Energy evaluation of hydrogen production integrated into the ethanol and sugar production process

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Abstract:

The sugarcane industrial sector is one of the main Brazilian economic activities due to its high efficiency and competitiveness, producing ethanol and sugar for internal and external markets. On the other hand, green hydrogen, produced from renewable energy, has emerged as a promising climate-neutral energy carrier over the last years; thus, several countries have published hydrogen roadmaps and are supporting the development of a hydrogen economy. Currently, hydrogen is produced mainly from natural gas through a reformation process; the refineries and the chemical industry are the main hydrogen consumers on the demand side. This hydrogen, produced from natural gas or methane without capturing the greenhouse gases made in the process, is classified as Grey hydrogen. In this way, in this study, the integration of Green hydrogen production into the conventional ethanol and sugar production process is proposed to use in the hydrotreatment of bio-oil produced via fast pyrolysis of sugarcane straw. Nevertheless, the sustainability and efficiency of the integrated process depend on the route adopted for hydrogen production. Thus, this study aims to perform an energy evaluation of different routes of hydrogen production and their integration into the ethanol and sugar production process from sugarcane. The different alternatives evaluated are: i) electrolysis using the surplus electricity in the process; ii) steam reforming of biogas produced from vinasse; iii) steam reforming of part of the ethanol produced. Furthermore, the impacts on the cogeneration system of the production process will also be evaluated.From the evaluated cases, ethanol reforming presented the lowest water consumption (14.1 L/t cane) and the lowest impact in cogeneration system (-6.3% in surplus electricity). Nevertheless Case III requires the consumption of 27.7% of the total ethanol produced in the mill.

Keywords:

Sugarcane; hydrogen; heat integration; hydrotreatment.

1. Introduction

In recent decades, debates have grown significantly about the use and dependence on fossil fuels as a result of the release of gases that intensify the greenhouse effect and global warming. Because of this, studies and research involving the use of alternative fuels have gained increasing prominence. Among these, hydrogen production has shown positive results and attracted the attention of the international market.

Hydrogen (H_2) has several advantages, such as its combustion only results in water, which makes its use especially attractive as a fuel since it is considered a clean energy. In addition, its heating value on a mass basis is significantly higher than that of fossil fuels, approximately three times that of fossil fuels [1], [2] . Given this, H_2 is an alternative energy source already widely studied, mainly for application in fuel cells. Moreover, H_2 is used as a reactant in the chemical and petroleum industries, for instance, ammonia production, petroleum processing and methanol production. However, H_2 is not found in free form in nature. Therefore, technologies such as water electrolysis, methane reforming and ethanol reforming have been

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widely studied in order to obtain hydrogen. Another possibility for applying H_2 is upgrading biofuels, such as the pyrolysis bio-oil.

Mechanical harvesting of sugarcane increased the availability of straw in the field, which can be used as fuel in boilers or as raw material for second-generation biofuel production through biochemical and thermochemical routes. Regarding the thermochemical routes, the fast pyrolysis allows to production of bio-oil from sugarcane straw that can be used for heating applications. However, there are limitations to the use of pyrolysis bio-oils as fuel in the transport sector because of its high oxygen content (35–40 wt%), which gives bio-oil unwanted properties such as low energy content, corrosiveness, high viscosity and aging [3].

There are several technologies for bio-oil upgrading, according to Sharifzadeh et al. [4], these processes can be classified into physical and chemical technologies. Concerning the chemical processes, hydrodeoxygenation (HDO), also known as hydrogenation or simply hydrotreatment, is the leading technology for upgrading pyrolysis oils, moreover compounds contained in gasoline and diesel can be obtained through this process; however, significant amounts of hydrogen are required as well as high temperatures and pressures.

In the existing literature, there are several studies regarding H_2 production in sugarcane production plants; however, these studies do not compare technologies, nor evaluate heat integration between processes or impacts in the cogeneration system. Thus, this work aims to evaluate the possibilities and opportunities of integrating hydrogen production into the sugarcane processing plants to use the produced hydrogen to upgrade pyrolysis bio-oil aiming at the production of synthetic gasoline and diesel. For this purpose, three technologies for H_2 production were studied: water electrolysis, methane reforming and ethanol reforming. Thus, mass and energy balances were performed with the objective of analysing how much H_2 is necessary for the upgrading process, as well as how much it is possible to obtain through each technological route, from the raw materials available in sugarcane factories, in addition to the possibility of analysing the impacts within the sugar and ethanol production process. The novelty of this study is to present the potential of renewable H_2, from feedstocks available from a sugarcane processing plant, for the specific application of bio-oil upgrading in the context of a biorefinery, as well as investigating the opportunities of heat integration aiming at a more efficient and sustainable production process.

2. Hydrogen production processes and feedstocks

According to IEA [5], in 2021, almost total global H2 production came mainly from fossil fuels, 62% from natural gas without CCUS (Carbon Capture, utilisation and storage), 19% from coal, mainly in China and 18% as a by-product from naphtha reforming at refineries, approximately 0.7% from oil and approximately 0.04% from water electricity. Regarding the low emission H2 production, it accounted for less than 0.7%, almost all from fossil fuels with CCUS.

There are several technologies and routes for hydrogen production, which depends mainly on the material that contains the hydrogen (hydrocarbon or non-hydrocarbon), energy source and catalyst material. The selection of feedstock and production pathway determines the cleanness, cost-effectiveness, efficacy, and feasibility of hydrogen production [6]. The cleanness of a hydrogen production pathway depends on the GHG emissions associated with the life cycle of produced hydrogen determined through LCA (Life Cycle Assessment). Furthermore, some studies in the literature classify the hydrogen production pathways in colours based on their associated emissions. For instance, grey hydrogen is associated with dirty and polluting production, such as natural gas reforming without CCUS, blue hydrogen considers the use of CCS (Carbon Capture and Storage), while green hydrogen refers to renewable energy for hydrogen production.

This study focused the hydrogen production from renewable raw materials and energy sources that are products and by-products of sugarcane processing, such as ethanol, the biogas produced from anaerobic digestion of vinasse, and the surplus bioelectricity from cogeneration system that can be used for water electrolysis. Next, there is a summary description of the production routes that were assumed in this study:

2.1. Water electrolysis

Water electrolysis is the process responsible for the breakdown of the H_2O molecule into H_2 and O_2 from the application of a continuous current of electricity that, through redox reactions, dissociates the water. It is considered an endothermic process because energy is absorbed and converted into heat in the electrodes, subsequently converted into chemical energy resulting in gaseous H_2. This technology can be described by the reaction:

$$H_2O_{(l)} + \text{energy} \rightarrow H_{2(g)} + 1/2\ O_{2(g)} \qquad (1)$$

The reactions that take place at the cathode and anode, respectively, are:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

$$2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^- \qquad (3)$$

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According to [2], modern electrolysers have the capacity to reach an efficiency that varies from 75% to 90%, which is equivalent to a consumption of 4.0 to 5.0 kWh/Nm^3 of H_2.

2.2 Methane reform from biogas

Biogas is the result of the anaerobic digestion process, and their main components are methane (CH_4) and carbon dioxide (CO_2). Because of its high methane content (between 50 and 60 % in molar basis), biogas can be subjected to methane reforming to produce hydrogen. The methane reforming processes that can be applied for hydrogen production are: steam reforming, partial oxidation, autothermal reforming and dry reforming. Among them, steam reforming is one of the most used, representing 48% worldwide [7]. This process can be described globally through the following reaction:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

2.3 Ethanol reforming

Ethanol is considered a raw material with a strong potential to produce hydrogen. This is due to its well-established handling, transport and storage technologies, low toxicity and volatility characteristics, and economic and thermodynamic viability.

To obtain hydrogen from ethanol, steam reforming of ethanol is used. This is an endothermic process characterized by the reaction of ethanol with water when they are in the presence of catalysts. In this environment, the reactions will be intensified, producing a gas mixture (syngas) that contains H_2, CO and H_2O [8].

According to Teixeira et al. [8], the ethanol conversion into hydrogen has an efficiency of 93.7%, and the suitable temperature range for this process took place is between 800 K and 1000 K. However, the conversion depends on the physic-chemical characteristic of fuel and the conditions of temperature, pressure, fuel-steam ratio and reforming techniques.

Two stages mark the steam reforming of ethanol: steam reforming reactions and water-gas shift reactions, the first of which is characterized by high temperatures and the second by low temperatures.

The reactions below represent the two steps, respectively:

Steam reforming: $C_2H_5OH_{(v)} + H_2O \rightarrow 2CO + 4H_2$

Water-gas shift reaction (WGS): $2CO_{(g)} + 2H_2O \rightarrow 2CO_2 + 2H_2$

The reaction that encompasses the entire process can be written as follows:

Overall reaction: $C_2H_5OH_{(v)} + 3H_2O_{(v)} \rightarrow 2CO_2 + 6H_2$, $\Delta H = 207.7$ kJ/mol

The choice of catalysts and supports is an important factor to be considered since their choice will impact the amount of H_2 that will be obtained. According to [8], the combination of Cu and Ni achieved the best efficiency: 90% H_2.

3. Methods

In order to analyse the feasibility of hydrogen production in sugar and ethanol production plants, mass and energy balances were performed in order to quantify the amount of H_2 that is possible to produce from available inputs through the proposed methods. The first analysis focuses on the potential of H2 production. In contrast, the second aims to evaluate the amount of raw materials and energy necessary to produce a certain amount of H_2, which is needed for a hydrotreatment plant that upgrades the bio-oil produced from the fast pyrolysis of sugarcane straw.

3.1. Evaluated cases

3.1.1. Case 0 – Base case

The base case corresponds to the production process of sugar, ethanol and bioelectricity from sugarcane. In it, the starting point is the processing of 500 t/h of sugarcane. Mass and energy balances in this process were performed in previous research studies [9],[10]. Figure 1 shows the main flows of the production process.

In this process, it was assumed that 50% of total recovery sugars from sugarcane were sent to sugar production while the remaining was directed to hydrous ethanol production. Regarding the bagasse usage, from the total produced (136 t/h), 5% (6.8 t/h) is reserved for start-up operations, 5 kg/t cane, equivalent to 2.5 t/h, is used in filters, while the remaining (126.7 t/h) is used as fuel in the boiler of the cogeneration system, which is based on a steam cycle with condensing extracting steam turbines (CEST) in order to maximise the electricity production; thus no surplus bagasse is obtained. The cogeneration system supplies steam and power to the production process (Fig. 1), and the main parameters of the cogeneration system are presented in Table 1.

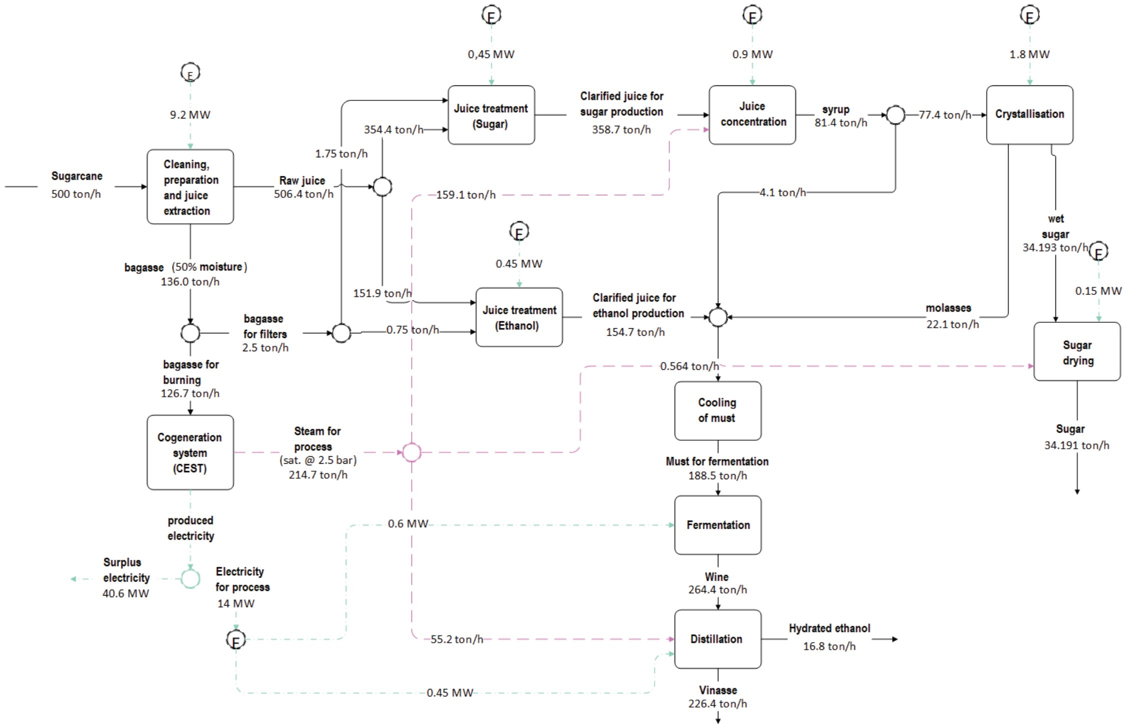

Figure. 1. Fowsheet of the conventional ethanol and sugar production process

Table 1. Main parameters of the cogeneration system of conventional process

Parameter	Value
Steam consumption, kg/t cane	437.6
Bagasse LHV (50% moisture content), MJ/kg	7.64
Electricity consumption in the conventional process, kWh/t cane	28
Boiler thermal efficiency, LHV basis,%	85
Isentropic efficiency of turbines and pumps, %	80
Condensing pressure, kPa	10
Temperature of live steam, °C	520
Pressure of live steam, bar	65
Process steam pressure, bar	2.5

Source: Palacios-Bereche et al. [10]

3.1.1. Case I - Water electrolysis

Table 2 presents the main parameters assumed for water electrolysis evaluation. The specific electricity consumption was assumed from the manufacturer Norsk Hydro A.S. according to [2] and [11].

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Table 2. Main parameters of water electrolysis assessment

Parameter	Value
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 requirement[b,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 standard[b], %	75
Energy consumption in water treatment system [b,d], kWh/m^3 of water	2
Energy consumption related to cooling water system, kWh/m^3 cooling water	0.0465

[a]Norsk Hydro A.S., [b]Madsen [11], [c]For evaporative cooling tower, [d]For groundwater,

Concerning to the water treatment, it was assumed a pre-treatment with standard filtration and further polishing to achieve the ultrapure standard. Water consumption for electrolysis as well as make-up water for the cooling water system in an evaporative tower, were taken into account.

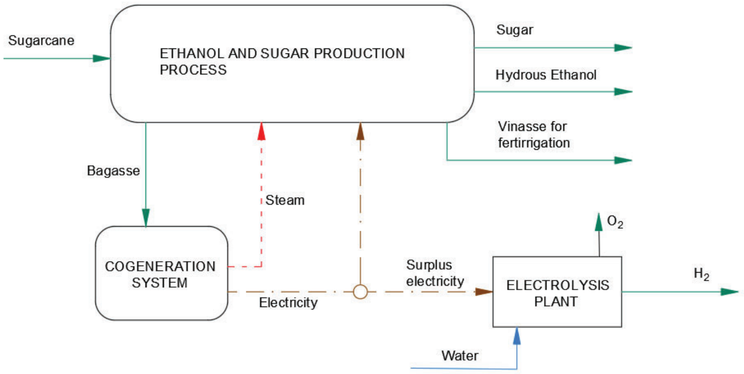

Figure. 2. Hydrogen production through water electrolysis using the surplus electricity of the mill

3.1.2. Case II - Biogas reforming

The biogas production from sugarcane was estimated according procedure presented in [10], which resulted in 2359.1Nm^3/h of raw biogas. In order to prevent reformer catalyst poisoning, a dessulphurisation system is necessary to remove H_2S; thus, a chemical scrubbing system (THIOPAQ system) was assumed in this study. Figure 3 presents a flowsheet for the H_2 production from biogas produced from vinasse biodigestion, while Table 3 shows the main parameters considered for simulation and evaluation.

Table 3. Main parameters assumed for biogas reforming

Parameter	Value
Biogas dessulphurisation	
Flow reduction in dessulphurisation process[a], %	15
Specific power consumption[a], kWh/Nm^3 of raw biogas	0.024
Biogas reforming[b]	
Reforming reactor temperature,°C	850
Reforming reactor pressure, bar	20.1
Steam/Carbon ratio in reforming (mol/mol)	2.87
Water-gas-shift reactor temperature[c], °C	400
Conversion of CO in WGS reactor[d], %	75
Efficiency of pumps and compressors, %	70
Hydrogen recovery in PSA (% of inlet H2)	75
H2 inlet concentration for PSA (% molar)	74
Temperature of preheated air, °C	315
Temperature of exhaust gases at burner outlet, °C	1400

[a]Flores-Zavala [12]; [b]Nakashima [13]; [c]Operating pressure 20.05 bar; [d]tese Peters

The desulphurised biogas composition was assumed in 64.4% of CH_4, 35% of CO_2, 0.6% N_2 and 40 ppm of H_2S in molar basis according to [12]. The biogas reforming process was simulated in Aspen Plus software according to the flowsheet and specifications supplied by [13] and [14]. In order to maximise the hydrogen production, it was assumed that all available biogas would be sent to the reforming reactor while the heating requirements of the process were fulfilled by burning the off-gas from the PSA system with sugarcane bagasse. Heat integration through Pinch Analysis was applied in order to determine the minimum requirements of external utilities, thus minimising the amount of bagasse necessary.

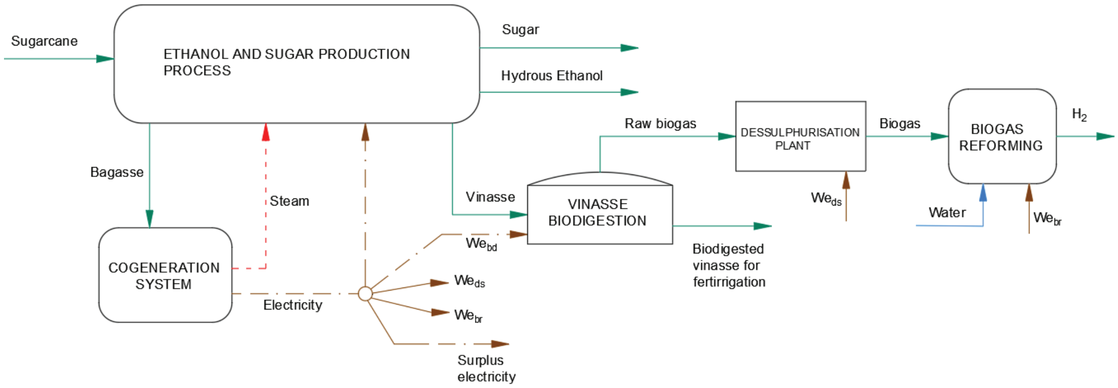

Figure. 3. Hydrogen production through biogas reforming

3.1.3. Case III - Ethanol reforming

Ethanol reforming was another technology analysed to obtain H_2. For this analysis, data from Souza et al. [15] was used to estimate the H_2 production and their energy requirements. In the same way, as in Case II, ethanol is sent to the reforming reactor, while the thermal energy demands were fulfil burning the off-gas from PSA and sugarcane bagasse. Using the simulation supplied by [15] performed in Aspen Hysys, it was possible to apply the heat integration procedure to determine the minimum amount of bagasse necessary. Figure 4 presents the flowsheet of H_2 production from ethanol, while Table 4 shows the main parameters adopted from [15] for evaluation

Table 4. Main parameters assumed for ethanol reforming [15]

Parameter	Value
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

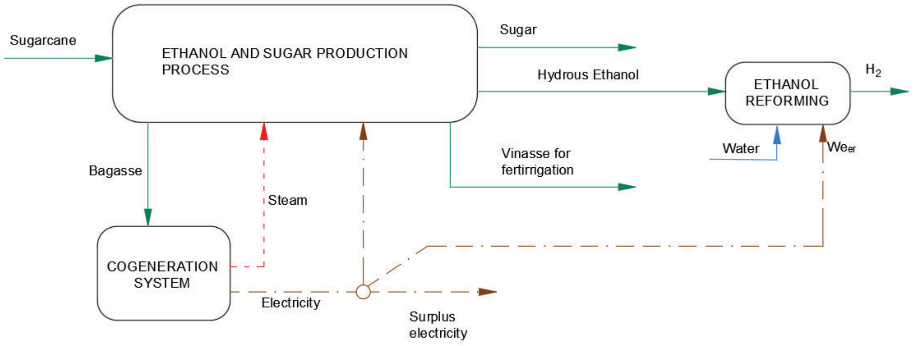

Figure. 4. Hydrogen production through water electrolysis using the surplus electricity of the mill

3.2. Hydrogen consumption in hydrotreating and hydrocracking

This analysis aims to evaluate the raw materials and energy requirements necessary to produce hydrogen for a bio-oil upgrading plant, which processes bio-oil produced from the fast pyrolysis of sugarcane straw. The fast pyrolysis of straw was simulated in Aspen Plus software in a previous study [16], while the hydrotreatment was simulated according to Peters [17]. Figure 5 presents the flowsheet of the hydrotreatment process followed by the distillation step with hydrocracking of the bottom product of the C-DIST2 column. Table 5 shows the main parameters assumed for hydrogen production analyses. Figure 5 shows that the organic phase produced in hydrotreatment is depressurized in a flash. The gaseous stream (FLSHGAS) has a significant amount of hydrogen recovered in a PSA system. This study assumed an H2 recovery of 85% in the PSA system; thus, hydrogen make-up results in 0.04651 kg H_2/kg bio-oil equivalent to 10,938 Nm^3/h.

Table 5. Main parameters assumed in the bio-oil upgrading system

Parameter	Value
Sugarcane straw recovery from field, %	50
Sugarcane straw processing rate in pyrolysis plant[a], t/h	47
Bio-oil produced in pyrolysis plant[b], t/h	21.1
Specific consumption of hydrogen in hydrotreatment[c], kg H_2/kg bio-oil	0.09
Specific consumption of hydrogen in hydrocracking[c], kg H_2/kg bio-oil	0.0032
Mass flow of FLSHGAS, kg/s	1.43
Hydrogen content in FLSHGAS, wt.%	22.6
Recycling rate of H_2 [d], %	55.8

[a] 15% of moisture content, [b] artigo Fernando, [c] Tese Peters; [d] Simulation

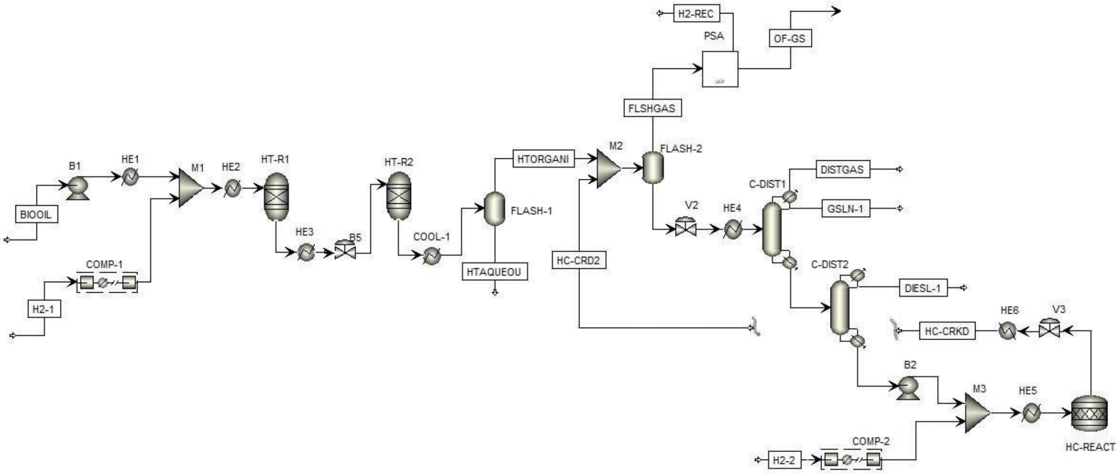

Figure. 5. Flowsheet of upgrading boi-oil plant in Aspen Plus software.

4. Results

4.1. Potential of hydrogen production from products and by-products of sugarcane processing plant

Figure 6 presents the results of hydrogen production from available inputs in the mill; it can be observed that only Case III (ethanol reforming) can supplied all the hydrogen necessary for hydrotreatment.

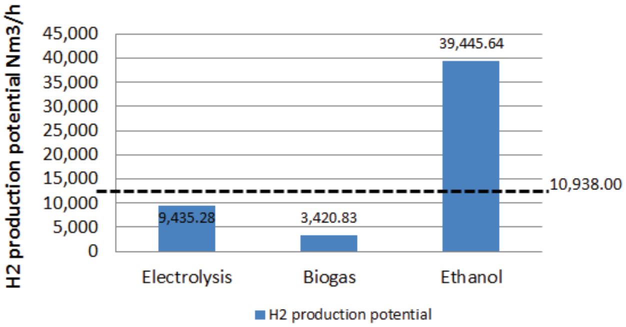

Figure. 6. Hydrogen production potential from available inputs in sugar and ethanol production process.

Thus, surplus electricity from the cogeneration system (40.6 MW) can produce 86.3% of the H2 necessary (Case I). Biogas reforming can achieve 31.3% (Case II) while considering all available ethanol produced in the plant (16.2 t/h), it is possible to produce 3.6 times the amount of hydrogen necessary (Case III). It represents a specific hydrogen production of 18.9, 6.8 and 78.9 Nm^3 of H_2 per t of cane for cases I, II and III, respectively. Regarding ethanol reforming, to produce the necessary hydrogen for hydrotreatment would be required only 4.5 t/h, which is equivalent to 27.7% of the ethanol produced in the mill.

Figure 7 shows the Grand Composite Curves obtained from Pinch Analysis for (a) biogas reforming (2,359.1Nm^3/h of raw biogas) and ethanol reforming (4.5 t/h of ethanol). Stream data for CC and GCC construction is presented in Appendix A

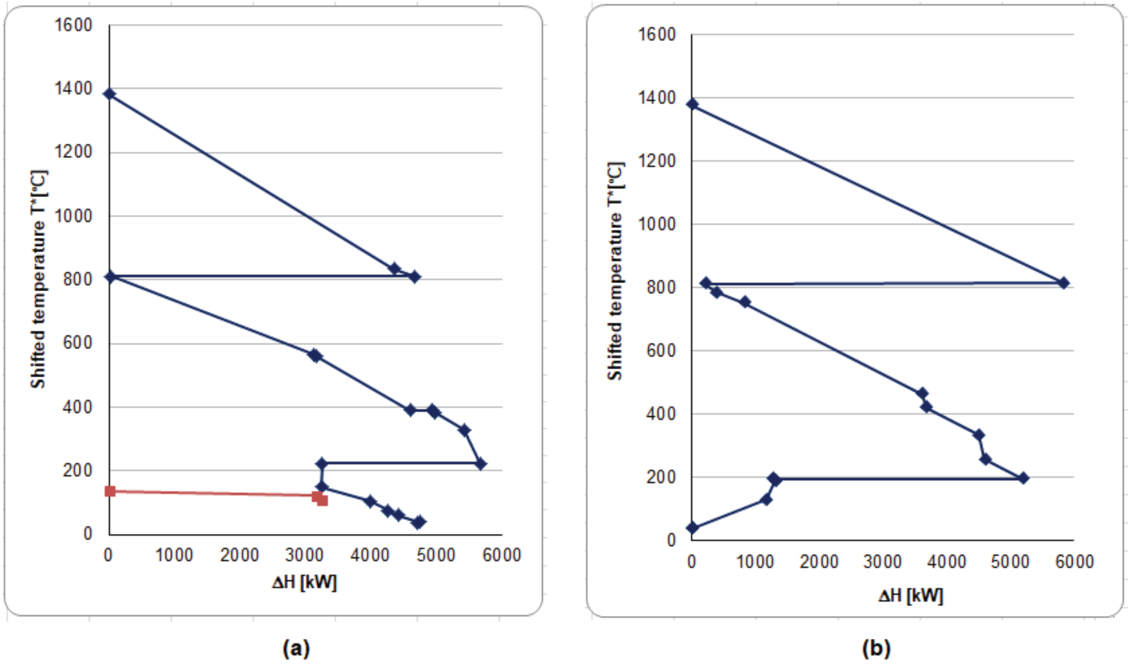

Figure. 7. GCC for (a) biogas reforming and (b) ethanol reforming process

From Fig. 7a, it can be observed that there is a significant amount of heat available at a relatively high temperature (below the reformer reactor temperature, 850°C); thus, it is possible to produce steam (at 2.5 bar and 127.4°C) and use it in ethanol and sugar production process, the red line in Fig. 7a represents this heat recovery potential. On the other hand, in Fig. 7b, better integration is observed because this configuration needs more heat at low temperatures (no hot and cold utilities are required for this case). Moreover, the heat integration procedure allows determining the amount of bagasse necessary to complete the heat demand in the reforming process for these cases. Table 6 presents the main results for these cases.

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Table 6. Main results for H_2 production potential

Parameter	Case I	Case II	Case III
H_2 production, Nm^3/h	9,435.3	3,420.8	10,938.0
% of the total H_2 required	86.3	31.3	100.0
Biogas consumption[a], Nm^3/h	0	2,359.1	0
Ethanol consumption, t/h	0	0	4.5
Electricity consumption, kW	40,600	423	198
Water consumption, m^3/h	10.9	4.6	7.0
Bagasse consumption[b], t/h	0	2.0	4.0
Impacts in the cogeneration system			
Steam supplied for the production process[c], t/h	0	5.1	0
Surplus electricity, kW	0	39,443	38,023

[a]Raw biogas; [b]Bagasse to fulfil the heat demand in the reforming process, 50% of moisture content, wet basis, [c]Saturated steam at 2.5 bar.

4.2. Production of H2 necessary for bio-oil upgrading plant and its impact in the cogeneration system

Table 7 presents the main results of this analysis. Regarding Case I, it would be necessary to buy from the electrical grid 6,466 kW (12.9 kWh/tcane) to achieve the required H_2 production. This electricity represents 11.8% of the total power produced by steam turbines of the cogeneration system. On the other hand, Case II requires an additional supply of 5,184 Nm^3/h of biogas or an equivalent of 2940.7 Nm^3/h of natural gas or biomethane (CH_4 content of 96.5% mol).

Regarding water consumption, biogas reforming presents the highest value, equivalent to 29.4L/t cane. According to Pina et al. [18], this value represents 7.1% of effective water collecting in the sugarcane processing plant (414 L/t cane). Finally, the case with the lowest impact in surplus electricity as well as water consumption is Case III; however, this case requires 27.7% of the total hydrated ethanol produced in the mill.

Table 7. Main results for H_2 production necessary to meet the bio-oil upgrading plant

Parameter	Case I	Case II	Case III
H_2 production, Nm^3/h	10,938.0	10,938.0	10,938.0
Biogas consumption[a], Nm^3/h	0	7,543.2	0
Ethanol consumption, t/h	0	0	4.5
Electricity consumption, kW	47,066.4	1,353.0	198
Water consumption, m^3/h	12.6	14.7	7.0
Bagasse consumption[b], t/h	0	6.4	4.0
Impacts in the cogeneration system			
Steam supplied for the production process[c], t/h	0	16.3	0
Surplus electricity, kW	-6,466	36880	38,023
ΔSurplus electricity[d] %	-115.9	-9.2	-6.3

[a]Raw biogas; [b]Bagasse to fulfil the heat demand in the reforming process, 50% of moisture content, wet basis, [c]Saturated steam at 2.5 bar, [d]In comparison to the Base Case (surplus electricity of 40.6 MW).

5. 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. Furthermore, its integration to the conventional sugar and ethanol production process was analysed as well as the impacts in cogeneration system. All evaluated cases presented feasibility; however there are advantages and disadvantages in each one. Case I (electrolysis) presented a significant impact in cogeneration system because the high electricity consumption of this technology. Case II (biogas reforming) presented the highest water consumption (29.4 L/t cane), while Case I presented the second highest (25.2 L/t cane), moreover, it would be necessary to acquire a significant amount of external biogas or natural gas, because the biogas available from anaerobic digestion of vinasse only can produce 31.3% of the required hydrogen for the upgrading plant. Case III (ethanol reforming) presents the lowest water consumption (14.1 L/t cane) and the lowest impact in cogeneration system (-6.3% in surplus electricity). Nevertheless Case III requires the consumption of 27.7% of the total ethanol produced in the mill, impacting significantly the revenues of the plant. In this way a more detailed analysis is needed, for instance an economic assessment or an exergoeconomic analysis to help in choosing the best proposal or proposals.

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Appendix A

Table A.1 Stream data for heat integration – Case II – Biogas reforming (2,359.1 Nm^3/h)

Stream Name	Supply Temp.	Target Temp.	dT Min Contrib.	Heat Duty
	°C	°C	°C	kW
Biogas preheating - HE1	60	550	15	609.2
Water heating HE2	25.31	212.6	10	1024.0
Water vaporization HE2	212.6	212.61	10	2413.0
Water superheating HE2	212.6	550	10	997.3
Product of reforming reactor - HE3	850	400	15	2097.8
Product WGS reactor - HE4 (1)	400	163.4	15	1046.7
Product WGS reactor - HE4 (2)	163.4	55	15	2346.3
Reforming reactor - REFORM	800	800,01	10	4625.3
Water-Gas-Shift reactor - WGS	400	399,9	10	331.6
Off-gas and air preheater - HE6	45.37	315	15	1563.9
Exhaust- gases - HE5	1400	120	15	10125.0

Table A.2 Stream data for heat integration – Case III – Ethanol reforming

Stream Name	Supply Temp.	Target Temp.	dT Min Contrib.	Heat Duty
	°C	°C	°C	kW
Ethanol preheating (2=>4)	25,22	740	15	3327
Product reforming reactor (13=>14)	800	350	15	3737
Product WGS-HT reactor (15=>16)	436.4	200	15	1874
Water heating (22=>25)	25.08	179.9	15	1283
Water vaporization	179.9	179.9	15	3939
Water superheating	179.9	800	15	2696
Product WGS-LT reactor (15=>16)	245.4	450	15	1651
Reforming reactor	799.1	800	15	5636
Exhaust gases	1400	150	20	12921

References

[1] P. D.A.F., "Produção de hidrogênio por eletrólise alcaline da água e energia solar," Universidade Federal de Uberlândia, 2016.

[2] J. R. L. Neto and J. R. S. Moreira, "Geração e Combustão do Hidrogênio Obtido Através do Processo de Eletrólise da Água," *Trab. conclusão Curso. Univ. São Paulo*, pp. 1–9, 2007.

[3] S. Czernik and A. V. Bridgwater, "Overview of applications of biomass fast pyrolysis oil," *Energy and Fuels*, vol. 18, no. 2, pp. 590–598, 2004, doi: 10.1021/ef034067u.

[4] M. Sharifzadeh *et al.*, "The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions," *Prog. Energy Combust. Sci.*, vol. 71, pp. 1–

80, 2019, doi: https://doi.org/10.1016/j.pecs.2018.10.006.

[5] IEA, “Global Hydrogen Review 2021,” 2021. doi: 10.1787/39351842-en.

[6] F. Dawood, M. Anda, and G. M. Shafiullah, “Hydrogen production for energy: An overview,” *Int. J. Hydrogen Energy*, vol. 45, no. 7, pp. 3847–3869, 2020, doi: 10.1016/j.ijhydene.2019.12.059.

[7] E. Léo Schultz, I. P. Soares, and F. B. Noronha, “Produção de hidrogênio a partir do biogás,” 2013. [Online]. Available: https://www.embrapa.br/documents/1355242/0/BiogásFert+-+Resultados+PA06.pdf.

[8] A. C. R. TEIXEIRA, C. H. G. de BRITO, C. B. MAIA, and J. R. SODRÉ, “Uma revisão sobre a reforma de etanol a vapor com foco na produção de hidrogênio,” in *XXIV Simpósio Internacional de Engenharia Automotiva*, 2016, pp. 541–550, doi: 10.5151/engpro-simea2016-pap76.

[9] M. C. Palacios-Bereche, “Análise energética e exergética de diferentes processos de disposição/aproveitamento energético da vinhaça em usinas sucroalcooleiras,” Universidade Federal do ABC, 2019.

[10] M. C. Palacios-Bereche, R. Palacios-Bereche, and S. A. Nebra, “Techno-Economic Evaluation and GHG Emission Assessment of Different Options for Vinasse Treatment and Disposal Aiming at Reducing Transport Expenses and Its Energy Use,” *BioEnergy Res.*, 2021.

[11] H. T. Madsen, “Water treatment for green hydrogen: what you need to know.” [Online]. Available: https://hydrogentechworld.com/water-treatment-for-green-hydrogen-what-you-need-to-know.

[12] B. A. Flores-Zavala, “Beneficiamento do biogás produzido em biodigestores anaeróbios para produção de biometano e energia elétrica,” Universidade Federal do ABC, 2016.

[13] R. N. Nakashima, “Modelling, simulation and optimization of biogas conversion routes integrated with fuel cell technology,” University of Sao Paulo, 2022.

[14] R. Nogueira Nakashima and S. Oliveira Junior, “Multi-objective optimization of biogas systems producing hydrogen and electricity with solid oxide fuel cells,” *Int. J. Hydrogen Energy*, no. xxxx, 2021, doi: 10.1016/j.ijhydene.2021.08.195.

[15] T. A. Z. de Souza *et al.*, “Exergoenvironmental assessment of hydrogen water footprint via steam reforming in Brazil,” *J. Clean. Prod.*, vol. 311, no. February, p. 127577, 2021, doi: 10.1016/j.jclepro.2021.127577.

[16] F. H. Salina, F. B. Molina, A. G. Gallego, and R. Palacios-Bereche, “Fast pyrolysis of sugarcane straw and its integration into the conventional ethanol production process through Pinch Analysis,” *Energy*, vol. 215, p. 119066, 2021, doi: 10.1016/j.energy.2020.119066.

[17] J. F. Peters, “Pyrolysis for biofuels or biochar? A thermodynamic, environmental and economic assessment,” Universidad Rey Juan Carlos, 2015.

[18] E. A. Pina, R. Palacios-Bereche, M. F. Chavez-Rodriguez, A. V. Ensinas, M. Modesto, and S. A. Nebra, “Reduction of process steam demand and water-usage through heat integration in sugar and ethanol production from sugarcane – Evaluation of different plant configurations,” *Energy*, vol. 138, pp. 1263–1280, 2017, doi: 10.1016/j.energy.2015.06.054.