COBEM 2021
26th International Congress of Mechanical Engineering
ABCM
Associação Brasileira de Engenharia e Ciências Mecânicas
November 22-26, 2021, Virtual Congress, Brazil

COB-2021- 0359

EXERGY ANALYSIS OF A HYDROGEN PRODUCTION PLANT WITH CO_2 CAPTURE.

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Abstract. *The increase in greenhouse gas emissions, in addition to the global need to reduce the use of fossil fuels, has motivated the use of renewable fuels. Among them, sugar-cane biomass has proved to be an attractive alternative for producing clean fuels, such as hydrogen. However, this raw material has been widely used as fuel for boilers, thus losing the capacity to generate other by-products. For this reason, this article proposes an exergetic analysis of hydrogen production with CO_2 capture. In this context, a chemical plant was designed and modelled. Its components are a circulated double bed gasifier, a synthesis gas treatment unit, a gas purification unit that uses selexol® to capture CO_2, and a hydrogen recovery unit. The entire system was modelled and simulated in Aspen plus® v8.8. The irreversibility generated by the gasification unit has a relevant influence on the whole plant's exergy efficiency. Therefore, this internal irreversibility induces an overall exergy efficiency of approximately 41.68%. On the other hand, the chemical plant can generate an overall emission balance is -1.16 kg CO_2/Nm^3H_2, which means remove an amount of about 15 t CO_2/h*

Keywords: *Biomass Gasification, Decarbonization, Hydrogen, Production, Exergy Analysis.*

1. INTRODUCTION

Hydrogen is a clean and efficient secondary energy source conventionally produced from fossil fuels, such as coal, natural gas, and oil. To reduce the consumption of fossil resources and the environmental hazards, the use of renewable energy to produce hydrogen attracts increasing attention in recent years. Biomass has been considered as one of the potential resources, which is abundant and renewable.

As Brazil is one of the world's largest sugar cane producers, about 8.38 million hectares (7.9%) (CONAB, 2020) of the land area devoted to primary food crops was used for sugar cane. So, the large quantities of sugar-cane residues, like bagasse, produced by the sugar and alcohol industries have formed the basis for developing new technological applications. Biomass is an important source of renewable energy that may help reduce fossil fuel dependency and CO2 emissions, especially in countries such as Brazil with enormous biomass potential. In recent years, biofuels have accounted for almost 70% of renewable energy production globally (IEA, 2017), and biomass was responsible for 25.5% of Brazilian domestic energy supply (EPE, 2016).

Andersson & Lundgren, (2014) presented a more environmentally benign method, hydrogen production by lignocellulosic biomass gasification. In addition, an economic analysis was conducted in this study on ammonia production based on biomass gasification. This study concluded that according to the economic analysis and performance analysis, the designed methodology was favourable. Uzi et al., (2019) focused on the pyrolysis and gasification of woody biomass and performed an experimental investigation to analyze chemical characterization. Sikarwar et al., (2016) presented a comprehensive review study on the advancements in biomass gasification. This study also presented a strategy to improve the sustainability and feasibility of biomass gasification via technological advancement and minimization of the environmental effects. Nakashima et al., (2019) studied the production of hydrogen and biomethane from vinasse and residual bagasse. The authors' focus was on the optimized integration process between the chemical plant and utilities plant. Finally, Flórez-Orrego and de Oliveira Junior, (2016) performed a comparative study between fossil fuel and biomass-based routes for ammonia production. Through the optimization process, the authors' shown biomass routes can present an overall emission balance until -2.3 tCO_2/tNH_3. However, while different options have already been proposed for each biomass wastes, there are few studies dedicated to analyzing the destroyed exergy and the CO_2 capture in the chemical plant. Thus, this paper presents a systematic approach of exergy analysis and decarbonization process to assess a chemical plant for hydrogen production using residual bagasse from biorefineries.

2. PROCESS DESCRIPTION

Figure 1 shows the production route proposed and analyzed in this work. The control volume assumed is only the chemical plant, so all utilities are imported to it. The process starts with an amount of moisture removed in a rotary dryer with a specific power consumption of 15 kWh per wet ton of biomass, where the water content of the biomass is reduced from 50% to 10%. Furthermore, in the chipping process, it is estimated that between 2% or 3% of the thermal input of the biomass (based on LHV) is required in terms of specific electricity consumption for the grinding to 0.5mm particle diameters. Therefore, in this work, it is assumed 3%.

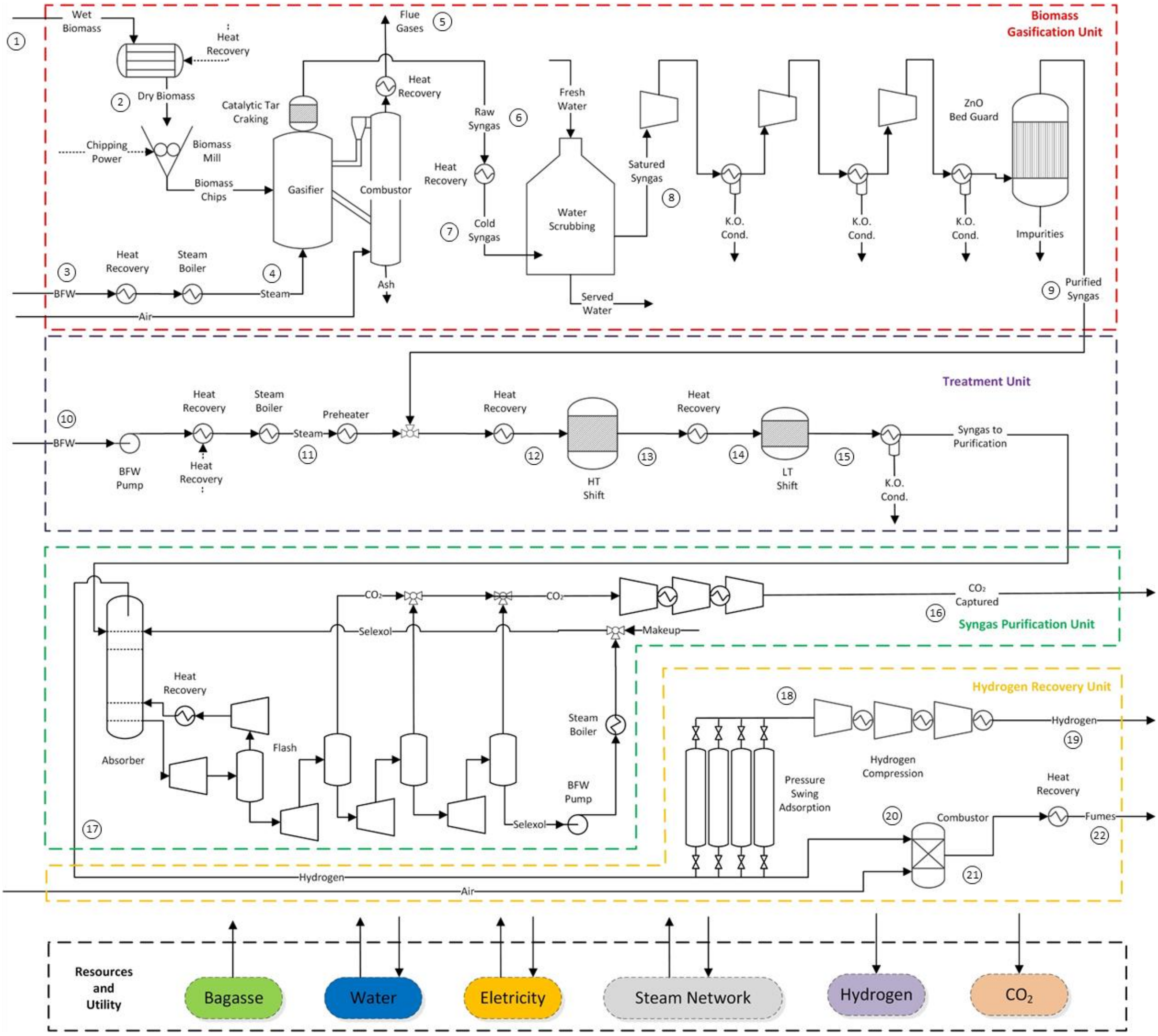

Figure 1: The integrated model used to assess hydrogen production from the sugar-cane bagasse gasification process.

The next step of the model is the gasification unit. The ultimate and proximate analysis of sugar-cane bagasse utilized is shown in Table 1 (Nakashima et al., 2019). It is used the proposed model by Battelle Columbus Laboratory (BCL). Furthermore, this model is based on an indirect gasifier at atmospheric pressure, which avoids dilution between the nitrogen of the syngas produced and the combustion gases. The combustion and gasification processes occur in a separate double column system. Steam is used as the gasification medium. In addition, in the combustion process is used a fraction of the char produced in the bagasse pyrolysis step provides the heat needed for endothermic drying, pyrolysis, and gasification reactions. Afterwards, the syngas is produced and exits the gasifier, and the tar produced is subjected to thermal catalytic cracking. The syngas is cooled to 400°C, scrubbed with water to remove impurities that may affect downstream equipment, and then compressed to 30 bar.

The next step is the treatment unit because the syngas still contains high CO levels, can be converted to hydrogen-rich syngas. In this unit, two sequential high (390°C) and low (212°C) temperature shift reactors are used to increase hydrogen concentration through the water-shift exothermic reaction. In this step, the hydrogen-rich mixture is intercooled by using a heat recovery system in order to control the maximum attainable reaction temperature.

The water-gas shift reaction helps increasing the hydrogen content and simultaneously produces more CO_2. Thus, the additional CO_2 produced is removed by using physical absorption with dimethyl ethers of polyethylene glycol (DEPG, commercially named the Selexol®) and pressure swing adsorption (PSA) systems syngas purification unit. Finally, the purified hydrogen is compressed (200 bar) with intercooling for commercialization.

Proximate Analysis		**Ultimate Analysis**	
Moisture	50%	C	46.70%
Ash	2.14%	H	6.02%
Volatile	83.54%	O	44.95%
Fixed carbon	14.32%	N	0.17%
		S	0.02%

Table 1: Proximate and Ultimate analysis used for sugar-cane bagasse.

3. METHODOLOGY

Mass, energy, and exergy balances for the unit operations of the studied case are carried out in Aspen Plus software. The exergy analysis and CO_2 capture are used to assess the performance of hydrogen production. A detailed model description is presented in the following sections.

3.1 Process modelling

The evaluation of the thermodynamic properties of each flow, as well as the mass, energy, and exergy balances of each operating unit, is performed using the Aspen Plus® V8.8 software. The thermodynamic model used in the gasification unit, the treatment unit, and the hydrogen unit is the Peng-Robinson EOS with Boston-Mathias modifications (ASPENTECH, 2011). On the other hand, the CO_2 recovery unit with DPEG, is used on the Thermodynamic model of the Theory of the Statistical Association of the Chain (PC-SAFT) (Adams et al., 2014; Field & Brasington, 2011; Flórez-Orrego et al., 2019).

The base of gasification is composed of sequential process pretreatment (dryer and chipping), pyrolysis, reduction, and combustion processes. Besides, the moisture removal simulation is done by using a FORTRAN subroutine (Flórez-Orrego et al., 2019). To estimate the yield rates of H_2, CO, CO_2, methane, tar, char, and water in the pyrolysis reaction step one uses empirical correlations reported in the literature as a function of temperature (Puig-Arnavat et al., 2012). For this, it is employed an Aspen-embedded Excel spreadsheet.

Compressors and pumps are modelled based on isentropic efficiencies of, respectively, 60% and 80%. The PSA is simplified as a black-box model assuming a hydrogen recovery efficiency of 95% mol, based on previous works (Kuo et al., 2021). As a simplification, the adsorption systems consumptions are assumed too small in terms of the overall system and the temperature swing adsorption was assumed as lossless. Furthermore, pressure and heat losses are not considered in any process. The ratio of specific chemical exergy to the lower heating value is calculated employing the correlation proposed by (Szargut et al., 1987) for solid fuels with specified mass ratios, Eq. 1.

$$\beta = \frac{b^{ch}}{LHV} = \frac{1.0438 + 0.1882\frac{y_H}{y_C} - 0.2509(1 + 0.7256\frac{y_H}{y_C})}{1 - 0.30350.1882\frac{y_O}{y_C}} \tag{1}$$

where the bagasse lower heating value (LHV, MJ/kg) is estimated based on the correlations reported by (Channiwala & Parikh, 2002) in Eq. 2.

$$LHV = 349.1y_C + 1178.3y_H + 100.5y_s - 103.4\,y_O - 15.1y_N - 21.5y_{ashes} - 0.0894h_{lv}y_H \tag{2}$$

and y_i are the mass fractions of carbon (C), hydrogen (H), sulfur (S), oxygen (O), nitrogen (N), and ashes (A) in the dry biomass, and h_{lv} is the enthalpy of evaporation of water at standard conditions (2442.3 kJ/kg). The so-calculated lower heating value and chemical exergy of dry bagasse are equal to 17.3 and 19.5 MJ/kg, respectively. The physical and chemical exergies and efficiencies based on the work of (Flórez-Orrego and de Oliveira Junior, 2016) are assessed using Excel add-ins embedded in Aspen Plus.

3.2 CO_2 Emissions

Two CO_2 emissions balances were performed: the overall CO_2 emissions and the net one. The overall CO_2 balance considers overall CO_2 emitted (either fossil or biogenic) minus CO_2 captured by the gas purification unit. In contrast, the net value subtracts the amount of CO_2 embodied by the crops, assumed as circular emissions. The indirect fossil CO_2 emitted considers the indirect emissions due to the upstream supply chains of electricity (62.09 gCO_2/kWh) and bagasse (0.0043 g CO_2/kJ Bagasse) (Flórez-Orrego et al., 2015). The biogenic emissions comprise the emissions related to the combustion of bagasse, based on the carbon content of the biomass.

3.3 Validation

The most important unit for this study is gasification because syngas has an essential impact on the final product. Therefore, the results obtained by the gasification system are validated using the study of Marcantonio et al., (2019). The comparative results are shown in Fig. 2. The most significant error finds between validation and simulation is of the element CO_2 with approximately 5%. On the other hand, the others elements show an error of less than 3%.

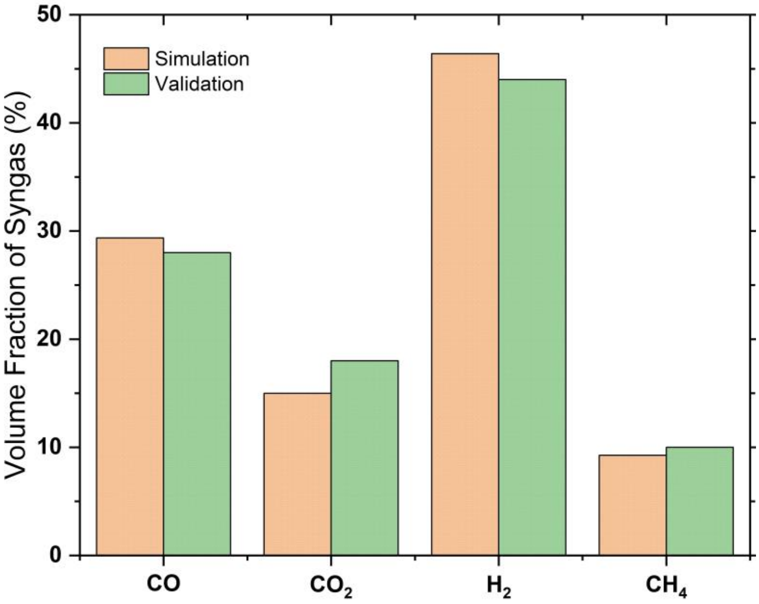

Figure 2: Validation results for gasification unit

4. RESULTS

As said previously, only biomass and electricity are considered resources to the chemical plant. Thus, without the utilities, the overall exergy consumption is 28.93 GJ/Nm^3H_2. Remembering that, the utilities are regarded as high steam, medium steam, and low steam, and as was described, the plant imports the utilities. Therefore, the effective overall exergy consumption is higher because this study assumed as the control volume only the chemical plant. Thus, all of the energy integration with the power plant is disregarded. In other words, the exergy consumption to produce the utility is not determined in this work. Moreover, it is noteworthy that the opportunity for importing ‘greener’ Brazilian electricity leads to a strikingly lower overall exergy consumption for hydrogen production compared to the autonomous cases.

The syngas composition, as well as exhaust gases, are shown in Figure 3. Each column represents the mass fraction of the most important streams of the plant. The numbers on the bottom of each column are identification tags inserted in Figure 1. In this way, it is observed that after the water gas shift reaction, the CO_2 fraction increased substantially compared to the syngas produced from the gasifier as expected. This fact happened because the combustor of the hydrogen plant burn 5% of residual hydrogen from PSA; in this way, different products are generated like water.

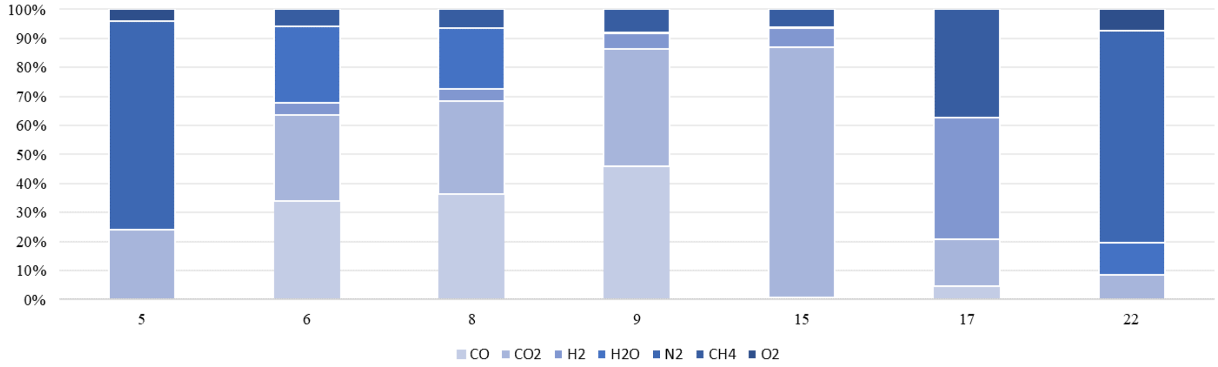

Figure 3: Composition of principal streams (Mass Fraction)

Figure 4 shows the distribution of exergy destroyed in chemical plant components. Thus, the gasification unit has the most significant amount of the exergy destroyed (67.1%). This fact emphasizes that the highest irreversibility rate is due to combustion, reduction, and pyrolysis processes. Along with that, the heat transfer with temperature difference are the most important irreversibilities for this unit and also to the chemical plant. Equally, the hydrogen recovery unit shows the second-highest exergy destruction (25.8%) due to the gases combustion process

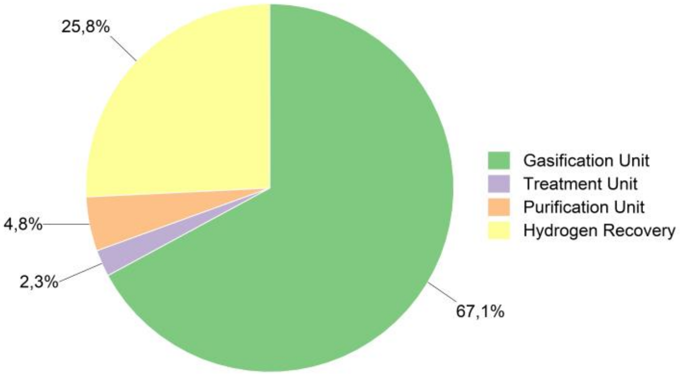

Figure 4: Exergy destruction for each unit of the plant

Figure 5 depicts the percentage of the exergy destroyed per equipment of the plant. It should be stressed that the gasification process typically presents the most exergy destruction (62.10%) among it. Then the flue gases (10.76%) come, followed by the hydrogen recovery unit (9.83%), the chipping process (4.61%), and the compression process (3.88%). Moreover, the dryer process and the scrubber process show lower values (0.77% and 0.72%, respectively). However, the purification unit exhibits exergy destruction of around 4.8%. Furthermore, with the use of turbines, it was possible to reduce irreversibilities in the expansion of this unit. In this way, the Table 2 complements the values shown previously, where it can be observed the exergy destroyed rate for each component of the plant.

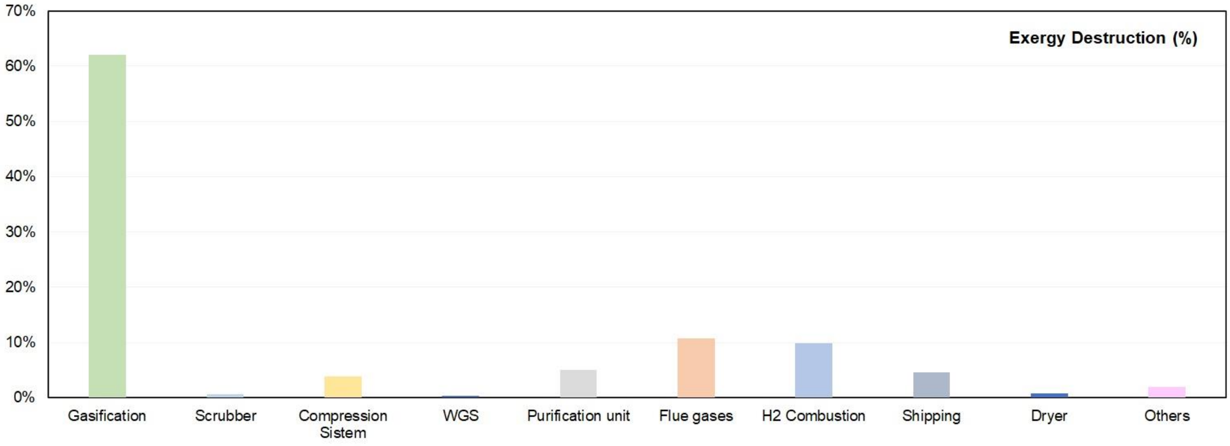

Figure 5: Percentage of exergy destruction for each equipment of the plant

Component of the Plant	Exergy Destroyed Rate	
Gasification	32371.51	kW
Scrubber	375.25	kW
Compression Sistem	2025.02	kW
WGS	199.03	kW
CO2 Removal unit	2612.24	kW
Flue Gases	5609.85	kW
H2 Combustion	5124.77	kW
Shipping	2404.56	kW
Dryer	399.60	kW
Others	1006.92	kW

Table 2 - Exergy destroyed rate for each component of the plant.

The overall exergy efficiency of the studied chemical plant is 41.68%, proximate of the exergy efficiency found by Nakashima et al., (2019). The units that presented substantial efficiency values are the treatment and purification units (97.44% and 94.76%, respectively). As introduced before, the gasification unit has the most exergy destruction. Thus, among the units, it shows lower efficiency (57.41%). Furthermore, the hydrogen recovery presented an efficiency value of about (69.59%), as shown in Fig. 6.

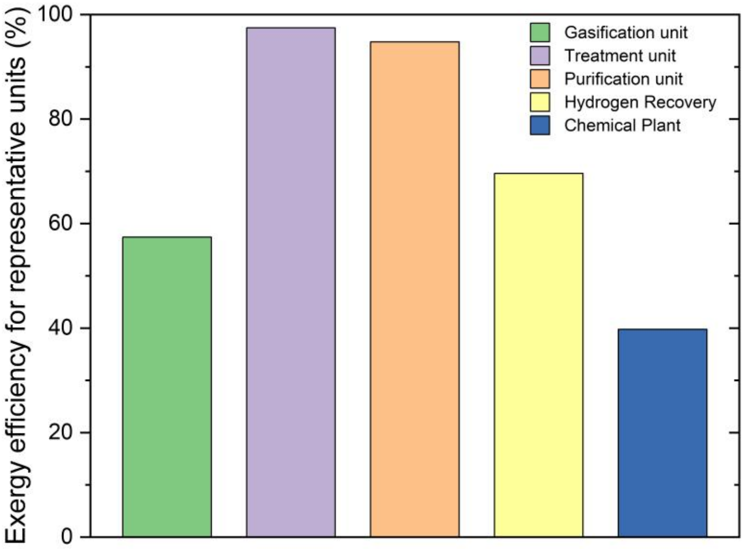

Figure 6: Exergy efficiency for representative units

Figure 7 presents the overall and detailed CO_2 emission balance. The overall emission balances achieve -1.16 kg CO_2/Nm^3H_2 in the chemical plant. The negative value indicates a net positive impact on the depletion of the CO_2 present in the atmosphere. As a result, the indirect emissions from biomass utilization are offset by the captured biogenic emissions. The import of ‘greener’ Brazilian electricity leads to a mitigation of CO_2 emissions. Furthermore, the purification unit captured about 15 t/h of CO_2 that would be emitted directly into the atmosphere.

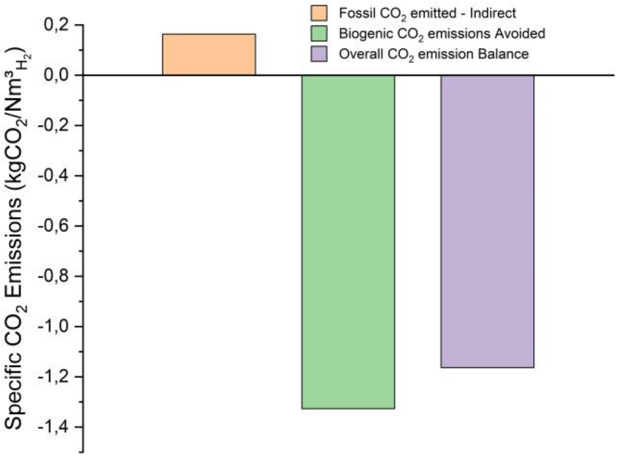

Figure 7: Overall and detailed (biogenic and fossil, directly and indirectly, emitted, and avoided) CO_2 emissions for the hydrogen plant

5. CONCLUSION

This work performed a modeling, simulation and an exergy analysis, in Aspen plus v8.8 ®, of hydrogen production with CO2 capture. The exergy analysis results allowed spotlighting the main points of irreversibility for each unit. As a result, the exergy efficiencies of the chemical plant and the more representative units, like gasification and hydrogen recovery, are 41.68%, 57.41%, and 69.59%, respectively, whereas the overall emission balance is -1.16 kg CO2/Nm^3H_2. This negative value points towards the environmental benefits brought by the production of chemicals through alternative energy sources, such as biomass and electricity, in integrated chemical plants. In order to minimize the destruction of exergy an energy integration approach can reduce the consumption of steam and electricity and increasing the plant's efficiency. The results of such analysis will be presented in a next paper.

6. ACKNOWLEDGEMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The first author acknowledges CAPES for his PhD grant. The second author acknowledges CNPq (Brazilian National Council for Scientific and Technological Development) for the grant 306484/2020-0.

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8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.

9. APPENDIX

Table A.1 summarizes the process data of the conversion section of biomass shown in Figure 1.

Stream	$\dot{m}$ (kg/s)	T (°C)	P (bar)	B (kW)
1	26640	25	1	144273.84
2	18400	120	1	80152.13
3	3182	25	2	900.10
4	3182	121	2	1442.95
5	29731.88	100	1	2634.62
6	15703.49	850	1	197209.89
7	15703.49	400	1	194380.37
8	14641.82	63	1	207259.80
9	11579.99	35	35	262606.02
10	8845.50	25	1	900.00
11	8845.50	390	35	3842.70
12	20425.49	390	35	153741.62
13	20425.49	502	35	152101.68
14	20425.49	180	35	150142.94
15	20425.49	230	35	149644.41
16	12571.50	35	1	28087.27
17	2374.55	36	35	27629.04
18	796.75	36	35	237067.69
19	796.75	35	200	237559.67
20	1577.78	36	1	420857.62
21	34539.89	1579	1	12797.43
22	34539.89	100	1	92.68

Table A.1 - Process data of the conversion section of biomass.