

TECHNICAL AND ECONOMICAL STUDIES OF INTEGRATION OF HYDROGEN PRODUCTION IN BRAZILIAN SUGAR CANE INDUSTRY

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Abstract: One of the biggest challenges today is to develop clean fuels, which do not emit pollutant and with feasible implementation. One of the options currently under study, it is highlight the hydrogen production process. In this context, this paper aims to study the technical and economical aspects of the incorporation process of hydrogen producing by ethanol steam reforming in the sugarcane industry. Therefore, it has been proposed a modification in the traditional process of sugarcane industry, in order to incorporate hydrogen production, besides the traditional products (sugar, ethylic and anhydric alcohol). For this purpose, a detailed theoretical study of the ethanol production process, describing the considerations to incorporate the hydrogen production will be performed. After that, there will be a thermodynamic study for analyzing the innovation of this production chain, as well as a study of economic engineering to allocate the costs of products of the new process, optimizing it and considering the thermoeconomics as being as an analysis tool. This proposal aims to improve Brazil's position in the ranking of international biofuels, corroborating the nation to be a power in the hydrogen era.

Keywords: Hydrogen, renewable energy, sugarcane industry

Nomenclature:

| | |
|-------------|---|
| C_{comb} | Fuel cost (sugarcane bagasse) [US\$/kWh]; |
| C_{EtOH} | Ethanol cost [US\$/kWh]; |
| C_{H_2} | Hydrogen production cost [US\$/kWh]; |
| C_{MAN} | Maintenance cost [US\$/kWh]; |
| C_{OP} | Operational cost [US\$/kWh]; |
| E_{comb} | Energy provided by sugarcane bagasse [kW]; |
| E_{EtOH} | Energy provided by ethanol [kW]; |
| E_{H_2} | Energy provided by Hydrogen [kW]; |
| f | Annuity factor [1/year]; |
| H | Equivalent period of operation [h/year]; |
| Inv_{ref} | Reference investment for hydrogen production [$\times 10^4$ US\$]; |
| k | Payback period [year]; |
| K | Equilibrium constant |
| m_{H_2} | Production capacity of hydrogen [Nm^3/h]; |
| r | Annual interest rate [%]; |
| α | Advance degree; |
| ΔG | Gibbs energy [kJ/kgmol]; |

1. INTRODUCTION

Economic and social reasons have increased the ethanol use as alternative fuel to avoid environmental problems (such as increase of greenhouse effect), specially in the cities. Renewable fuels can be obtained from biomass such as

sugarcane, contributing to carbon sequestration. According to Ioannides (2001), ethanol is less toxic than methanol and besides that Brazil has the largest and most successful biofuel programs in the world, involving production of ethanol from sugar cane. Silveira J. L., Leal E. M. (2001) and Vasudeva et al. (1996) have shown that the better application of hydrogen is in a fuel cell. It can be a promising technology alternative for energy generation, specially in replacement of technologies that use natural gas and oil products (such as LPG, gasoline, etc.).

Hydrogen is the simplest, lightest and most plentiful element in the universe. It is made up of one proton and one electron revolving around the proton. In its normal gaseous state, hydrogen is colorless, odorless, tasteless, non-toxic and burns invisibly (in the case of air mixture). It should not be considered a “fuel”, but instead, should be considered as an energy transport mechanism. Currently, most hydrogen is made from natural gas through a process known as reforming. Reformers are reactors that produce mixtures containing hydrogen, carbon dioxide, and some other compounds, through the process called steam reforming, where superheated water and hydrocarbons react to produce a mixture with hydrogen, carbon monoxide, and carbon dioxide. This process is endothermic. Hydrogen can also be produced from a variety of sources including water and biomass [Silveira, 2009].

This work has studied the process incorporation of hydrogen producing by ethanol steam reforming in the sugarcane industry, according to the Fig.1. In this case, in addition to the production of sugar and ethanol, the Brazilian sugarcane industry would be able to produce biohydrogen.

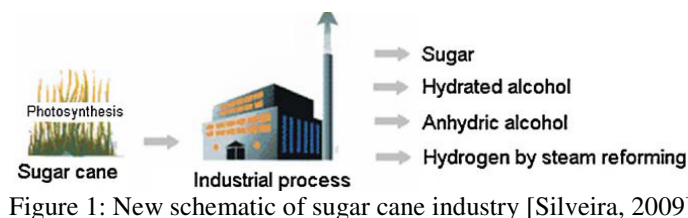


Figure 1: New schematic of sugar cane industry [Silveira, 2009]

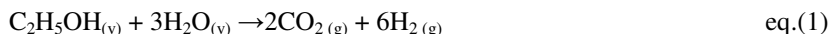
2. ETHANOL STEAM REFORMING

For hydrogen production, several technologies may be studied. Steam reforming is one of the most usual technologies installed in chemical industries. The reforming efficiency is obtained through studying of physical-chemical properties of feedstock, thermodynamic conditions (temperature and pressure of reaction, technical configurations of reformer such as dimensions and catalysts, and feedstock and water flows). The method to be utilized depends on the suggested fuel cell, which will use the reforming products. The fuel cell technology determines hydrogen purity and other reforming product rates. Steam reforming occurs in the presence of a catalyst, the syngas produced includes hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), among others. Some arrangements to minimize some reactions that can contribute to decrease the hydrogen production are necessary. Since this reaction is endothermic, heat from external sources is necessary. To minimize losses, some products of the steam reforming such as non-reacted fraction of reactants might be utilized to heat reactants burning them through after-burners [Silveira, 20].

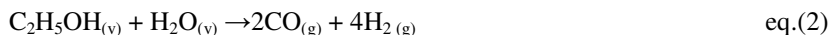
One of the most important is steam reforming of methane. One alternative is steam reforming of alcohols, specially ethanol. The use of this fuel is interesting in Brazil case, whereas is a greatest production of this fuel in the world and it is the best way to guarantee the volume of production necessary in the Brazilian case. The integration or association of hydrogen production with sugar industry, certainly, can put Brazil in a good classification in the “Hydrogen Era”, in the near future.

In the global reaction of hydrogen production utilizing ethanol, 6 mole of hydrogen for 1 mole of ethanol are produced.

(1) Global Reaction is shown in Equation 1 (eq.(1)). At high temperatures, this one consists in a reaction of ethanol and water in gaseous state resulting in the production of carbon dioxide and hydrogen, as shown by Appleby A. J. (1993):



(2) Steam Reforming Reaction. Equation 2 (eq.(2)) shows the steam reforming reaction, which is, an endothermic reaction of ethanol with water, resulting in the production of carbon monoxide and hydrogen. This reaction may occur through an external reforming:



(3) Water Gas Shift Reaction. It is an exothermic, reversible reaction (as shown in eq.(3)), that can occur at lower temperatures than the latter reaction. However, the CO conversion is incomplete and an additional process to remove it is necessary:



(4) Methanation. Several chemical reactions can occur simultaneously with the steam reforming of ethanol reaction. Equation 4 (eq.(4)) shows a representative equation, that is, production of methane from carbon monoxide:



(5) Boudouard Reaction. In this reaction, the production of carbon is described through the carbon monoxide decomposition, as shown, in eq. (5):



3. PHYSICAL-CHEMICAL ANALYSIS

The equilibrium constants associated with reactions previously studied may be expressed as follows (eq.(6)-eq.(9)):

$$K_1 = \frac{Y_{\text{CO}_2}^2 Y_{\text{H}_2}^6}{Y_{\text{EtOH}} Y_{\text{H}_2\text{O}}^3} P^4 \quad \text{eq.(6)}$$

$$K_2 = \frac{Y_{\text{CO}}^2 Y_{\text{H}_2}^4}{Y_{\text{EtOH}}^2 Y_{\text{H}_2\text{O}}} P^4 \quad \text{eq.(7)}$$

$$K_3 = \frac{Y_{\text{CO}_2} Y_{\text{H}_2}}{Y_{\text{CO}} Y_{\text{H}_2\text{O}}} \quad \text{eq.(8)}$$

$$K_4 = \frac{Y_{\text{CH}_4} Y_{\text{H}_2\text{O}}}{Y_{\text{CO}} Y_{\text{H}_2}^3} P^{-2} \quad \text{eq.(9)}$$

where P is the pressure, and y_i (eq.(10)) is a molar fraction of gaseous species, expressed as follows (in Pa):

$$Y_i = \frac{n_i}{n_{\text{tot}}} \quad \text{eq.(10)}$$

where n_i is the number of moles of each species, and n_{tot} is the sum of moles of all reactants or all products of reforming.

The equilibrium constants of reactions are linked with free energies of molecules in equilibrium.

Temperature Influence. The dependence of Gibbs energy with temperature may be expressed by several parameters, following these expressions (eq.(11), eq.(12)):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{eq.(11)}$$

$$d\left(\frac{\Delta G^0}{T}\right) = -\frac{\Delta H^0}{T^2} \quad \text{eq.(12)}$$

As steam reforming is an endothermic reaction, ΔH_0 is positive as equilibrium constant increases when temperature also increases. Fig. 2 shows Gibbs energy changes as function of temperature.

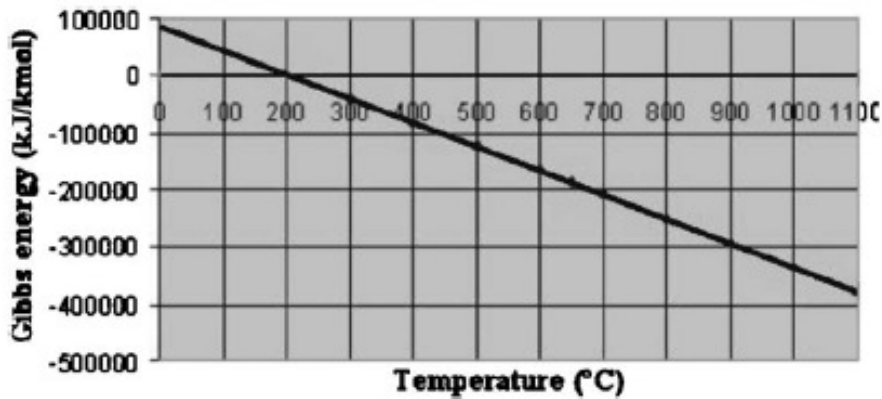


Figure 2: Gibbs energy as function of temperature

At 480 K (207°C), ΔG_0 is null, showing that the global reaction is possible only at high temperatures. According to the Le Chatelier principle, higher volume of products is formed at higher temperatures.

Equilibrium Composition. The reaction advance and Gibbs energy depletion continues to the equilibrium. The equilibrium composition as function of temperature can be determined, as shown in Table 1.

Table1: Chemical equilibrium of global reaction of steam reforming of ethanol

| $C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$ | | | | |
|---|---------------------------------|----------------------------|------------------------|------------------------|
| Input | | | | |
| Number of moles n_i | n | $3n$ | 0 | 0 |
| Overall number of moles $n_{tot}^{(in)}$ | $n_{tot}^{(in)} = n + 3n = 4n$ | | | |
| In equilibrium | | | | |
| Number of moles n_i | $n(1-\alpha)$ | $3n(1-\alpha)$ | $2n\alpha$ | $6n\alpha$ |
| Overall number of moles $n_{tot}^{(eq)}$ | $n_{tot}^{(eq)} = 4n(1+\alpha)$ | | | |
| Molar fractions y_i | $1/4(1-\alpha)/(1+\alpha)$ | $3/4(1-\alpha)/(1+\alpha)$ | $1/2\alpha/(1+\alpha)$ | $3/2\alpha/(1+\alpha)$ |

Supposing ideal behavior and excluding fugacity coefficient, the equilibrium coefficient is equal to K_p (equilibrium constant as function of partial pressure of each component). Knowing the molar fractions of each species is determined by the equilibrium coefficients (see eq. (6) and degree advance (α) of reforming, as shown, in equations 16 and 17 (eq. (16), eq. (17)). The equilibrium constant values, advance degrees, and molar fractions of hydrogen and ethanol as function of temperature in the range of 0–1200 K and at 1 atm are calculated through equations 13 and 14.

$$K = \frac{3^3 \alpha^8 p^4}{(1+\alpha)^4 (1-\alpha)^4} = \frac{27\alpha^8}{(1-\alpha^2)^4} p^4 \quad \text{Equilibrium constant} \quad \text{eq.(13)}$$

$$\alpha = \frac{\sqrt[8]{K}}{(\sqrt[4]{K} + \pm \sqrt{27p})^{1/2}} \quad \text{Advance degree} \quad \text{eq.(14)}$$

The behavior of advance degree as function of temperature can be seen in Fig. 3.

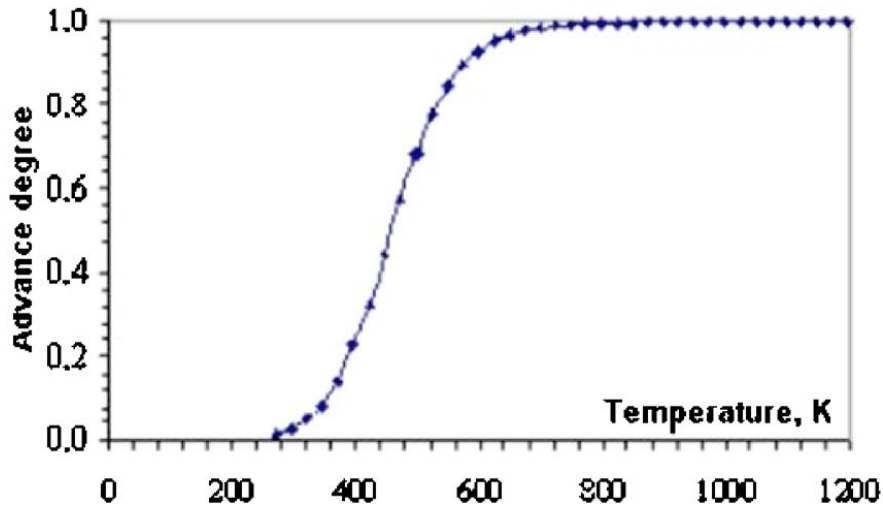


Figure 3: Advance degree of global reaction of steam reforming of ethanol as function of temperature

The increase of temperature contributes to global reaction progress and, hence, the hydrogen production. In the Fig.3 is shown that the best temperature of reformer is near 600 K.

4. ECONOMIC ANALYSIS

The methodology of economic analysis is based on calculations engineering economics developed by Silva M. E. (2010), considering the feasibility of the sugarcane industry to produce 1500 [Nm³/h] of hydrogen using ethanol. In order to reach this proposal, an economic analysis based on the investment of the hydrogen production system was developed, where were considered the input costs, operating cost, maintenance cost, operation period, interest rate and annuity factor.

According to Souza, A. C. C. (2005) and Silveira J. L. (1998), to determinate the cost of hydrogen production, the following equation were used (eq.(6)-eq(10))

The global equation for hydrogen cost is shown below (eq.(15))

$$C_{H_2} = \frac{Inv_{ref} \cdot f}{H \cdot \dot{E}_{H_2}} + C_{OP} + C_{MAN} \quad \text{eq.(15)}$$

where:

Operational cost using bagasse as fuel is shown below (eq.(16)) and According to Kothari et al (2008), the maintenance cost of steam reformer was estimated as 3% of investment (eq.(17)):

$$C_{OP} = \frac{E_{Comb} \cdot C_{Comb}}{E_{H_2}} + \frac{E_{EtOH} \cdot C_{EtOH}}{E_{H_2}} \quad \text{eq.(16)}$$

$$C_{MAN} = 0,03 \cdot \frac{Inv_{ref} \cdot f}{H \cdot \dot{E}_{H_2}} \quad \text{eq.(17)}$$

The equations of annuity factor (f) is shown in the eq.(18) and the equation of capital value is shown in eq.(19)

$$f = \frac{q^k \cdot (q-1)}{q^k - 1} \quad \text{eq. (18)}$$

$$q = 1 + \frac{r}{100} \quad \text{eq. (19)}$$

The reference investment (Inv_{ref}) was estimated using Boehm technic (1987), and its application is according to Fig.4:

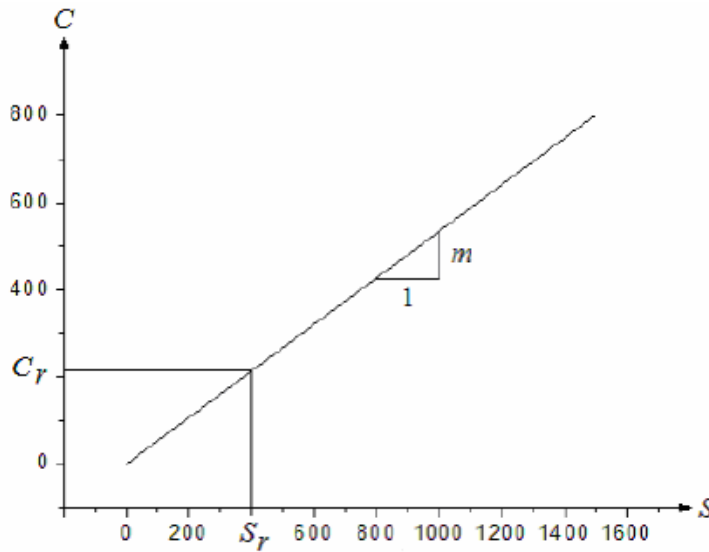


Figure 4 - Auxiliary curve to determine the reference cost

Through the figure 2 was be able to obtain the following equation eq.(20)

$$C = C_r \left(\frac{S}{S_r} \right)^m \quad \text{eq. (20)}$$

Silva M.E. (2010) has adapted the reference investment for steam reform process with hydrogen production range of 1 to 1500 [Nm³/h], resulting in the eq. (21)

$$Inv_{ref} = 400 \left(\frac{m_{H_2}}{750} \right)^{0,5304} \quad \text{eq.(21)}$$

5. RESULTS AND DISCUSSIONS

To calculations were utilized the value 0,7961 [l/h] obtained by Silva (2010) as experimental result of anhydrous alcohol amount for producing 1Nm³/h. Based on this previous study, it was obtained the value 0,8597 [l/h] for hydrated alcohol.

With these two parameters and adopting the hydrated alcohol cost is 70% of anhydrous alcohol, it was possible to make a comparison between them. All the figures below (Fig.5-11) presents an equivalent period of operation (H) of 4000 [h/year]

The Fig. 5 presents the hydrogen production cost as function as payback period for anhydrous alcohol. The annual interest rate (r) ranged from 4 to 12%. As expected, the results show that the production cost decreases with the increase of payback period (k). In relation to interest rate, as much higher will be the production cost.

The Fig. 6 presents the hydrogen production cost as function as payback period for hydrated alcohol. The result shows the same behavior obtained for anhydrous alcohol.

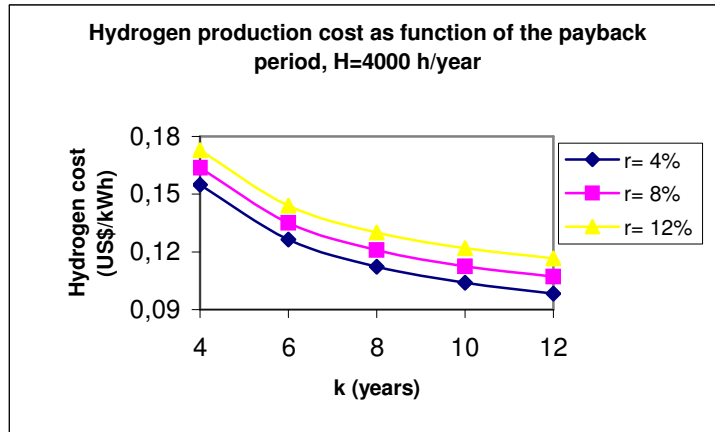


Figure 5. Hydrogen production cost for anhydrous alcohol as function of payback period for different annual interest rate

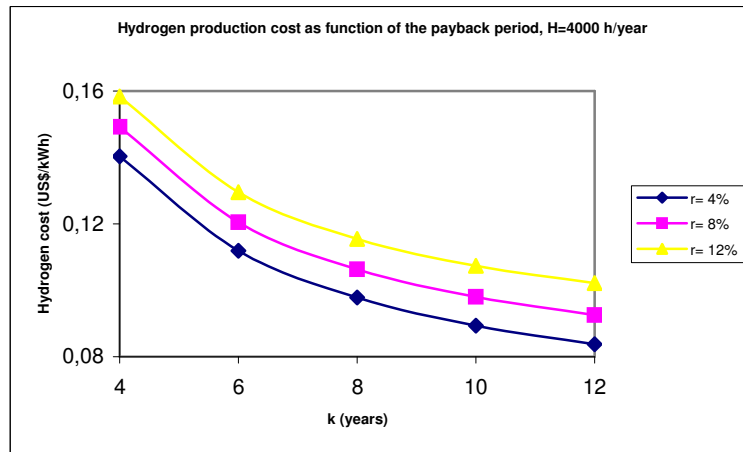


Figure 6. Hydrogen production cost for hydrated alcohol as function of payback period for different annual interest rate

On the Fig. 7 is shown the hydrogen production cost as function of annual interest rate, with different payback period for anhydrous alcohol, this result is in accordance with previous results. The same behavior is presented on Fig. 8 for hydrated alcohol.

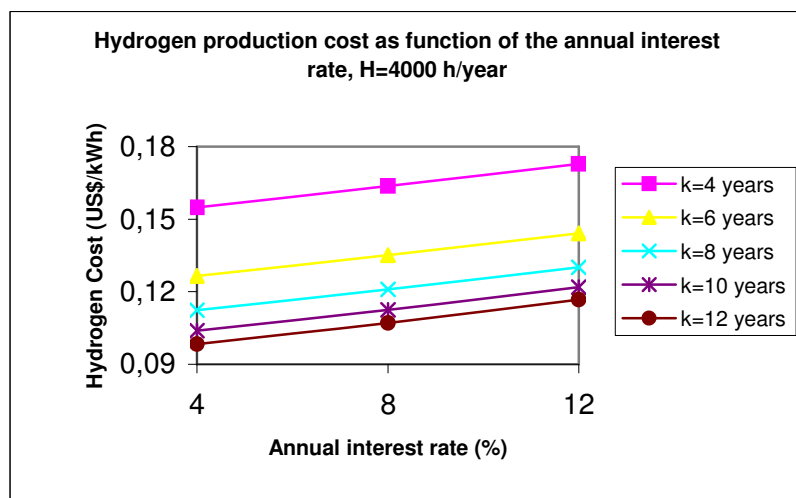


Figure 7. Hydrogen production cost as function of annual interest rate with different payback period for anhydrous alcohol.

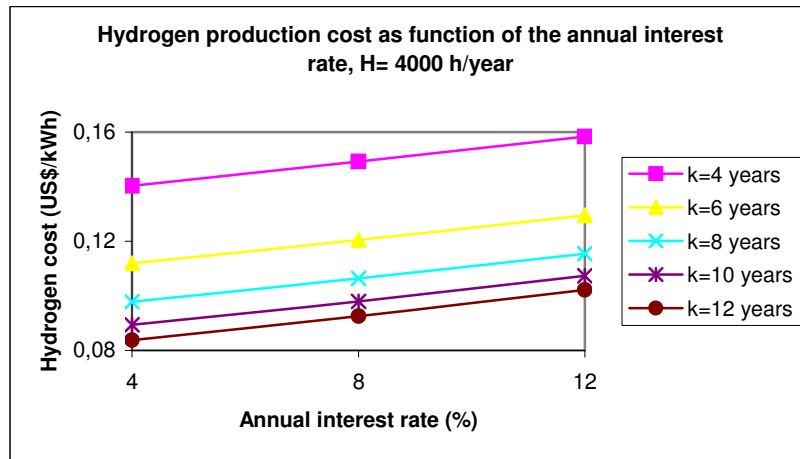


Figure 8. Hydrogen production cost as function of annual interest rate with different payback period for hydrated alcohol.

On Fig. 9 is shown the hydrogen production cost as function of annual interest rate with different equivalent period operation, for payback period of 8 years. The same features are shown for hydrated alcohol, as can be seen on Fig. 10.

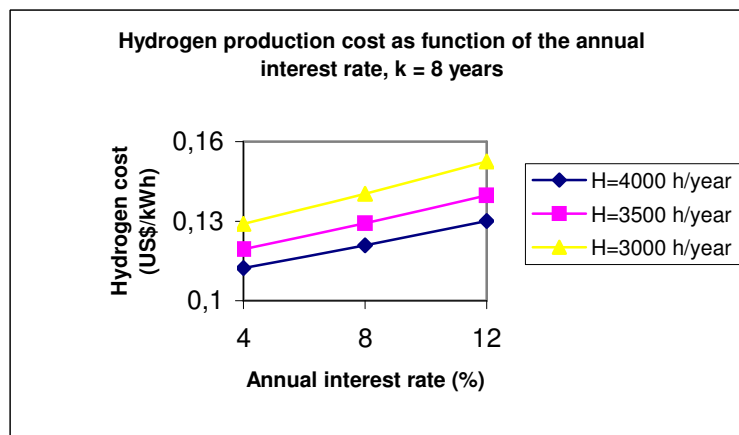


Figure 9. Hydrogen production cost as function of annual interest rate for anhydrous alcohol with different utilization period.

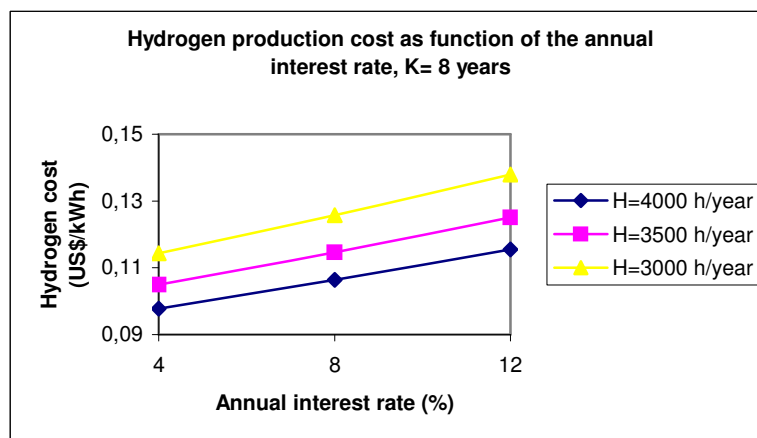


Figure 10. Hydrogen production cost as function of annual interest rate for hydrated alcohol with different utilization period.

On Fig. 11 is show the comparison between hydrogen production cost for anhydrous and hydrated ethanol as function of payback period. It is noticeable that hydrated alcohol presents hydrogen production cost lesser than anhydrous alcohol because the hydrated alcohol price was considered 70% of anhydrous alcohol price.

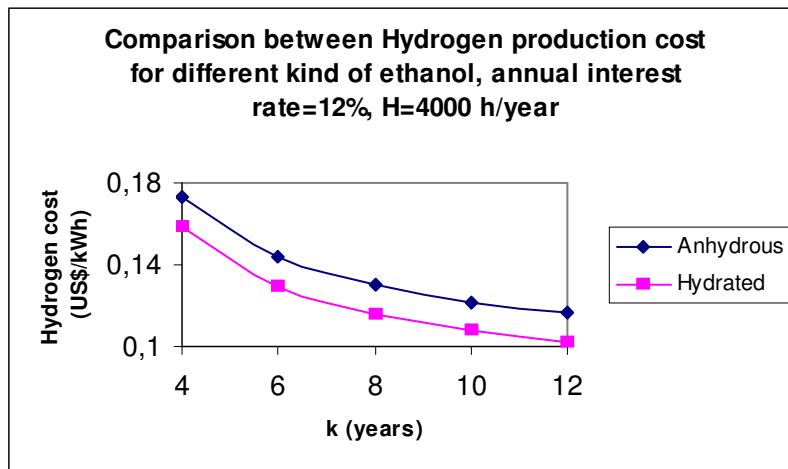


Figure 11. Comparison between hydrogen production cost for different kind of ethanol as function of payback period.

6. CONCLUSIONS

This paper was developed to show the advantages of hydrogen producing from ethanol steam reforming and show what kind of ethanol would be more feasible to hydrogen production: the anhydrous or hydrated. Although the anhydrous alcohol has higher lower heating value and demanded less alcohol amount to produce 1 [Nm³/h] of hydrogen, the results of economic analysis showed that hydrated alcohol is more viable than anhydrous alcohol. The main reason for this behavior was the cost difference between anhydrous and hydrated alcohol, in the specific situation of this work, the hydrated alcohol cost was adopted as being 70% of anhydrous value. The results showed that hydrated alcohol is the best alternative to produce hydrogen in the production chain of sugarcane industry.

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