Exergy based evaluation of large-scale hydrogen production from African palm rachis

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A B S T R A C T

Background: The valorization of residual biomass generated in the palm oil extraction process as palm cake and empty palm fruit bunches of rachis, is a topic of interest due to the possibility of increasing the sustainability of the process. For this reason, the residual biomass use as a feedstock for high value products has been evaluated using experimental and Computer Aided Process Engineering for exploring behavior of emerging technologies in large-scale. However, production of renewable energy blocks must be evaluated from energy point of view. **Objective:** In this work, hydrogen production from rachis of African Palm is analyzed as a promising biotech alternative, using process simulation and exergy analysis methodologies, in order to quantify the irreversibilities of the process and define possibilities of improvement. **Methodology:** Simulation was performed using specialized software and the effect of operating variables on exergy of residues and gasification stage were evaluated through a sensitive analysis. By exergy assessment, total irreversibilities, exergy from industrial services, exergy of residues and overall exergy efficiency of the process were quantified, based on palm rachis and carbon composition. **Results:** Through this study it was found that for 42300 t/year of wet biomass, 576.78 kmol/h of hydrogen may be obtained. It was observed that although the exergetic efficiencies of the main stages were considerably higher (cooling and hydrogen separation stages presented 98.7 % and 97.4 %, respectively), overall efficiency found to be 27.1 %, which is low in comparison to other processes, being biomass drying and hydrogen purification identified as critical stages, and exergy for industrial services represents 53 % of the total inlet exergy to the process. In addition, the sensitivity analysis showed that exergy of residues in the gasification stage decreases with increasing input ratios African Palm Rachis/Carbon and O_2/Carbon, while the efficiency of this stage is proportional to the relationships mentioned. **Conclusion:** Process can be improved for increasing exergy efficiency, by using all gasification effluents and diminishing external services, it is proposed the analysis of energy integration based on the flows of discarded water in the system, ensuring its sustainability.

INTRODUCTION

In the last years, industrial activities associated with extraction of minerals or organic substances have increased, which subsequently leads to wastes generation (Saedi, Aremu and Idris, 2012). For instance, in the oil palm industry it is obtained a residual biomass known as Rachis (Goncalves, Cruz, Sales, Souza, Silva, Guimaraes, Mattedi and Jose, 2016), which should be considered as new renewable resource of energy due to its

lignocellulosic nature (Mat, Wahad, Mohd, Moktar, Mhd, Abdul and, Yusoff, 2013). Several researches have been developed regarding its use for the production of value added products such as pulp used in papermaking (Rios and Vesga, 2008) or hydrogen via biomass gasification (Mendoza, Bula, Gómez and Corredor, 2012). Currently, hydrogen is one of the main inputs in the oil industry due to its use in the production of diesel and naphtha, as well as on enriching CH_4 biogas in order to improve the quality of gas combustion (Cavinato, Gottardo, Micolucci, Bolzonella, and Pavan, 2016; Kumar, Banerjee and Deb, 2011). Also it is used in ammonia plants for the Haber-Bosch process (Vojvodic, Medford, Studt, Abild-Pedersen, Suvra, Bligaard and Nørskov, 2014). On the other hand, in the transportation sector is focusing attention on it as its use as fuel, due to propose a more sustainable environmental and economic option (SIC, 2013). Due to hydrogen demand, an alternative for its production is the gasification of oil palm rachis. In America, the largest oil producers are Colombia and Ecuador. Colombia is the first palm oil producer of Latin America and the fourth in the world, with domestic production of 753,000 tons, and about 500,000 hectares of oil palm (SIC, 2011), for this reason the palmist sector has become one that produce waste in the country (Gómez Mendoza, 2014). Despite the promising benefits from an economic and environmental point of view of the process in question, this technology is under investigation due to the assembly on an industrial scale requires further technological development and studies to know efficiencies expected and its sustainability (Pérez Sánchez, 2010).

Computer-aided simulation has been successfully used for evaluation and improvement of emerging technologies and exergy analysis has been usually applied to thermal processes integration and optimization (Carrasquer, Martínez-Gracia and Uche, 2016). For instance, Tolga Balta, Kizilkan and Yilmaz (2016) used exergy analysis to study the thermodynamic performance of solar-driven integrated high temperature steam electrolysis for hydrogen production. From the results of the analyses, the overall energy and exergy efficiencies of the considered system are found to be 24.79 % and 22.36 % for power generation section and 87 % and 88 % for hydrogen production section respectively. Also it is found that without any auxiliary equipment, the considered hydrogen production process consumes 1.98 kWh at 230 °C, generates 0.057 kg/s H_2.

In order to justify that a technology which use renewable resources is more efficient and sustainable than other, evaluations and comparisons of the processes can give a clear insight regard how energy is utilized. In this sense, exergy efficiency concept is more meaningful than energy efficiency because it gives a true measurement of how closely the actual performance of production process approaches ideality. In particular, exergy analysis clearly identifies the causes and locations of energy degradation in a process thereby facilitating process and technology improvements (Teng Tan, Teong Lee and Rahman Mohamed, 2010).

In this work, process simulation is used coupled with exergy analysis for the evaluation of hydrogen obtaining process from African Palm Rachis, in order to quantify exergy losses that can lead to improve the potential production chain.

MATERIALS AND METHODS

Characterization of the raw material:

The biomass composition used in this research (rachis palm oil) as well as gasification residues (tars and solid) is found in Tables (1) and (2) respectively, based on data reported by Bicer and Dincer (2015) and Ogi, Nakanishi, Fukuda and Matsumoto (2013).

Table 1: Palm rachis composition

Properties	% wt
Moisture (wb)	55.6
Moisture (db)	5.18
O (db)	45.66
N (db)	1.21
C (db)	46.62
H (db)	6.45
S (db)	0.035
Ash (wb)	3.45
Volatile matter (db)	1.84

Table 2: Composition and properties of the carbon

Properties	Carbon (% wt)	Solid waste (% wt)	Tar (% wt)
LHV (kJ/kg)	25.08	-	-
HHV (kJ/kg)	27.13	-	-
O	6.88	13.73	-
N	1.25	-	-
C	63.75	1.10	94.30
H	4.50	1.60	6.30
S	2.31	-	-
Ash	9.70	83.57	-
Moisture	11.41	-	-

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Process simulation:

Process simulation was performed using Unisim design based on a plant with capacity of 42300 t/year of african palm rachis (RPA). Figure (1) shows the process diagram for obtaining hydrogen from RPA. First, the pretreatment step consisted of biomass milling (to a particle size of 0.3 mm) and drying (374.15 K), to increase gasifier efficiency and reduce tars production. The gasifier selected was a circulating fluidized bed model, which ensures good contact of the solid-gas, tars underperforming (< 0,1 % wt) (Ogi *et al*., 2013) and high conversion of biomass. At this stage enters O_2 pure liquid at 80 K, product of air separation. The main limitation of this step lies in the concentration of metals in ash due to the high production of solid particles, in addition to the wide variety of reactions that occur, which depend on the operating conditions and gasifying agent used (Linares Hurtado and Fernández González, 2009). The ratio of O_2/C and RPA/Carbon were taken as 0.35 and 0.82, respectively. Optimum operating conditions of 1173.15 K and 60 bar were established, considering the process as isothermal. The biogas obtained is subjected to a cooling step which passes through a heat exchanger (out to 333.28 K) and an electric cooling (industrial services), lowering the temperature of 1173.15 K to 283.15 K, in order to condition the biogas for displacement shift reactor, where the hydrogen concentration will be increased. In this simulation, two shift reactors were used, one at low (283.15 K) and other at high (643.15 K) temperature. It was also assumed that occurs two reactions where hydrogen is produced from methane and water ($CuO/ZnO/Al_2O_3$ as catalyst) and carbon monoxide and water (Fe_3O_4/Cr_2O_3 as catalyst) (Bell, Towler and Fan, 2011). The synthesis gas obtained in the reactor goes through a cooling stage to 553.15 K. Then, the water present in it is separated by condensation. The resulting stream is mixed with Selexol to dissolve the undesired components (CH_4, CO and CO_2) and finally it is subjected to a flash separation process where the H_2 is obtained in one of the output currents.
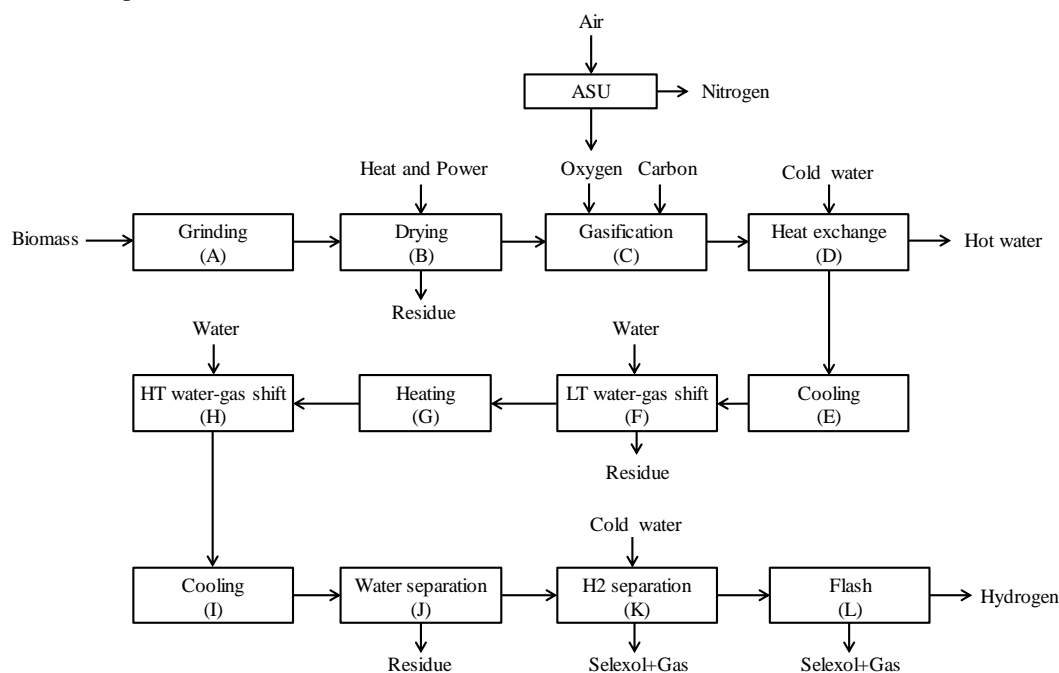
Fig. 1: Process diagram of hydrogen obtaining process from RPA.

Exergy analysis:

Exergy is defined as the maximum amount of theoretical work that can be obtained from the interaction between a thermodynamic system to certain conditions and stable reference environment. If there is a difference between these two states, there is the possibility of producing work; otherwise, this possibility is reduced. In this sense, the exergy analysis becomes a powerful tool to identify potential areas for process improvement in terms of reducing unnecessary resources or replacing a unit for a one with a better thermodynamic performance, due to allows quantifying the major inefficiencies and system performance (Ruiz de la Cruz, Orozco Muñoz, Bonilla Correa and Peralta Ruiz, 2015). For an exergy balance in steady state, exergy destruction is related to net mass transfer irreversibility, work and heat by equation (1).

$$Ex_{destroyed} = Ex_{mass\text{-}net} + Ex_{heat\text{-}net} + Ex_{work\text{-}net}$$

(1)

Exergy related to mass transfer in the absence of electrical, magnetic, nuclear and surface tension effects is defined as the sum of physical, chemical, kinetic and potential irreversibilities (equation 2). In most of industrial

processes, the kinetic and potential irreversibilities tend to be neglected by low contribution to the total exergy (Kumar, Singh, Jithu, Mural, Revuru and Das, 2016) physical and chemical irreversibilities are given by the equations (3) to (5), where equation (4) can be use when stream behaves like an ideal gas mixture and equation (5) if stream is in solid or liquid state. In equation (6), allows calculating the chemical exergy of a compound, where ΔG_f^0 is the standard Gibbs free energy of formation of the substance, Ex_{ch-j}^0 is the chemical exergy of the jth pure element of the substance and v_i is the number of atoms of the jth pure element of the compound. In the case of a mixture, Chemical exergy is defined by its components and their concentration as shown in equation (7). If the stream is an energy source, can be defined exergy conversion coefficients, for the case of fuels (coal, oil, gas), exergy at 1 bar and 298.15 K can be obtained by equation (8), where LHV is the calorific power, w is the moisture percentage of coal and h_{fg} is the latent heat of water at 25°C. In addition, the term φ_{dry} can be calculate by equation (9), where X_H, X_O, X_N, X_S and X_C are the mass fraction of hydrogen, oxygen, nitrogen, sulfur and carbon present in the coal (Yan, Yue and He, 2015).

$$Ex_{mass}=Ex_{phy}+Ex_{ch}+Ex_{pot}+Ex_{kin} \tag{2}$$

$$Ex_{phy}=(H-H_0)-T_0(S-S_0) \tag{3}$$

$$Ex_{phy-ig}=C_P(T-T_0)-T_0\left(C_P Ln\frac{T}{T_0}-R Ln\frac{P}{P_0}\right) \tag{4}$$

$$Ex_{phy-liq}=C_P\left[(T-T_0)-T_0 Ln\frac{T}{T_0}\right]-v_m(P-P_0) \tag{5}$$

$$Ex_{ch-i}=\Delta G_f^0+\sum_j v_j Ex_{ch-j}^0 \tag{6}$$

$$Ex_{ch-mixture}=\sum_i y_i Ex_{ch-i}+RT_0\sum_i y_i ln(y_i) \tag{7}$$

$$Ex_{fuel}^{ch}=(LVH+wh_{fg})\varphi_{dry}+9{,}417X_s \tag{8}$$

$$\varphi_{dry}=0.1882\frac{X_H}{X_C}+0.061\frac{X_O}{X_C}+0.0404\frac{X_N}{X_C}+1.0437 \tag{9}$$

The exergy associated to work in a system where there is no volume change is equal to the own work the system (equation 10). Regarding exergy by heat transfer, this can be calculated based on Carnot efficiency, which represents the fraction of energy transferred from a heat source at temperature T, which can become a work environment, to the reference temperature T_0, using equation (11). On the other hand, the total exergy input to a system may be associated with the process streams input and/or industrial services required by the system (equation 12), while the total exergy output can be associated with product flows and/or waste streams as shown in equation (13).

$$Ex_{work}=W \tag{10}$$

$$Ex_{heat}=\sum_i\left(1-\frac{T_0}{T}\right)Q_i \tag{11}$$

$$Ex_{total-in}=\sum_i Ex_{mass-in}+\sum_i Ex_{utilities-in} \tag{12}$$

$$Ex_{total-out}=\sum Ex_{products-out}+\sum Ex_{wastes-out} \tag{13}$$

Exergy losses or exergy destroyed refers to the irreversibilities in the process, that is, the potential of the system to produce work that there was not used, and can be calculated by subtracting total exergy input and exergy associated with the output stream of products, which was the potential used (equation 14). Finally, the exergy efficiency of a process or a stage within the process can be calculated based on the irreversibility and the total exergy input to the system by the equation (15) and the percentage of total process irreversibilities that was destroyed in a stage i can be calculated using equation (16).

$$Ex_{destroyed} = Ex_{total\text{-}in} - \sum Ex_{products\text{-}out}$$

(14)

$$\eta_{exergy} = 1 - \left(\frac{Ex_{destroyed}}{Ex_{total\text{-}in}} \right)$$

(15)

$$\% \ Ex_{destroyed, \ i} = \left(\frac{Ex_{destroyed, \ i}}{Ex_{total \ destroyed}} \right) x100\%$$

(16)

## RESULTS AND DISCUSSION

Exergy efficiency per stage:
Figure (2) shows the exergy efficiency, residues exergy and irreversibilities for the stages of hydrogen obtaining process from palm rachis. It is observed that the exergetic efficiency of the dryer was the lowest of all (33.1%) since temperature changes and water separation increased useful energy loss, while the most efficient ones were cooling and H_2 extraction stages by Selexol (98.81 % in average) due to the low contribution of the heat exergy. Regarding residues exergy losses, in the gasification, these represent 91% of total losses in the process (588,023 MJ/h), because of multiple reactions that occur as well as physical and chemical changes in the system. This waste stream of 20,332 ton/h leaves at 1173.15 K, so this heat could be used in the process. In the other hand, the 47,5 % of total irreversibilities were in the H (second reactor shift) and J (water separation) stages, where in the first case are equivalent to 71,319 MJ/h of exergy losses due to high temperatures at the entrance (643.15 K) and for the second, 40,484 MJ/h.
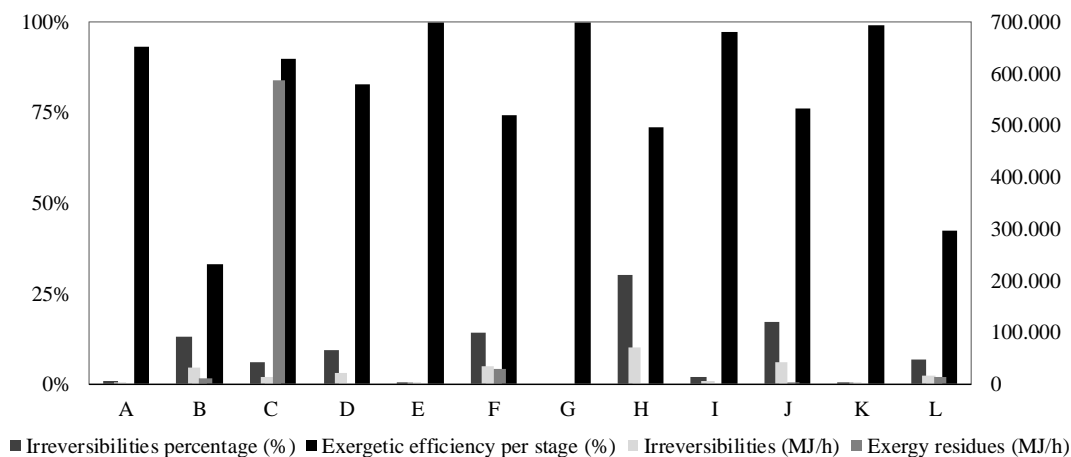
Fig. 2: Exergy analysis per stage of hydrogen obtaining process from African palm rachis

Global exergy efficiency:
Figure (3) presents the overall results for the exergetic analysis for the process. It is observed that although the efficiencies of the main stages were considerably higher, overall efficiency found to be low (27.1 %), mainly due to exergy for industrial services represents 53 % of the total inlet exergy to the process. Even though the process generates significant amounts of hydrogen (86.8 kmol/h) it does not mean that it is efficient enough, since a large proportion of the energy consumed in the system comes from external sources, as well, the residues exergy is greater than the product of interest (11,717 MJ/h in the output of L stage), the waste of energy capacity affects the low performance of the process.
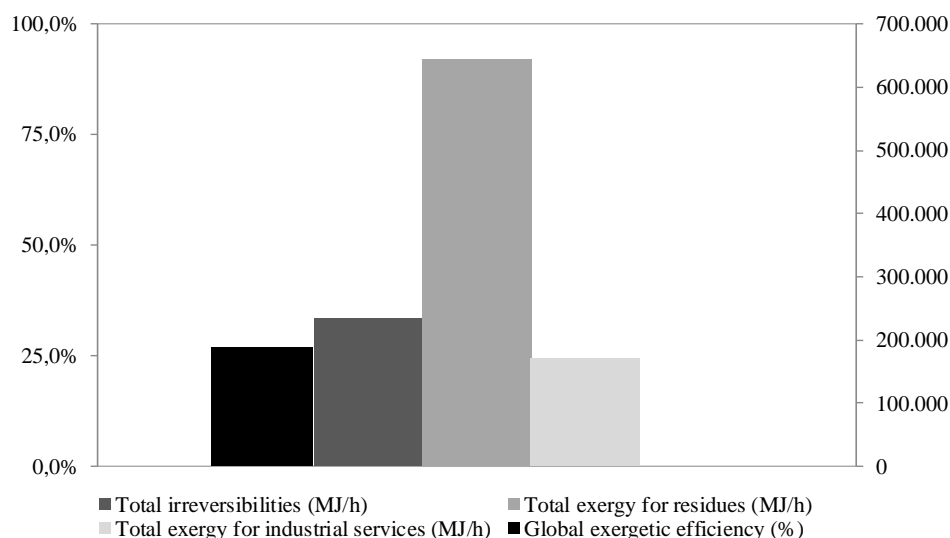
Fig. 3: Global exergy analysis of hydrogen obtaining process from african palm rachis

Sensitivity analysis:

    A sensitivity analysis was performed by varying the ratio of the percentage w/w of O_2/C and RPA/Carbon to model the change in residues exergy and exergetic efficiency of the gasification step. Figure (4a) shows that the residues exergy decreases with increasing input proportions of RPA/Carbon and O_2/C. At low ratios of RPA/Carbon (from 0 to 3), exergy is highly sensitive to these changes, however after a ratio of 3 that effect is not significant. Regarding the ratio O_2/C, it can be said that decrease the oxygen amount entering to the gasification is directly related to the products generation that might be undesirable, which could in turn increase the residues exergy. Otherwise to this tendency occurs with the exergetic efficiency of the stage, which is proportional to the ratios mentioned as is shown in Figure (4b). It is observed that the oxygen amount is a critical variable in the process and the efficiency is quite sensitive to variations on it, therefore, by controlling the oxygen entering to the system can be generated a substantial improvement in the stage efficiency and in general on process efficiency. Moreover, under ideal scenarios, the objective would be to take advantage of the carbon present in the rachis to reduce the inflow of additional sources of it, however, the latter is essential. In such case, increase this ratio allows greater advantage of rachis amount and increase stage efficiency and process.

(a)   (b)
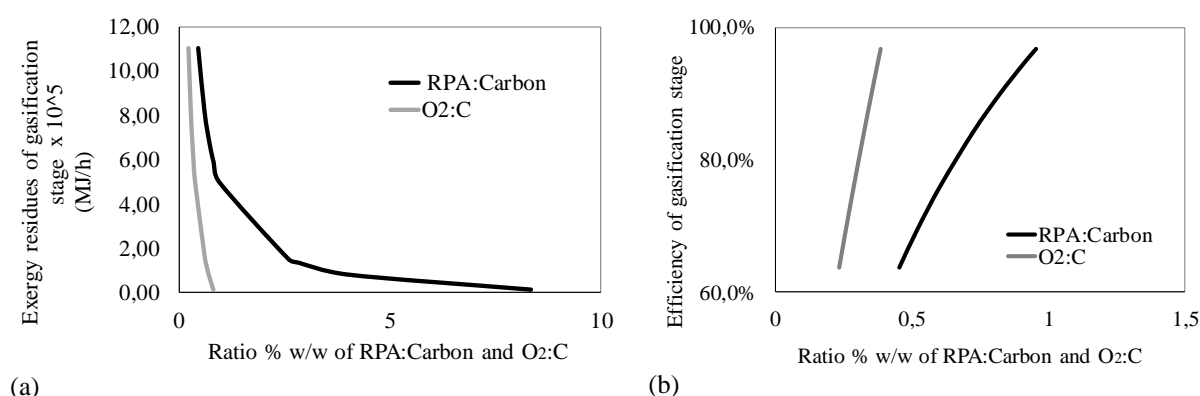
Fig. 4: Influence of RPA:Carbon and O_2:C ratios on a) residues exergy and b) exergetic efficiency of gasification stage in the hydrogen obtaining process

Conclusions:

    Application of exergy analysis for the evaluation of materials and biomass to obtain values products such hydrogen, constitutes a useful tool for generating and designing alternatives towards sustainable development. In this study, a hydrogen obtaining process from african palm rachis with a basis calculation of 40.84 t/h of wet biomass was simulated, where was produced 2.876 t/h of hydrogen. Then, it was analyzed from an exergy perspective in order to identify the main irreversibilities steps, and know the exergy of wastes and utilities, and

exergy efficiency for each step. Finally, a sensitivity analysis was performed in order to evaluate the effect of O_2/C and RPA/Carbon ratios on residues exergy and exergetic efficiency of the gasification step.

Results showed a global exergetic efficiency of 27.1 %. Although, this process presents similar exergetic efficiency for hydrogen obtaining process from a solar-driven integrated with high temperature steam electrolysis, where authors found an overall exergy efficiency of 22.36 % for power generation section and 88 % for hydrogen production section, respectively. In addition, the stage that had the highest efficiency was the cooling (E) with 99.93%. In the other hand, the total irreversibilities were estimated on 235,526 MJ/h, where high temperature water-gas shift (H) and water separation (J) steps contributes to the 47 % of the total exergy destroyed in the process, showing losses of 71,319 and 40,484 MJ/h, respectively, which makes them to be the ones with major energy sinks. Also, the exergy calculated for industrial services was 171,136 MJ/h. The analysis carried out allows to consider the use of residues, especially those generated in the gasification step (588.024 MJ/h) as a new biotechnology alternative due to the composition of the synthesis gas makes it a potential source for generating electricity, fuel and fertilizers. Finally, sensitive analysis showed that exergy of wastes on gasification step decreases with increasing input proportions of RPA/Carbon and O_2/C and the efficiency of the stage is quite sensitive to variations on oxygen amount, therefore, by controlling the oxygen entering to the system can be generated a substantial improvement in this stage efficiency and in general on process efficiency.

Results obtained suggest that would be beneficial to implement technical improvements or apply optimization methodologies such as process integration and technical specifications of equipment, in order to reduce the amount of exergy destroyed along the stages of the process as well as to decrease industrial services required for hydrogen production. It is proposed the analysis of energy integration based on the flows of discarded water in the system that ensure its sustainability and give a positive use to wastes and byproducts streams.

This analysis is a valuable method in discussing the thermodynamic performance of a system due to guide to identify the units where the most profit can be made by replacing the specific unit by a one with thermodynamically better performing. Including exergy analyses in the study of novel chemical process might help in the suggestion of the use or reduction of utilities, which, ultimately, it is reflected in an economic and environmental impact. From the exergy analysis applied in this paper, more detailed and useful information was obtained to reveal the system improvement potential points, regard to residues and steps.

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