HYDROGEN PRODUCTION INTEGRATED IN THE ETHANOL PRODUCTION PROCESS

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ABSTRACT

Because of the increase in gas emissions that intensify the greenhouse effect and the need for diversification of the world energy matrix that arises from this context, debates and research on energy sources that reduce environmental impacts and replace fossil fuels. Among them, two alternatives to the use and dependence on these fuels, which have gained visibility, are biofuels and hydrogen. The Brazilian sugar and alcohol industry is responsible for producing first and second generation ethanol, in addition to enabling the production of other biofuels and electricity from the use of residues from the ethanol production process itself, such as sugarcane bagasse and straw. For instance, fast pyrolysis of straw can produce bio-oil, which after an appropriate treatment can be used as a fuel for transport sector. Thus in this study, the integration of hydrogen production into the ethanol and sugar production process is proposed to use in the hydrotreatment of bio-oil produced through fast pyrolysis of sugarcane straw. Therefore, this study aims to perform energy and exergy assessments of different alternatives of hydrogen production and their integration into the ethanol and sugar production process from sugarcane. The different routes studied were: electrolysis, steam reforming of biogas and steam reforming of the ethanol. In addition, the impacts on the cogeneration system of the production process are also analyzed.

Keywords: Sugarcane, Hydrogen, Integration, Hydrotreatment, Bio-oil

Introduction

International debates on the demand for renewable fuels and those that have less environmental impact have gained strength in recent years. Due to global warming, which is a result of the increase in the gas emissions that intensify the greenhouse effect, the need to diversify the world's energy matrix has increased. This is because such a matrix has main sources are fossils fuels, which in addition to being pollutants, are finite. In this context, the need for biofuels has increased globally. So investments and development of new technologies that enable and enhance the production of these fuels expanded. In the midst of this situation, of particular note is the production of second-generation biofuels.

On the other hand, hydrogen stands out worldwide as an alternative fuel to fossil fuels, mainly due to its combustion generating just water vapour [1]. Besides, H_2 can be used as a reactant in the chemical and petroleum industries. Another possibility for applying H_2 is upgrading biofuels, such as the pyrolysis bio-oil. Bio-oil is one of the products of fast pyrolysis of sugarcane straw, so it is possible to treat it in order to obtain biofuels with higher added value such as synthetic gasoline or synthetic diesel, fuels composed of renewable hydrocarbons that can be used in internal combustion engines.

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Among bio-oil treatments, hydrotreatment and hydrocracking can be highlighted for upgrading pyrolysis oils. However, significant amounts of hydrogen are required. Furthermore, it is important to emphasize that H_2 is not found in free form in nature. Because of that, technologies such as water electrolysis, methane reforming and ethanol reforming have been studied to obtain hydrogen.

Thus, the objectives of this study include studying three alternatives for hydrogen production (water electrolysis, methane reforming and ethanol reforming) and its incorporation in the sugar and alcohol plants aiming at an integrated production of second generation biofuels.

Technologies and raw materials for obtaining hydrogen – Evaluated cases

Hydrogen produced from renewable sources has been seen as a strong contributor to the decarbonization of energy systems, such as the industrial and automotive sectors. However, it is important to point out that the environmental benefits of using hydrogen as an energy source are too dependent on the technologies used to produce H_2. Hydrogen can be produced from different primary energy sources. To differentiate these different ways of obtaining H_2, colors are used [2]. The present study focused on the production of H_2 obtained from renewable raw materials and renewable energy sources. In this case, these are the products and by-products of sugarcane processing, such as ethanol, biogas produced from the digestion of vinasse and surplus bioelectricity from the plant's cogeneration system that can be used for water electrolysis. The technologies analyzed in this study are presented in the following sections.

Case I - Water Electrolysis

The electrolysis of water consists of a process in which the water molecule is broken, thus forming O_2 and H_2 by means of a continuous electric current that makes the water dissociate from redox reactions. This is an endothermic process in which the energy is absorbed in the process and is converted into heat at the electrodes releasing the hydrogen and oxygen in gas phase. In this study it was assumed the use of surplus electricity for H_2 production.

According to [3], modern electrolysers have a energy consumption between 4.0 to 5.0 kWh/Nm^3 of H_2.

Case II - Biogas from vinasse biodigestion

The main component of biogas is methane, CH_4, there are several conversion process that can be used to produce H2 from CH4: steam reforming, partial oxidation, autothermal reforming and dry reforming. This study assumed the biogas production from vinasse biodigestion, a cleaning process for raw biogas for H2S removal and the steam reforming for H_2 production being that steam reforming being the most used technology, representing 48% of world production [4].

Case III - Ethanol reforming

Ethanol is considered a fuel that is easy to handle, transport, store, with low toxicity and volatility, together, these characteristics make it desirable for use in obtaining H_2. The technology assumed in this study was the ethanol reforming, which is an endothermic process formed by the reaction of ethanol with water in the presence of catalysts, which increase the reaction rates resulting in a mixture of gases composed of H_2, CO and H_2O [5]. Still according to [5], the process consists of two steps, the first under high temperature conditions (steam reforming reactions), and the second at low temperatures (water-gas shift reactions).

Methods

For this study, mass and energy balances were structured, from the raw materials available at the plant, with the objective of analyzing the feasibility of hydrogen production.

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It was assumed a sugarcane plant that process 500 tonnes of sugarcane per hour and produces sugar (68.4 kg/t cane), hydrated ethanol (21.1 L/t cane) according [6]. For this study the vinasse production was 247.8 m^3/h and the surplus electricity was 40.600 kW for a cogeneration system with back-pressure steam turbines. Table 1 presents the main parameters assumed in modeling and simulation, additional data was assumed from [7].

Table 1 – Main parameters assumed for analysis. Source: [7]

Parameter	**Value**
Electrolysis	
Energy consumption of electrolyser[a], kWh/Nm^3 of hydrogen	4.3
Ultrapure water requirement for electrolysis[b], L of water/kg of hydrogen	9
Cooling water requirementb,c, (L/h) per MW of electrolyser capacity	400
Water recovery in standard filtration (pre-treatment)b,d, %	98
Water recovery in polishing to ultrapure standardb, %	75
Biogas reforming	
Power consumption in dessulphurisation[a], kWh/Nm^3 of raw biogas	0.024
Reforming reactor temperature,°C	850
Reforming reactor pressure, bar	20.1
Steam/Carbon ratio in reforming (mol/mol)	2.87
Water-gas-shift reactor temperaturec, °C	400
Conversion of CO in WGS reactord, %	75
Hydrogen recovery in PSA (% of inlet H2)	75
Ethanol reforming	
Specific H_2 production from ethanol, kg H2/kg ethanol	0.219
Water consumption, kg water/kg ethanol	1.6
Additional heat supply, kWh/kg ethanol	1.25
Specific power consumption, kWh/kg ethanol	0.0441

Regarding modelling and fast pyrolysis of sugarcane straw as well the hydrotreatment and hydrocracking process, data from Salina et al. [8] and Santos et al. [9] was assumed.

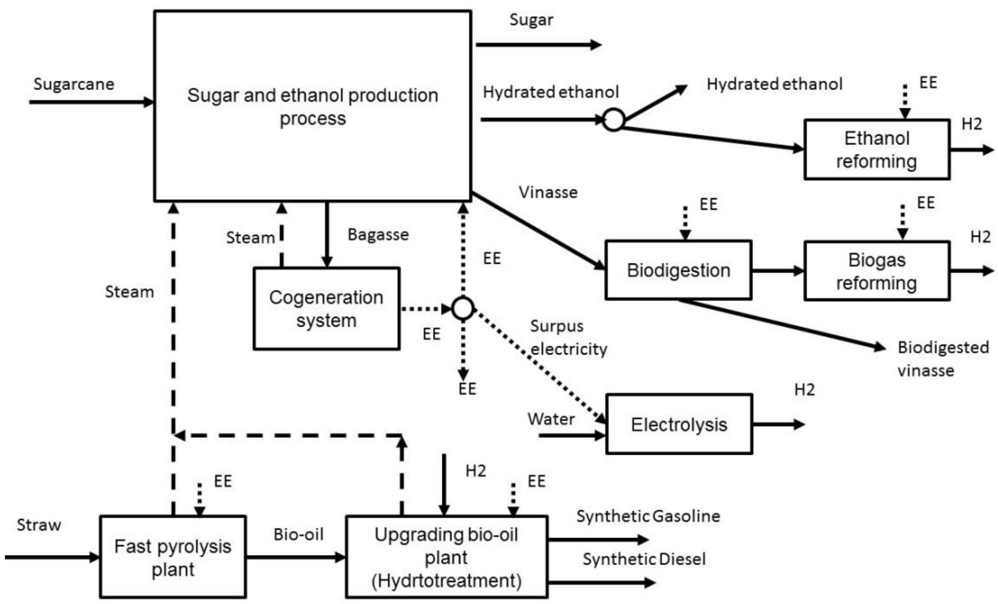

Figure 2 – Flow sheet of technologic alternatives for H_2 production and its integration with fast pyrolysis and the upgrading bio-oil plant

Results

Figure 1 presents the hydrogen production potential from raw materials available in sugar and ethanol production plant. These values can be compared with the H_2 necessary for make-up in the bio-oil upgrading plant, which is 10,938 Nm^3/h (for the treatment of 21.1 t of bio-oil from fast pyrolysis of sugarcane straw). Thus, the H_2 production represents 86.3%, 31.3% and more than 100% for cases I, II and III respectively.

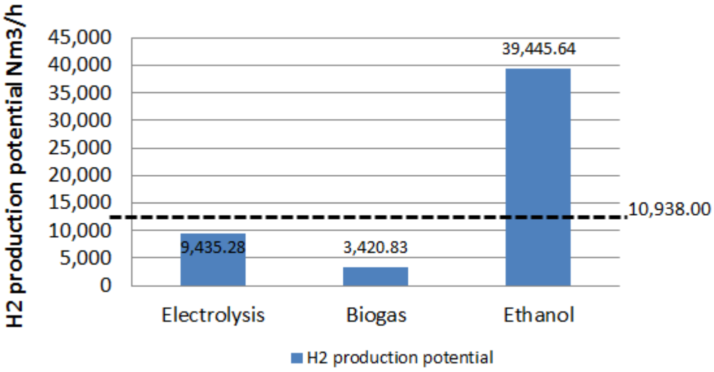

Figure 1 – H_2 production potential

Table 2 presents the main results of water, electricity, and raw materials necessary for H_2 production, as well as energy and exergy efficiencies. Efficiencies were calculated using input and product approach. Concerning Case II, in addition to H_2 production, there is the possibility of produce steam at 2.5 bar that can be sent to the conventional sugar and ethanol production process. The energy and exergy efficiency resulted 56.2% and 64.7% respectively, taking into account only the H_2 as a product, moreover taking into account the steam produced as well, the values resulted 80.1 and 71.9 for the energy and exergy efficiency respectively.

Table 2 – Main results of evaluation – Energy and exergy efficiencies

Parameter	Case I	Case II	Case III
Water consumption, m^3/h	10.9	4.6	7.0
Electricity consumption, kW	40,600	423,2	197,9
Bagasse consumption, t/h	-	2.0	4.0
Biogas consumption, Nm^3/h	-	2359.1	0
Ethanol consumption, t/h	-	-	4.5
Hydrogen production, Nm^3/h	9,435.3	3,420.8	10.938,0
Steam for process, t/h	-	7.2	-
Energy efficiency, %	69.6	80.1 (56.2)	79
Exergy efficiency, %	68.5	71.9 (64.7)	70.3

LHV of H_2: 33.33 kWh/kg; LHV of ethanol: 26,334 kJ/kg; LHV of biogas: 5.73 kWh/Nm^3; LHV of bagasse: 7.640 kJ/kg (50% of moisture content); specific exergy of H_2: 236,1 kJ/mol; specific exergy of hydrous ethanol: 27.620 kJ/kg; specific exergy of biogas: 18.499 kJ/kg; specific exergy of bagasse; 10,055 kJ/kg, specific exergy of water: 50 kJ/kg

Conclusions

Three routes of hydrogen production were evaluated in this study assuming as feedstock products and by-products available in sugar and ethanol production process aiming to match the hydrogen consumption of a bio-oil upgrading plant. Energy and exergy efficiencies were calculated as well. From the results obtained only with ethanol reforming (Case III) it is possible to achieve the H_2

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production necessary for hydrotreatment of 21.1 t/h of bio-oil. In this case is consumed 4.5 t/h of ethanol, which represents 27.7% of the ethanol produced in the plant. Moreover Case II presents the possibility of steam production that can be integrated to the conventional sugar and ethanol production process; taking into account this steam as a by-product in addition to the H_2 produced, Case II presents energy and exergy efficiencies of 80.1% and 71.9% respectively.

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