reforma} = \frac{\dot{m}_{H_2} * LHV_{H_2}}{\dot{m}_{biogas.SG} * LHV_{biogás} + \dot{m}_{biogas.ref.} * LHV_{biogas}} \quad (11)$$

Onde:

$\dot{m}_{biogas.SG}$: biogas mass flow in the boiler [kg/s]
$\dot{m}_{biogas.ref.}$: biogas mass flow in the reformer [kg/s]
$\dot{m}_{H_2}$: hydrogen mass flow [kg/s]
LHV_{biogas}: lower heating value of biogas [kJ/kg]
LHV_{H_2}: lower heating value of hydrogen [kJ/kg]
$\eta_{reforma}$: energetic efficiency of the biogas steam reform process [-]

According to Krich et al. (2005), the efficiency of the biogas steam generator varies from 75% to 85%. In this paper the value of 85% was considered. According to Braga (2014), the temperature of the steam for the reforming process is 700 ºC. Avraam et al. (2010) indicate a vapor / biogas molar ratio of 3.04.

Equation (12) can be used to calculate the flow of biogas necessary (to burn) in the steam generator and to produce the required of the steam in the reforming process.

$$\dot{m}_{biogas.SG} = \frac{\dot{m}_{steam} * \Delta h_{steam}}{\eta_{SG} * LHV_{biogas}} \tag{12}$$

Onde:
LHV_{biogas}: lower heating value of biogas [kJ/kg]
$\dot{m}_{biogas.SG}$: biogas mass flow consumption in the steam generator [kg/s]
$\dot{m}_{steam}$: steam mass flow produced in the steam generator [kg/s]
η_{SG}: steam generator efficiency [-]
Δh_{steam}: variation of specific enthalpy of water in the steam generator [kJ/kg]

3. RESULTS OF ENERGETIC ANALYSIS

The Table 2 shows the results of the biogas mass flow necessary to the internal combustion engine, the efficiency of the electrolyser and the energy efficiency of the electrolysis process for a biohydrogen production of 600 Nm^3 / h, obtained of energy analysis applied to the electrolysis process.

Table 2: Results of the energy analysis of the electrolysis process (Paulino, 2017)

Results	Values
Biogas mass flow in the ICE ($\dot{m}_{biogasICE}$) [Nm^3/h]	2548
Efficiency of the electrolyzer ($\eta_{electrolyzer}$) [%]	61.13
Energetic efficiency of the electrolysis process ($\eta_{eletro.el.ICE}$) [%]	26.35

The Table 3 shows the results of the energy analysis of the steam reform process.

Table 3: Results of the energy analysis of the biogas steam reforming process (Paulino, 2017)

Results	Values
Biogas mass flow in the steam generator ($\dot{m}_{biogas.SG}$) [Nm^3/h]	403.51
Biogas mass flow in the reformer ($\dot{m}_{biogas.ref.}$) [Nm^3/h]	520.32
Steam mass flow produced in the steam generator ($\dot{m}_{steam}$) [m^3/h]	0.991
Energetic efficiency of the biogas steam reforming process ($\eta_{reforma}$)[%]	63.39

The Fig. 3 shows the comparison of the energy efficiencies of the electrolysis and the steam reforming process.

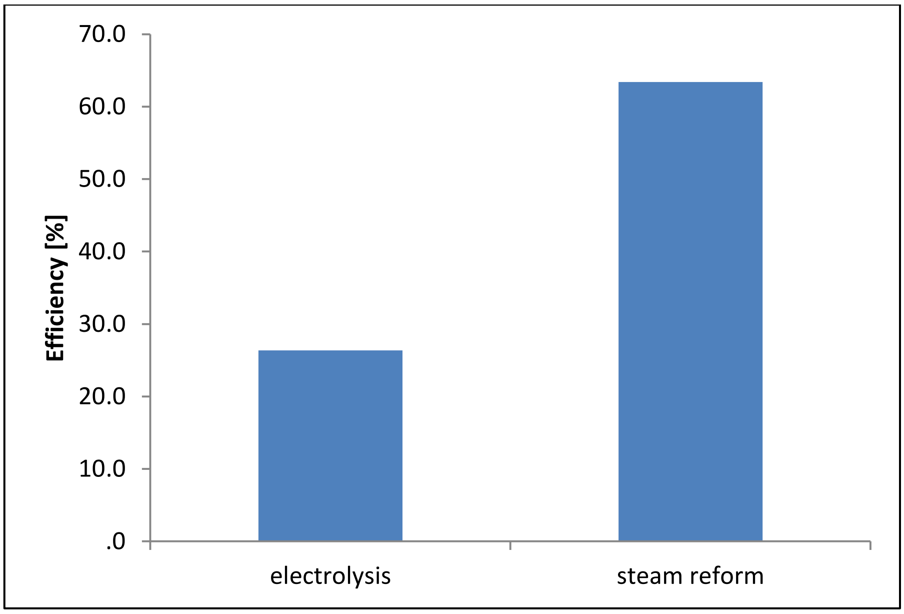

Figure 3: Process energetic efficiency

The Fig. 4 shows the comparison of the hydrogen production capacity in the city of São Paulo, considering the process of electrolysis and steam reforming of the biogas.

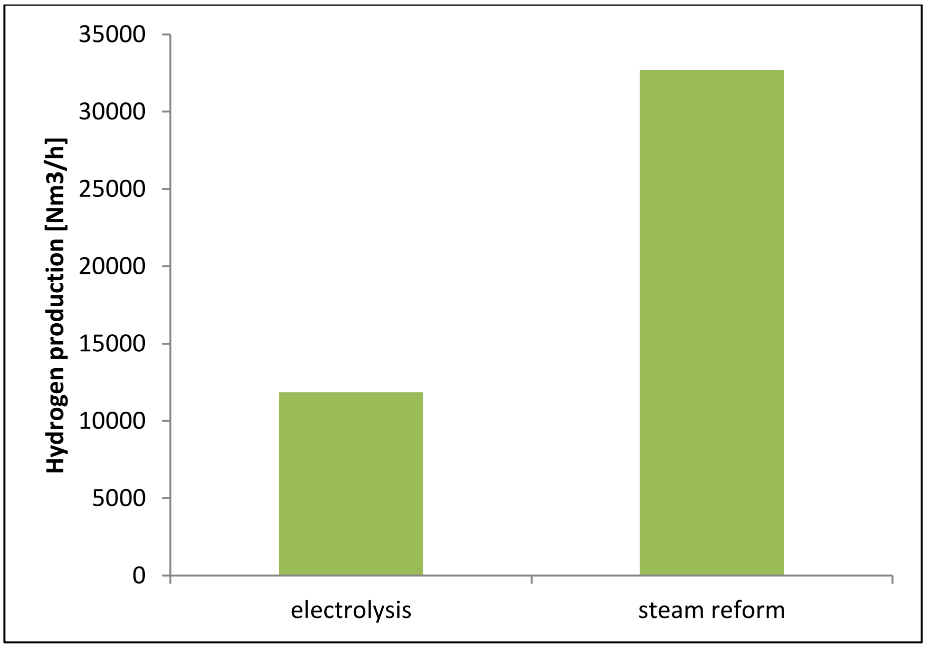

Figure 4: Hydrogen production potential

Through the Fig.4 is possible to observe that the hydrogen production capacity is higher when the steam reforming process is used, because this process presents greater energetic efficiency, according to Fig. 3.

4. CONCLUSIONS

The processes of electrolysis of the water operating with electricity obtained from the biogas burning in the internal combustion engine and the steam reforming of the biogas are important routes to obtain the biohydrogen.

The energy analysis showed that the biogas production (50,333 m3 / h) of the three landfills of the metropolitan region of the city of São Paulo, can produce 11852.15 Nm3 / h of hydrogen using the electrolysis process and 32688.51 Nm3 / h of hydrogen by the steam reform process. The steam reforming process is more energy efficient (63.39%) than the electrolysis process (26,34).

Finally, the city of São Paulo has great potential to produce biohydrogen from the biogas of its sanitary landfills, especially when it comes to the steam reform process.

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