PROCEEDINGS OF ECOS 2019 - THE 32ND INTERNATIONAL CONFERENCE ON
EFFICIENCY, COST, OPTIMIZATION, SIMULATION AND ENVIRONMENTAL IMPACT OF ENERGY SYSTEMS
JUNE 23-28, 2019, WROCLAW, POLAND

Exergoeconomic and environmental assessment of production and end use of sugarcane residues derivatives

***R. N. Nakashima*[a], *D. Flórez-Orrego*[b], *S. de Oliveira Junior*[c]**

[a] *University of São Paulo, São Paulo, Brazil, rafaelnnakashima@usp.br (CA)*
[b] *University of São Paulo, São Paulo, Brazil, daflorezo@usp.br*
[c] *University of São Paulo, São Paulo, Brazil, soj@usp.br*

Abstract:

The upgrade of sugarcane industry residues, such as vinasse and bagasse, has a notably potential for large scale production of biofuels in Brazil. Despite this fact, the biomass conversion into either electricity or biofuels requires various energy intensive processes that may drastically affect its technical and environmental competitiveness against their non-renewable counterparts. Accordingly, the mapping of the generation of the process irreversibility and their associated atmospheric emissions may help, by issuing appropriate mitigation tasks, in the reduction of exergy consumption rates and environmental impact. Therefore, in this paper, a comparative assessment between the total (c_t) and non-renewable (c_{nr}) exergy costs and specific CO_2 emissions (c_{co2}) of the electricity, methane and hydrogen produced from sugarcane vinasse and bagasse is presented and compared with the conventional (fossil fuel-based) supply chains. As a result, a strikingly high average renewable to non-renewable ratio ($\frac{c_r}{c_{nr}}$) of 15.2 is estimated for the biofuels derived from the waste upgrade plant. However, due to the larger number of process involved in the conversion of biomass resources, the total exergy costs of biofuels delivered vary from 2.6 to 2.2 times higher in comparison to those derived from fossil fuels. On the other hand, although hydrogen production from sugarcane wastes involves more processes, its unit exergy costs in the end-use stage (transportation service) were found to be the lowest among the studied biofuels, partially due to the higher efficiency of hydrogen-fueled transportation technologies. In general, the production of biofuels and electricity from sugarcane wastes can offer fuels with greatly reduced CO_2 specific emissions and low non-renewable energy consumption shares.

Keywords:
Biomethane, Ethanol, Hydrogen, CO_2 emissions, Exergy.

1. Introduction

The transportation sector is an important area of environmental improvement, since its responsible for a significant portion of energy consumption and greenhouse emissions in the world. In 2016, this economical sector produced a quarter of greenhouse emissions (8 GtCO_2) in the world, a value that has been steadily increasing in the last years [1]. In Brazil, for instance, the 2018 energy balance report indicates that the transportation sector already accounts for 45.8% of carbon dioxide emissions and 32.7% of the country energy demand [2]. A possible alternative to reduce the environmental impact of this sector is the gradual replacement of fossil fuels by biofuels or electricity. In fact, since they could be helpful to reduce or eliminate the CO_2 emissions derived from fuel combustion, their adoption seems an ideal way to achieve the sustainable development of the transportation sector. However, it is possible that these environmental gains in the end-use stage may be offset by the characteristics of upstream fuel production processes [3].

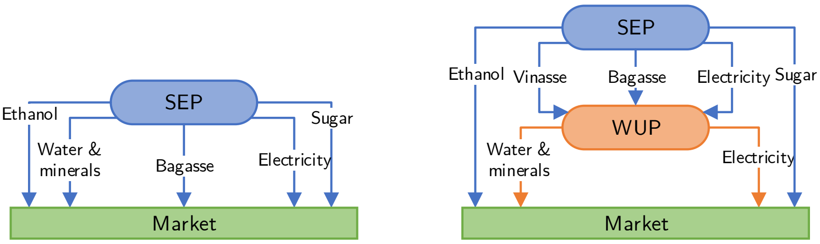
Some recent studies investigated this general concern evaluating the production and usage of renewable fuels. For instance, Piekarczyk, et al. [4] studied the thermo-ecological cost of several biofuels production. Their study indicate that the overall exergy efficiency of the system and the ecological costs are very sensitive to the utility system feedstock, which may couterweight their environmental positive effects. In other study, Floréz-Orrego et al. [5] evaluated the total, non-renewable and CO_2 exergy based costs for fuels produced in the Brazillian context using an exergoeconomy methodology. Their findings indicate that the total unit exergy costs of ethanol and biodiesel are much higher than their fossil-derived correspondents, but they are also mostly derived from renewable energy sources.

On the other hand, the adoption of gaseous fuels, such as methane and hydrogen, are indicated as a cleaner transition to a renewable energy economy. However, these fuels can not achieve environmental sustainability without the development of other technologies that reduce their associated fossil CO_2 emissions [6]. Alternative means for methane and hydrogen production from renewable sources include gasification and/or anaerobic digestion of organic residues from existing biofuel industries, such as the sugarcane ethanol mills.

In this way, the production of gaseous biofuels from wastes derived from sugarcane processing may increase the performance of the existing transportation sector in Brazil, while providing a framework to develop alternative production routes for gaseous fuels. Nevertheless, the impact of producing these biofuels along with sugar and ethanol has been seldom studied, which limits the comparison with their fossil-derived competitors. Therefore, acknowledging these research gaps, an analysis of the production of electricity, methane and hydrogen derived from residual bagasse gasification and anaerobic digestion of vinasse (ethanol distillery effluent) is presented. Furthermore, it is important to notice that the performance of upstream supply stage of sugarcane and its transformation processes into sugar and ethanol, as well as the end-use of those biofuels in transportation service, are also considered in this analysis.

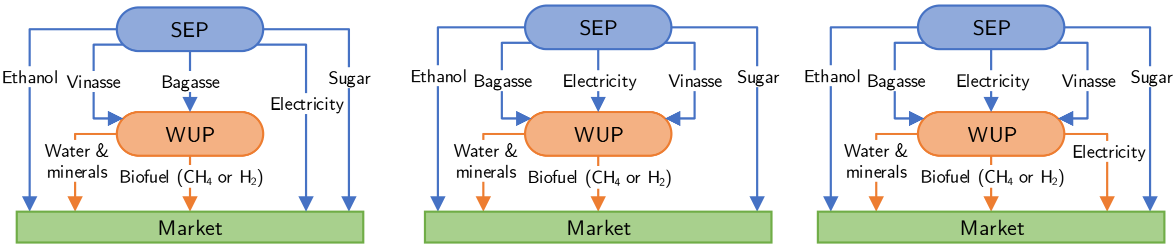
2. Description of study cases for biofuels and electricity production

A graphical summary of the studied cases is presented in Fig 1. The proposed problem consists in a sugarcane ethanol plant (SEP), which simultaneously produces sugar, ethanol and electricity; integrated to a waste upgrade plant (WUP) that uses bagasse and vinasse as main feedstocks. Both production plants have independent utility systems that internally provide electricity and heat by using a Rankine cycle with an extensive waste heat recovery system. In this way, the SEP consumes bagasse in the utility system to match its energy demands, while the WUP uses either purified syngas or vinasse-derived biomethane as fuels. Three possible products derived from vinasse and bagasse are conceived: electricity, methane and hydrogen. In the scenarios in which a biofuel is produced, the excess electricity produced in SEP can be used to partially supply the demand of the WUP. Otherwise, if such resource is not available, the WUP consumes purified syngas and/or vinasse-derived biomethane in order to match its energy demands, depending of which choice provides the minimum operational cost. Moreover, the WUP utility system can be enhanced to match only its own power demands or to generate excess electricity to the market. In summary, a scenario in which only sugar, ethanol and electricity are produced is adopted as the base case (case a, Fig 1) and seven additional study cases were conceived depending of the WUP configuration. Actually, the WUP can produce either only electricity (case b, Fig 1), only biofuel, with or without the consumption of SEP-derived electricity (cases c and d, Fig 1, respectively), or both (case e, Fig 1).



(a) Base case

(b) WUP electricity



(c) WUP biofuel without SEP electricity integration

(d) WUP biofuel with SEP electricity integration

(e) WUP biofuel and electricity

Figure 1: Summary of study cases for biofuel and/or electricity production. SEP: Sugar and ethanol plant. WUP: Waste upgrade plant.

2.1. Main processes description

An integrated sugarcane mill producing ethanol from a mixture of sugarcane juice, syrup (concentrated juice) and molasses (by-product of sugar production) is considered in this study. Bagasse is separated from sugars and water in milling process and used as feedstock in biomass boilers or exported as a byproduct. On the other hand, vinasse is the undesired portion of the alcoholic product of fermentation (wine), which is separated in distillation columns. This effluent is usually discarded in the sugarcane fields in a process called fertirrigation, as it contains an important concentration of water and potassium. In the proposed waste upgrade plant (WUP), vinasse and residual bagasse are used as main feedstocks to produce electricity and/or biofuels. Vinasse is sent to anaerobic reactors that reduce its chemical organic demand (COD) and produce biogas, a gaseous mixture mainly formed by methane and carbon dioxide. On the other hand, bagasse is grinded and converted into syngas (a mixture of hydrogen, carbon oxides and other impurities) in a indirectly heated gasifier. In this unit, a fraction of the char produced is use to provide enough heat for the gasification process that consumes steam as a gasifying agent. Next, biogas and syngas are converted into methane and/or hydrogen by means of purification processes (e.g. physical absorption, pressure swing adsorption) and chemical reactions (e.g. steam reform, water gas shift, methanization). The flowsheet of the SEP and WUP plants are shown in [5] and Appendix A flowsheet, respectively. A detailed description of the processes composing these production plants is provided in previous works [5, 7].

3. Methods

Due to the intricate relationship in terms of energy and mass transfer between material streams and unitary operations, different computational frameworks are used in order to properly model the mass, energy and entropy balances of the studied processes. The sugar-ethanol plant was modeled in the Engineering Equation Solver (EES) [8], while the WUP model is mostly developed in the Aspen Plus software [9]. Moreover, the anaerobic digestion model N°(ADM1) [**?**,10], composed of a set of ordinary differential equations, is solved by using Matlab and linked with Aspen Plus via MS Excel to estimate biogas flowrate and composition. On the other hand, the utility system of the WUP was designed based on the Equation Oriented (EO) approach in the OSMOSE Lua platform [11], developed by the IPESE group at EPFL in Switzerland, aiming the minimization of energy requirements and operation cost of the plant.

The obtained results are analyzed in the light of the exergoeconomy methodology proposed by [5], which consists of an adaptation of the available exergy costing methods [12,13] to allocate the total and non-renewable cumulative exergy consumption and specific CO_2 emissions of fuels, chemicals and electricity. This methodology is similar to other approaches, notably the thermo-ecological cost [14], and allows to pinpoint connections between the thermodynamic conversion quality and the environmental impact of the industrial processes.

3.1. Model assumptions

Sugarcane is composed of 70% of water, 14.5% of sacarose, 13.5% of fiber and 2% of other solids in mass basis, while bagasse is considered as containing 50% water and 50% fiber [15]. The sugarcane milling rate was fixed as 500 ton/day to represent an average sugar and ethanol production plant in Brazil [15]. On the other hand, vinasse is approximated by a mixture of water, inorganic substances (e.g. KOH, KCl, NH_3, among others) and organic material with average concentrations as reported in [16]. The vinasse chemical organic demand and sulfate concentrations are assumed as 31.5 gO_2/l and 0.03 gSO_4^{2-}/gO_2. Moreover, the vinasse disposal process (fertirrigation) is modeled as a black-box process with an average diesel consumption of 0.19 l/$m^3_{vinasse}$ to transport the effluent to sugarcane fields.

The thermodynamic properties of the studied mixtures are determined by using different correlations depending on their suitability. The sucrose-water solutions properties are estimated based on the methodology described by Nebra and Fernandez Parra [17]. Bagasse composition is set by using an ultimate composition (46.70% C, 44.95% O, 6.02% H, 2.14% ash, 0.17%N and 0.02%S) and a proximate analysis concentration of 83.54% volatile, 50% moisture (as-received), 14.32% fixed carbon and ash in balance [18]. Vinasse general components (e.g. sugars, lipids, organic inert, etc.), derived from the ADM1 methodology [16], were modeled as commonly observed substances (e.g. glucose, acetic acid, lignin) using the Non-Random Two-Liquid activity model (NRTL). Meanwhile, since the biogas dessulfurization involve electrolytic reactions, the adaptation of the NRTL model for electrolytes (ELEC-NRTL) is used to estimate properties of caustic solutions. On the other hand, the Perturbed-Chain Statistical Associating Fluid Theory was used to model the Selexol solvent (DEPG) [19]. For other unit operations, which mainly involve gaseous substances (e.g. gasification, methanization, flare, etc.), the Peng-Robinson EOS with Boston-Mathias modifications is used to derive their thermophysical properties.

Thermodynamic equilibrium with an approach-to-equilibrium temperature is assumed in most of the chemical reactors (e.g. steam reform, water gas shift, methanization and flare combustion) to reduce the deviations of the reaction products. An notably exception is the caustic scrubber used in the dessulfurization, which is modeled by using a rate-base calculation method [20]. Moreover, the anaerobic reactions are modeled as first order reactions with Monod equations and inhibition factors, assuming phase equilibrium and a perfectly mixed reactor [10]. On the other hand, the yield of the pyrolysis reaction products in the gasification process is estimated by means of empirical correlations [21].

All processes, excepting the anaerobic reactor, are considered as adiabatic and the pressure losses are neglected. Complementary dehumidification processes necessary to comply biomethane Brazilian legislation are not considered. The consumptions for fuel distribution and the conversion efficiencies for the end use stage conversion efficiencies (8.69% for hydrated ethanol used in flex fuel engines, 6.06% for compressed natural gas in adapted Otto cycle engines, 15.79% for hydrogen internal combustion engines), as reported by [22, 23], are used to determine the unit exergy costs and the specific CO_2 emissions of the transportation service of the produced biofuels.

3.2. Energy integration and operating cost minimization

The design of the utility system responsible to provide the combined heat and power requirements to WUP relies on the OSMOSE Lua platform. This computational framework is able to determine the best arrange of selected technologies and their respective operational loads, which satisfy the process plant energy requirements with the minimal production costs. This optimization problem can be written as the set of equations presented in (1)-(5), which constitute a Mixed Integer Linear Programming (MILP) optimization problem.

$$\min_{f^{\omega}, y^{\omega}, R_r} [(f^{\omega} \dot{B}^{CH} c)_{vinasse} + (f^{\omega} \dot{B}^{CH} c)_{bagasse} + (f^{\omega} \dot{V} c)_{water} - (f^{\omega} \dot{B}^{CH} c)_{\substack{\text{biofuel or} \\ electricity}}] t_{op} \tag{1}$$

Subject to the following constrains:

$$\sum_{\omega=1}^{N^{\omega}} f^{\omega} Q_r^{\omega} + \sum_{i=1}^{N} Q_{i,r} + R_{r+1} - R_r = 0 \quad \forall r = 1...N \tag{2}$$

$$\sum_{\omega=1}^{N^{\omega}} f^{\omega} W^{\omega} + W_{in} - W_{exp} = 0 \tag{3}$$

$$f_{min}^{\omega} y^{\omega} \leq f^{\omega} \leq f_{max}^{\omega} y^{\omega} \quad \forall \omega = 1...N^{\omega} \tag{4}$$

$$R_1 = 0,\ R_{N_r+1} = 0,\ R_r \geq 0 \tag{5}$$

Where:

- $\dot{B}^{CH}$: Chemical exergy flow rate (kW);
- c: cost of the feedstock consumed or prices of marketable fuels and electricity produced (EUR/h);
- $\dot{V}$: volumetric flowrate of water consumed (m^3/h);
- t_{op}: operational time (h);
- Q and R: heat transferred between the process streams (kW) and cascade heat flowrate (kW), respectively;
- N_{ω}: the number of units in the set of utility systems;
- f^{ω} and y_{ω}: load factor and integer variable, which represent, respectively, the load and existence of each utility unit selected by the optimization algorithm.

Apart from the rigorous chemical plant modeling performed in Aspen plus, additional mass and energy balances are included in the optimization framework for the utility systems considered. Moreover, representative costs for the Brazilian market are assumed for the main feedstocks and products considered [24–26], namely water (3.03 EUR/m^3), vinasse (0.0006 EUR/kWh), bagasse (0.0056 EUR/kWh), hydrogen (0.072 EUR/kWh), biomethane (0.032 EUR/kWh) and electricity (0.06 EUR/kWh). In summary, the optimal solution consists of the set of integer variables (y_{ω}) and load factors (f^{ω}) that satisfy the minimal energy requirement condition (2)-(5) with the minimal production costs (1).

3.3. Exergy analysis and unit exergy cost allocation

Physical and chemical exergy are evaluated neglecting the potential and kinetic exergy of the streams involved. On the other hand, some specific procedures were used to calculate the chemical exergy of sugarcane, bagasse and vinasse. Sugarcane chemical exergy is estimated based on the mass weighted average of the chemical exergy of its components, i.e. sacarose, fiber and water [23]. On the other hand, bagasse chemical exergy is determined based on its lower heating value, estimated by using the correlations of Channiwala and Parikh [27], and the

$\frac{b^c}{LHV}$ ratio is calculated in terms of its atomic composition [28]. The chemical exergy of organic components in vinasse is approximated by a correlation with the chemical oxygen demand, as previously described by Tai et al. [29], adapted by Nakashima and Oliveira Junior [16]. In order to avoid inconsistencies in the exergy balance of the distillation process, the exergy flow of vinasse organic substances was also included in the wine exergy flowrate [30]. For other common substances, the chemical exergy values reported by Szargut [28] are used.

As it has been mentioned, the unit exergy cost and specific CO_2 emissions are used to evaluate the thermodynamic performance (cumulative exergy consumption) and the environmental impact of the several possible products and processes, as proposed by [5]. This approach aims to calculate the total and non-renewable exergy costs (c_t and c_{nr} in kJ/kJ) and CO_2 emissions (c_{co2} in gCO_2/kJ) per unit of exergy of product, from the supply stage (e.g. sugarcane farming and transportation) up to its end-use (e.g. electricity or mechanical power consumption). The exergy costs are allocated following the procedures recommended by the thermoeconomy methodologies [12, 13].

3.4. Cost formation analysis

In order to identify and rank the contributions of each process and consumption in the formation of products costs, a cost allocation analysis is proposed in this paper similar to methods proposed by [31, 32]. A schematic explanation of the cost formation procedure is described in Fig 2, in which a certain process have multiple input (i) and output (o) streams. The exergy costs (c_T, c_{NR}) and specific CO_2 emissions (c_{CO2}) of the products can be determined by (6). It is important to notice that the exergy consumption and product terms, respectively, $\dot{B}_c$ and $\dot{B}_p$ may be either a total exergy flow ($\dot{B}_i$ or $\dot{B}_i$) or an exergy flow variation ($\dot{B}_i - \dot{B}_o$ or $\dot{B}_o - \dot{B}_i$), depending of the cost allocation criteria assumed for the process.

Furthermore, by considering the rational exergy efficiency of the process shown in Fig 2 as described in (7), the exergy cost of the products can be calculated as given by (8). Thus, the exergy costs of products can be determined as a function of the weighted average costs of consumption ($\sum \gamma_i c_i$) and the process efficiency ($\frac{1}{\eta}$). For the sake of illustration, these two factors can be readily separated with the aid of an auxiliary variable called $\Delta c_{process}$, which corresponds to the difference between the real product cost (ie. when $\eta < 1$) and the corresponding ideal value (ie. when $\eta = 1$), as shown in (9). In this way, the contributions of the process consumption and the process efficiency to the formation the product costs can be determined based on (9). This last equation can be adapted to calculate the specific CO_2 emissions (c_{co2}) by considering an additional term $\dot{m}_{co2}$ (gCO_2/MJ) that represents the emission associated to the direct combustion of fossil fuels, as shown in 10.

$$c_p = \frac{\sum_i B_i c_i}{\sum_p B_p} \tag{6}$$

$$\eta = \frac{\sum_p B_p}{\sum_i B_i} \tag{7}$$

$$c_p = \frac{\sum_i c_i \gamma_i}{\eta} \tag{8}$$

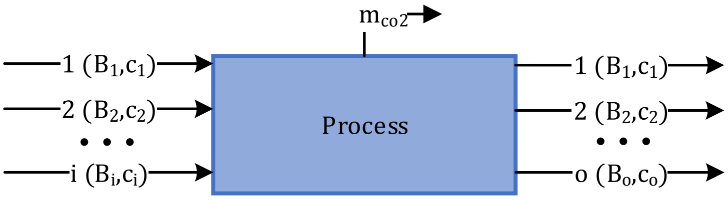


Figure 2: Simple example of cost balance

where $\gamma_i = \frac{B_i}{\sum_i B_i}$

$$c_p = \sum_i c_i \gamma_i + \Delta c_{process} \tag{9}$$

where $\Delta c_{process} = \left(\frac{1}{\eta} - 1\right) \sum_i c_i \gamma_i$

$$c_p = \sum_i c_i \gamma_i + \Delta c_{process} + \dot{m}_{co2} \tag{10}$$

Finally, it is important to notice that, since a consumption stream of one process may be the product of an upstream one, the analysis of cost allocation in a production route requires an iterative procedure to embrace multiple processes. Furthermore, it is also important to highlight that the $\Delta c_{process}$ term is not only dependent on the process efficiency, but it also takes into consideration the cost of the process consumptions. Therefore, the $\Delta c_{process}$ term can be influenced by multiple processes, since the costs of the consumption streams may be related with the efficiency of other processes. Nevertheless, the $\Delta c_{process}$ terms stress the direct cost contribution added to the given product in a certain process. This contribution can thus be reduced by either increasing the process efficiency or by reducing the use and/or costs of its consumptions.

4. Results and discussion

Table 1 shows the production remarks (ethanol, sugar, electricity, methane and hydrogen) for each case study described in Fig 1, whereas Table 2 summarize the fuel consumption in the WUP utility system. As it can be observed from Table 1, since the SEP design remains the same, the production of ethanol and sugar remains unchanged for all the cases studied. Particularly in case (b), the use of vinasse and excess bagasse from SEP to produce electricity substantially increase the power generation compared to the base case design (+353%). However, the biofuel production cases (c)-(e) still deliver more products (in the exergy basis) to the market, since they rely less on the highly irreversible process of combustion. Actually, among the selected products, the methane production appears as the most productive route for the WUP in terms of exergy yield, followed by hydrogen and electricity cases.

On the other hand, Table 2 shows that the use of excess electricity from SEP in the WUP (d)-(e) can avoid the consumption of purified syngas and vinasse-derived methane in the WUP utility system, creating a positive net effect in the overall exergy flow of upgraded products (as

Table 1: Exergy flow of main SEP and WUP products (MW) for each case in Fig. 1

	Cases							
Products	(a)	(b)	(c)CH_4	(d)CH_4	(e)CH_4	(c)H_2	(d)H_2	(e)H_2
Ethanol	124.29	124.29	124.29	124.29	124.29	124.29	124.29	124.29
Sugar	157.97	157.97	157.97	157.97	157.97	157.97	157.97	157.97
Electricity	4.23	19.16	4.23	0.30	1.60	4.23	0	1.47
Methane	0	0	57.99	67.74	67.74	0	0	0
Hydrogen	0	0	0	0	0	45.69	53.24	53.24

Table 2: Fuel exergy consumption (MW) the utility system of WUP for each case in Fig. 1

	Cases							
Fuel	(a)	(b)	(c)CH_4	(d)CH_4	(e)CH_4	(c)H_2	(d)H_2	(e)H_2
Methane (vinasse)	0	28.36	0	0	0	10.63	0	0
Syngas (bagasse)	0	47.7	11.79	0	0	0	0	0

evidenced in Table 1). In fact, as it can be seen in the (e) cases for methane and hydrogen production, the WUP utility system can even export electricity without consuming additional fuels by fully recovering the available waste heat energy.

The exergy costs calculated for the main products (i.e. ethanol, methane, hydrogen and electricity) in all the studied cases is shown in Fig. 3. As it may be expected, ethanol is the biofuel that presents the lowest unit exergy costs since its production uses less energy conversion processes and it is also independent of the downstream irreversible energy transformations occurring in WUP. Moreover, among the gaseous biofuels considered, methane is the waste-derived product that has the lowest unit exergy costs, partially due to its higher production yield. The results in Fig 3 also indicate that the co-production of electricity and biofuel, namely cases (e) for methane or hydrogen production, brings about lower unit exergy costs, mainly due the fact that most of the power generated is obtained from the exploitation of the available waste heat throughout the biofuel production plant.

Despite this fact, it is also worthy to notice that in the case of the gaseous biofuels produced by the WUP, the share of non-renewable unit exergy cost out of the total unit exergy cost is almost negligible when compared to the extent of the non-renewable unit exergy cost of the petroleum-derived fuels ($c_{nr} > 99\%$) [5]. Moreover, the results presented in Fig 3 for the non-renewable unit exergy cost are in agreement to the thermo-ecology costs reported by Piekarczyk et al. [4] for hydrogen and synthetic natural gas production from lignocellulosic biomass (0.232 and 0.135 MJ/MJ, respectively, for the best scenario).

The distribution of the exergy destruction rate among the different processes in the SEP and WUP is shown in Fig 4 for cases (a), (b) and optimal scenarios of biofuel production, cases (e) for hydrogen and methane. As it can be seen, the SEP utility system is responsible for most of the exergy destruction share, since it relies in the bagasse combustion to deliver the required heat and power demands of sugar and ethanol units. Certainly, since the SEP system is not not subject to optimization in the study cases, it may be possible to reduce its irreversibilities by using a optimized heat recovery system or more efficient power generation cycles [33]. In

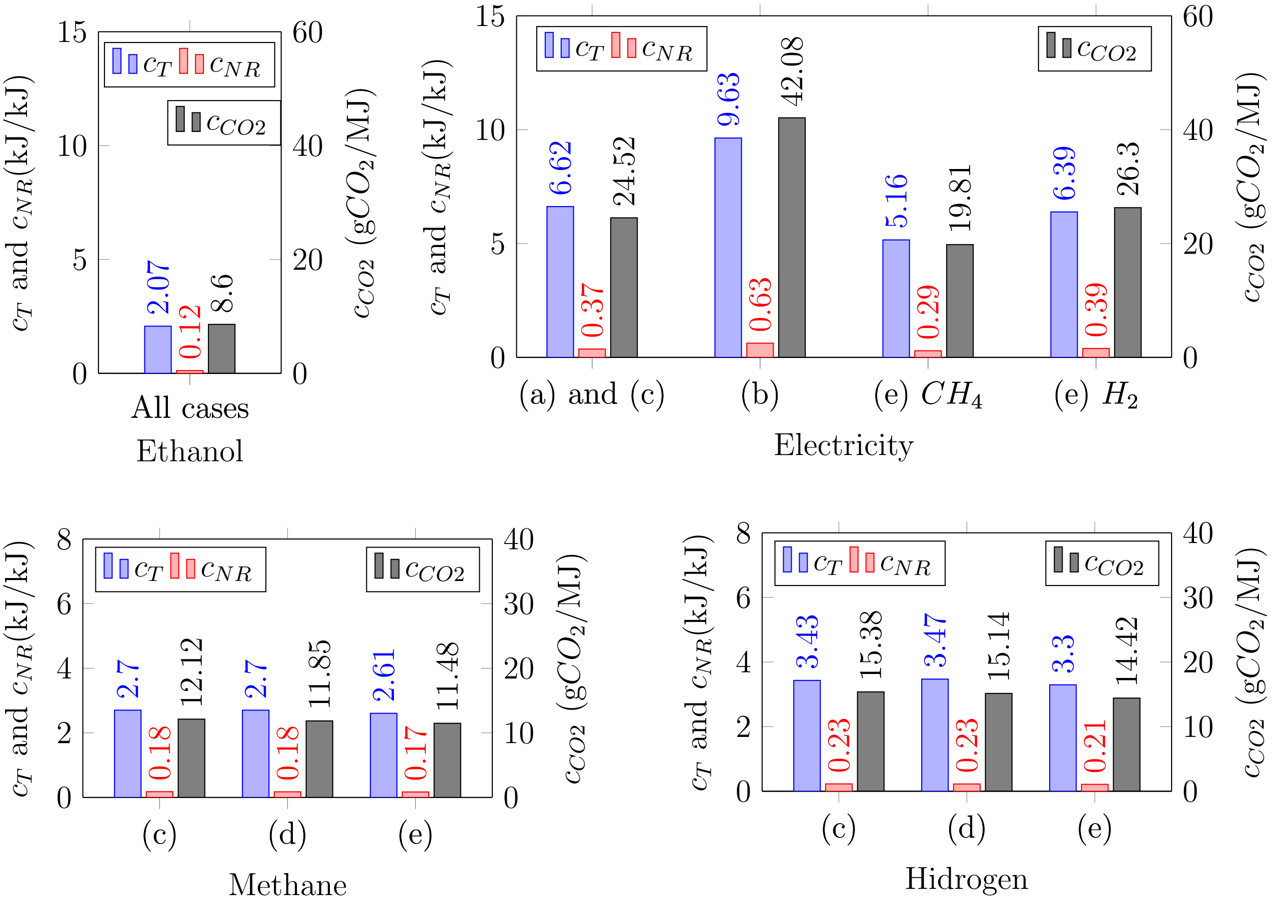


Figure 3: Exergy costs of the main products for each case study

general, the processes of the SEP are responsible for the majority of the exergy destruction in the overall system, since the exergy flowrate of the its streams are higher than the WUP streams. For instance, the fermentation, washing and milling processes are responsible for 9.7% to 10.9% of the overall exergy destruction. On the other hand, a significant portion of exergy destruction (6.3-15.5%) occurs in the fertirrigation process, since the exergy of the non-converted organic substances in vinasse is discarded to the environment. In fact, although the vinasse could be used to produce biogas in WUP, as proposed in cases (b) to (e), a great portion of the vinasse exergy is actually attributable to organic substances of difficult conversion in anaerobic digestion (e.g. lignin). Nevertheless, the exergy destruction in fertirrigation can be substantially reduced (53.4%) through the vinasse anaerobic digestion in WUP. Other units with high exergy destruction shares are the WUP utility system, mainly due to the fuel consumption, and the gasification system, which also includes highly irreversible reactions and substantial bagasse consumption to maintain the reactor conditions. It is also noticeable that, in the biofuels production scenarios (e), the WUP utility system destroys less exergy because it does not burn fuels, differently from the standalone electricity generation scenario (b). Fig 4 also shows that the introduction of a WUP does not necessarily reduce the overall exergy destruction,

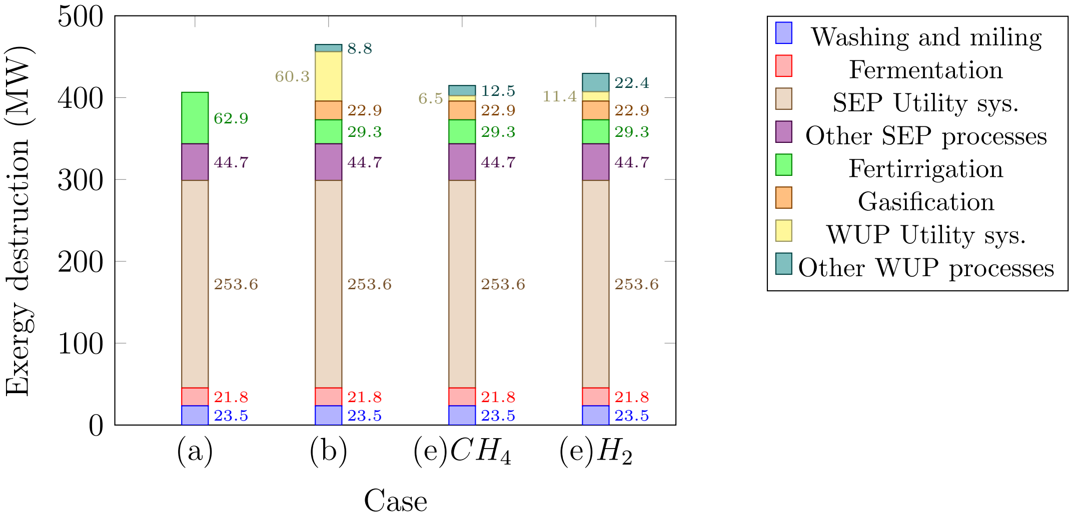


Figure 4: Exergy destruction breakdown for the SEP and WUP processes in selected cases (shown in Fig. 1)

since it consumes/transforms the residual bagasse that otherwise would be sold to the market. Therefore, the WUP objective is closer to yield value added products out of low grade exergy residues than to sole reduce the exergy destruction of the overall system.

The costs formation analysis, shown in Fig 5, gives other insight to the influence of some processes in the unit exergy costs of products. The result for the ethanol total exergy unit cost shares similarities with observations published by [34], in which the utility sytem (boiler), fermentation and destillation processes also are the main sources of the ethanol c_T cost. In general, the results is conected with the exergy destruction analysis, since highly irreversible processes impact negatively the exergy costs, but the influence of certain units are shifted. For example, the fertirrigation process does not affect the costs of any biofuel or electricity, because its products does not directly influence any other process. Furthermore, the influence of units closer to the end product have greater impact in the cost formation. For instance, although the gasification unit correspond to only 5.3-5.5% of total exergy destruction in the biofuel production cases, its direct influence in the cost formation its about 11.6-15.2%. Other important remark is the different impact of non-renewable consumptions (natural gas, diesel, NaOH and other chemicals) for each exergy costs. The exergy flow of these streams may not be relevant among the other feedstocks, but they are mostly composed by non-renewable sources and are linked with greater indirect fossil emissions.

The unit exergy costs and specific CO_2 emissions at the end-use stage are presented in the Fig 6 for the best biofuel production scenarios, namely ethanol production along with hydrogen or methane (cases e, Fig. 1). As it can be seen, all the costs are sharply penalized by the low exergy efficiency of fuel conversion in the transportation service. Nevertheless, differently from the the supply and transformation stages, biomass-derived hydrogen highlights as the biofuel with lowest exergy costs, since the conversion in the end use stage is more efficient compared with other fuels.

In summary, the results presented in Fig 3 and Fig 6 can be compared with those obtained

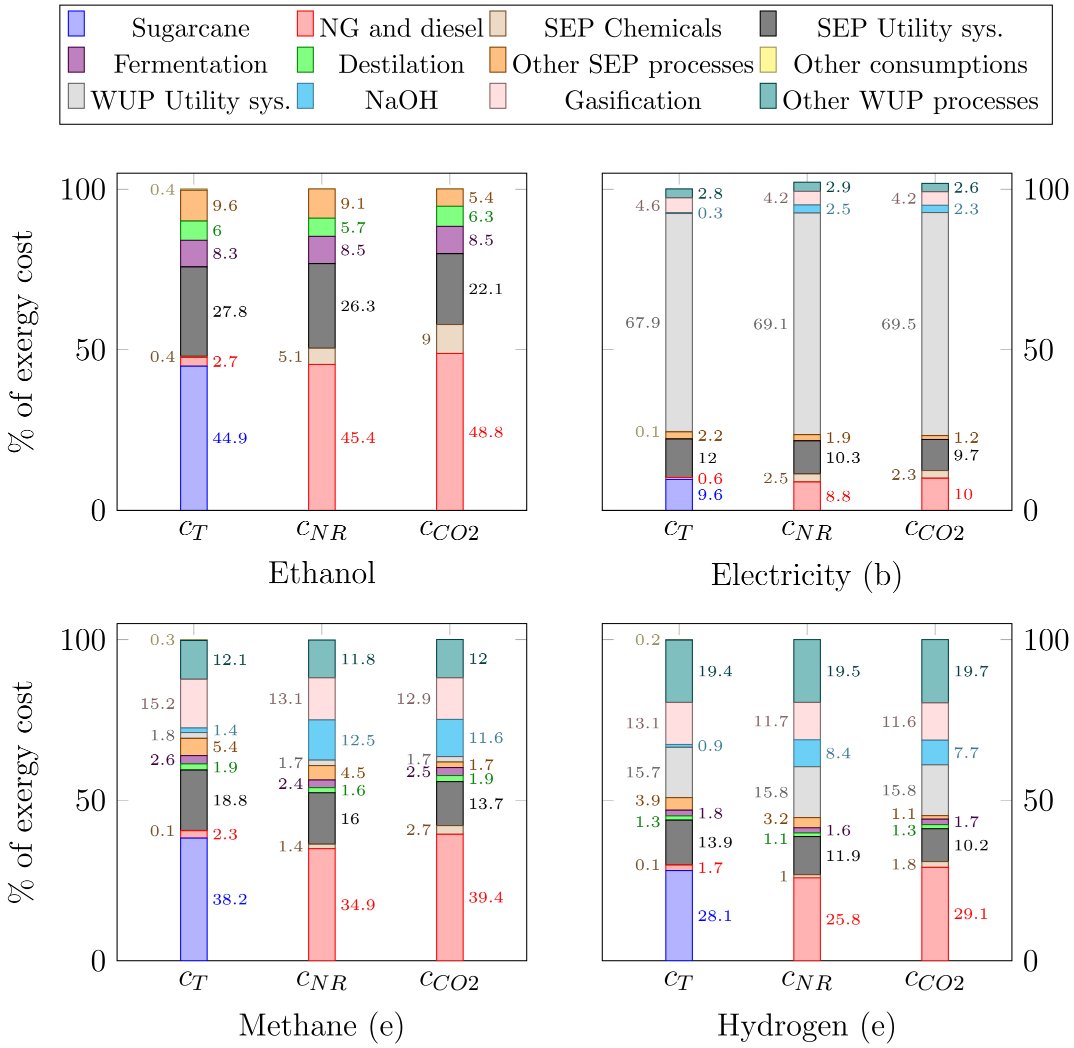


Figure 5: Cost formation breakdown of main products for selected cases

by [5, 22], which are shown in Table 3. This analysis indicate that the c_t and c_{co2} for waste derived biofuels are higher than fossil alternatives for the production stage. Nevertheless, as it has been previously mentioned, the non-renewable and end-use stage c_{CO2} are much lower than those fossil-derived. This fact indicates an overall environmental friendly perspective regarding the upgrade of biorefinery residues. In other words, the production and end use of biofuels produced from sugarcane wastes could actually improve the environmental performance of the natural gas and hydrogen fueled transportation. Another important remark is that the ethanol exergy costs are lower compared to those values reported by [5, 22], since the present study suitably considers the exergy flowrate of the organic substances embodied in vinasse, leading to a greater impact in cost balance of the ethanol distillation.

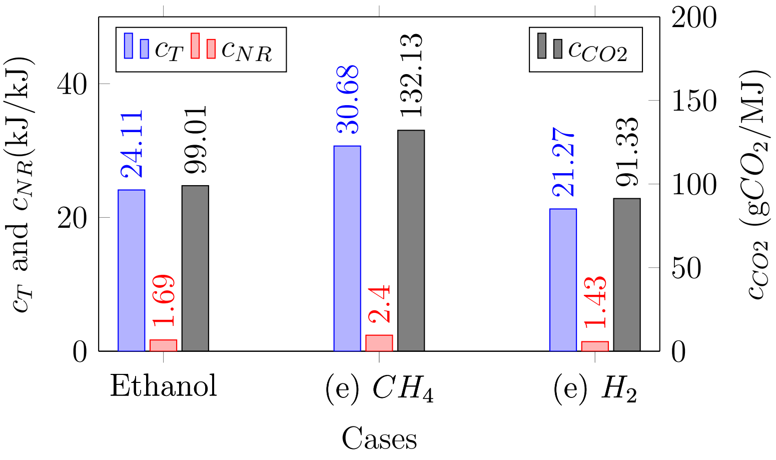


Figure 6: Unit exergy costs and specific CO_2 emissions for the biofuels end-use stage

Table 3: Unit exergy costs and specific CO_2 emissions reported by [5, 22]

Product	Production			End-use		
	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/MJ)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/MJ)
Ethanol	3.056	0.1802	12.7	35.4573	2.3638	166.93
Natural gas (fossil)	1.055	1.055	2.3	19.4394	18.6675	1045.23
Hydrogen (fossil)	1.5139	1.5137	73.9	9.9930	9.5940	471.79

5. Conclusion

In this paper, the analysis of the unit exergy costs and specific CO_2 emissions of the production and end-use of biofuel and electricity from sugarcane industry residues, vinasse and bagasse, was investigated. In total, eight possible production cases were studied varying the desired end products obtained in a waste upgrade plant (WUP), in which the WUP utility system was optimized based on the minimization of production costs and energy requirements. The results indicate that the methane production has the lowest unit exergy costs for the production stage, while hydrogen uprise as the most efficient route when the end-use stage is also considered. These best scenarios are obtained for a sugarcane biorefinery that enables the integration of the electricity produced in sugar and ethanol plant (SEP) to a separated waste upgrade plant (WUP). This allows to avoid the consumption of produced biofuel in the combustion process in WUP utility system. Certainly, the preliminary results may be subject to further optimization by varying the SEP utility system configuration, which was not performed in this paper.

As a result, in comparison with fossil fuel derived alternatives, the biofuel presented much lower non-renewable unit exergy costs and CO_2 specific emissions and higher total unit exergy costs. Thus, the production and usage of gaseous biofuels generate more irreversibility at the expense of the consumption of mostly renewable exergy sources with a lower indirect carbon footprint. The exergy destruction results indicate that further improvements can be obtained by improving the utility system efficiencies and/or by reducing the consumption of heat exergy and electricity in various chemical processes. On other hand, the cost formation analysis pinpoints the slight non-renewable dependency of biofuels production in the supply stage (e.g. natural gas and diesel in the agriculture and transportation stages) and due to chemicals consumption (e.g. NaOH, CaO, H_2SO_4). In summary, this research endorses the production of biofuels and electricity from sugarcane wastes based on environmental parameters and determines the main units with the highest improvement opportunities.

Acknowledgments

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 would like to thank the National Agency of Petroleum, Gas and Biofuels, ANP (PRH/ANP Grant 48610.008928.99) and the Colombian Administrative Department of Science, Technology and Innovation - COLCIENCIAS. At last, the third author thanks to the National Research Council for Scientific and Technological Development, CNPq (grant 304935/2016-6).

Appendix A - Waste upgrade plant flowsheet

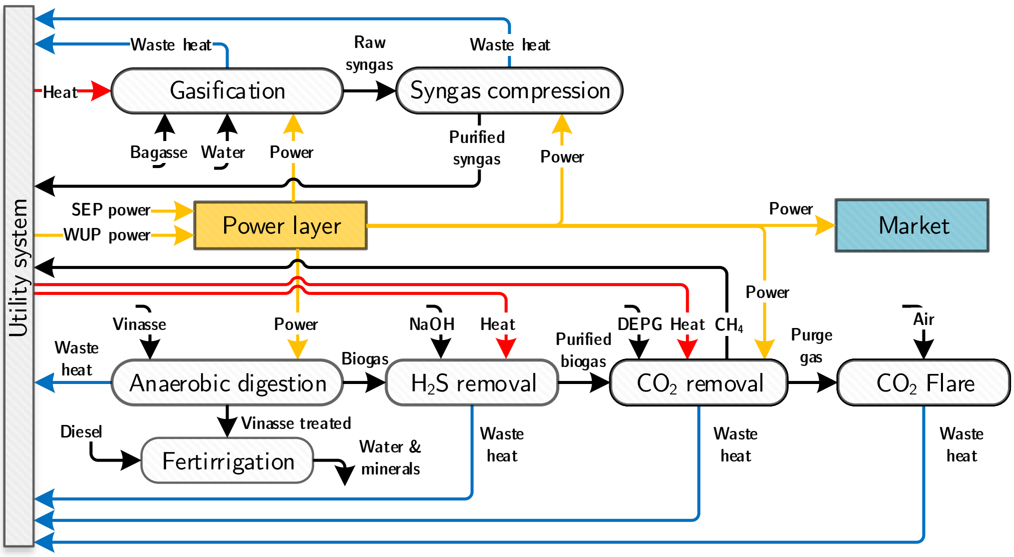


Figure 7: Flowsheet of the waste upgrade plant for power generation

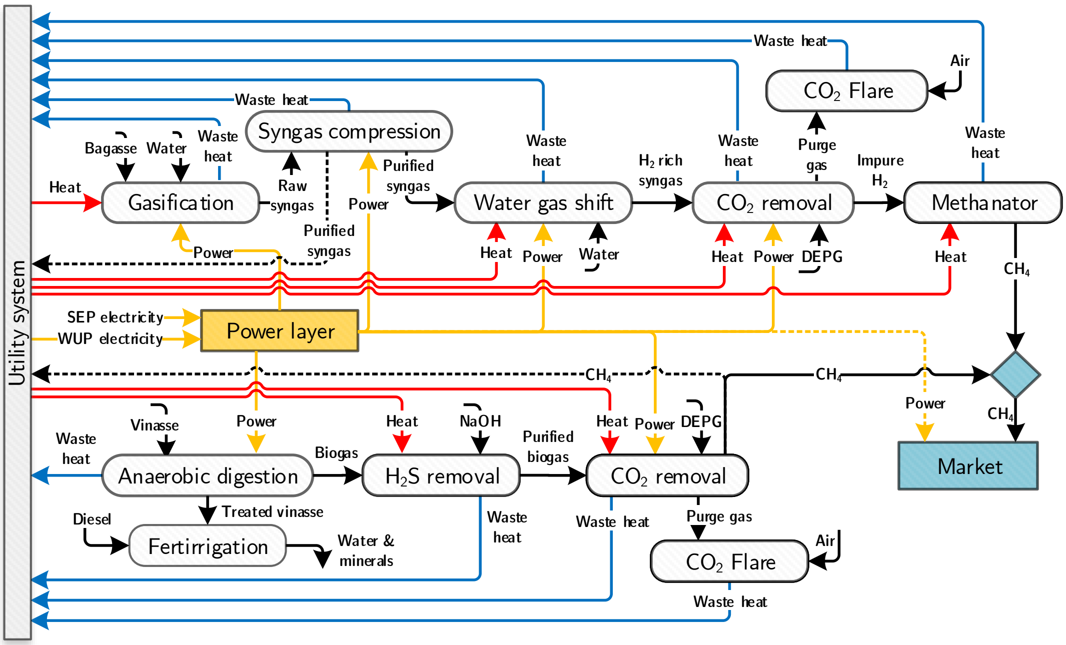


Figure 8: Flowsheet of the waste upgrade plant for methane production

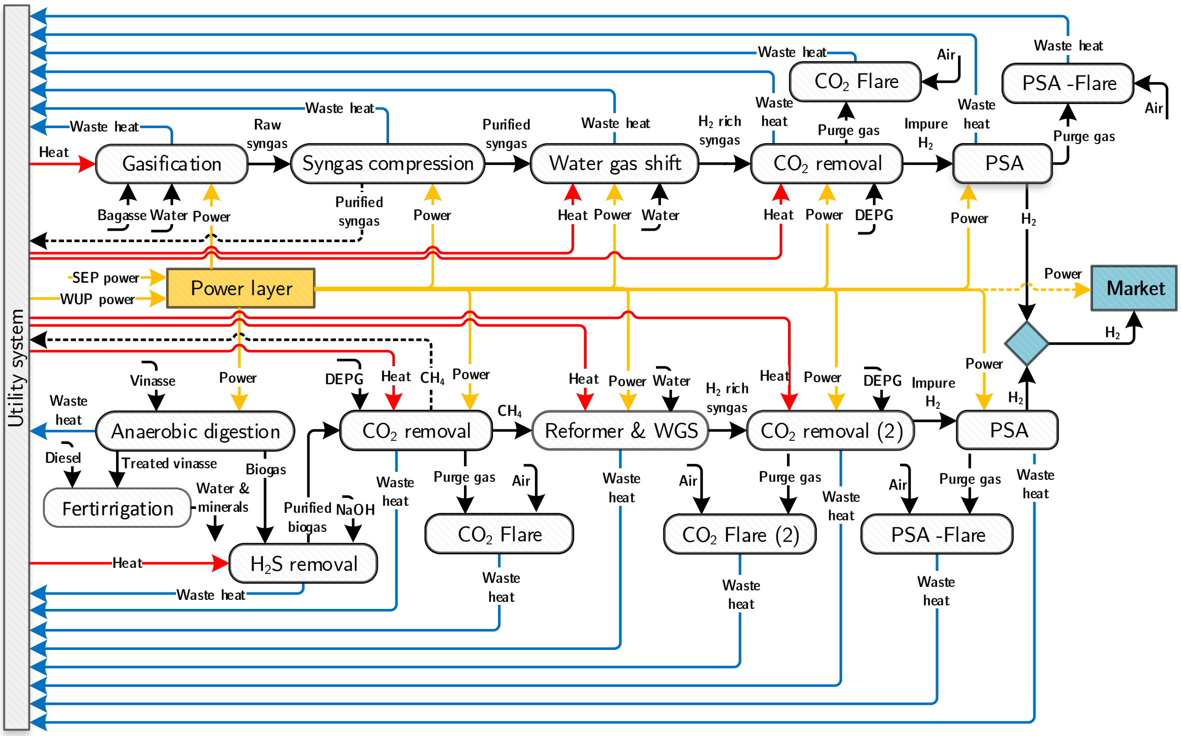


Figure 9: Flowsheet of the waste upgrade plant for hydrogen production

Nomenclature

$\dot{B}$	exergy flow rate, kW
c	specific cost, EUR/kWh, EUR/m^3, kJ/kJ or gCO_2/MJ
f	load factor
$\dot{m}_{co2}$	CO_2 emissions per exergy, gCO_2/kJ
N_ω	number of units in the set of utility systems
Q	heat flow, (kW)
R	cascade heat flow, kW
t_{op}	operational time, h
$\dot{V}$	volumetric flowrate of water consumed, (m^3/h)
y	integer variable
W	power, kW

Greek symbols

γ	exergy flow ratio
$\Delta c_{process}$	cost difference in a process, kJ/kJ or gCO_2/kJ
η	exergy efficiency

Subscripts and superscipts

ω	ω-th utility unit
CH	chemical
$co2$	carbon dioxide
exp	exported
i	i-th component or input
in	internally consumed
nr	non-renewable
o	output
p	product
r	r-th temperature interval
t	total

REFERENCES

[1] International Energy Agency (IEA). Co2 Emissions From Fuel Combustion 2018: Overview; 2018. Available from: `https://webstore.iea.org/co2-emissions-from-fuel-combustion-2018`.

[2] Empresa de Pesquisa Energética (EPE). Brazilian energy balance - Summary report: year base 2017; 2018.

[3] International Energy Agency (IEA). World Energy Outlook 2018: Executive summary; 2018. Available from: `https://webstore.iea.org/world-energy-outlook-2018`.

[4] Piekarczyk W, Czarnowska L, Ptasiński K, Stanek W. Thermodynamic evaluation of biomass-to-biofuels production systems. Energy. 2013;62:95–104.

[5] Flórez-Orrego D, da Silva JAM, Velásquez H, de Oliveira S. Renewable and non-renewable exergy costs and CO2 emissions in the production of fuels for Brazilian transportation sector. Energy. 2015 aug;88:18–36.

[6] World Energy Council (WEC). Natural gas perspectives: the role of natural gas; 2016. Available from: `https://www.worldenergy.org/wp-content/uploads/2017/11/WEC-PERSPECTIVES-Word-Gas-Report-WEB.pdf`.

[7] Nakashima RN, Flórez-Orrego D, de Oliveira Junior S. Integrated anaerobic digestion and gasification processes for upgrade of ethanol biorefinery residues. In: 5th International Conference on Contemporary Problems of Thermal Engineering. Gliwice, Poland; 2018. p. 11.

[8] Klein SA, Alvarado F. Engineering equation solver. F-Chart Software, Madison, WI. 2002;1.

[9] Aspen Plus v.8.8. Aspen Technology. 2015;.

[10] Batstone DJ, Keller J, Angelidaki I, Kalyuzhnyi SV, Pavlostathis SG, Rozzi A, et al. Anaerobic digestion model no. 1 (ADM1). London, UK: IWA Publishing; 2002.

[11] Yoo MJ, Lessard L, Kermani M, Maréchal F. OsmoseLua - An Integrated Approach to Energy Systems Integration with LCIA and GIS. In: Gernaey KV, Huusom JK, Gani R, editors. 12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering. vol. 37 of Computer Aided Chemical Engineering. Elsevier; 2015. p. 587 – 592.

[12] Lozano MA, Valero A. Theory of the exergetic cost. Energy. 1993;18(9):939–954.

[13] Lazzaretto A, Tsatsaronis G. SPECO: A systematic and general methodology for calculating efficiencies and costs in thermal systems. Energy. 2006;31(8-9):1257–1289.

[14] Stanek W, Czarnowska L. Thermo-ecological cost - Szargut's proposal on exergy and ecology connection. Energy. 2018;165:1050–1059. Available from: `https://doi.org/10.1016/j.energy.2018.10.040`.

[15] Ensinas AV, Nebra SA, Lozano MA, Serra LM. Analysis of process steam demand reduction and electricity generation in sugar and ethanol production from sugarcane. Energy Conversion and Management. 2007;48(11):2978 – 2987. 19th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems.

[16] Nakashima RN, de Oliveira Junior S. Exergy assessment of vinasse disposal alternatives : concentration , anaerobic digestion and fertirrigation. In: 31st International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact on Energy Systems ECOS; 2018. p. 15.

[17] Nebra SA, Fernandez Parra M. The exergy of sucrose-water solutions: proposal of a calculation method. In: 18th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact on Energy Systems ECOS; 2005. .

[18] Ardila YC, Figueroa JEJ, Lunelli BH, Filho RM, Wolf Maciel MR. Syngas production from sugar cane bagasse in a circulating fluidized bed gasifier using Aspen Plus: Modelling and Simulation. Computer Aided Chemical Engineering. 2012 jan;30:1093–1097.

[19] Field RP, Brasington R. Baseline flowsheet model for IGCC with carbon capture. Industrial and Engineering Chemistry Research. 2011;50(19):11306–11312.

[20] Cherif H, Coquelet C, Stringari P, Clodic D, Pellegrini L, Moioli S, et al. Experimental and Simulation Results for the Removal of H2S from Biogas by Means of Sodium Hydroxide in Structured Packed Columns. ICBST 2016: 18th International Conference on Biogas Science and Technology. 2016;.

[21] Puig-Arnavat M, Bruno JC, Coronas A. Modified Thermodynamic Equilibrium Model for Biomass Gasification: A Study of the Influence of Operating Conditions. Energy & Fuels. 2012 feb;26(2):1385–1394.

[22] Flórez-Orrego D, Silva JAM, Oliveira SD. Exergy and environmental comparison of the end use of vehicle fuels: The Brazilian case. Energy Conversion and Management. 2015;100:220–231.

[23] Flórez-orrego D. Thermodynamics and environmental comparison (CO2 emissions) of production and end use routes of vehicle fuels, derived from petroleum, natural gas, biofuels, hydrogen and electricity (electric vehicles) (In portuguese); 2014.

[24] Flórez-Orrego D, Sharma S, Oliveira SD, Marechal F. Combined Exergy Analysis and Energy Integration for Design Optimization of Nitrogen Fertilizer Plants. In: 30th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, ECOS 2017. San Diego, CA, USA; 2017. .

[25] Santos VEN, Ely RN, Szklo AS, Magrini A. Chemicals, electricity and fuels from biorefineries processing Brazil's sugarcane bagasse: Production recipes and minimum selling prices. Renewable and Sustainable Energy Reviews. 2016 jan;53:1443–1458.

[26] Hotza D, Diniz da Costa JC. Fuel cells development and hydrogen production from renewable resources in Brazil. International Journal of Hydrogen Energy. 2008 oct;33(19):4915–4935.

[27] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel. 2002;81(8):1051–1063.

[28] Szargut J, Morris DR, Steward FR. Energy analysis of thermal, chemical, and metallurgical processes. New York, NY: Hemisphere Publishing; 1988.

[29] Tai S, Matsushige K, Goda T. Chemical exergy of organic matter in wastewater. International Journal of Environmental Studies. 1986 oct;27(3-4):301–315.

[30] Nakashima RN. Exergy assessement of biogas production and usage in the sugarcane industry (In Portuguese); 2018.

[31] Cuadra CT. Symbolic thermoeconomic analysis of energy systems. Exergy, Energy System Analysis and Optimization-Volume II: Thermoeconomic Analysis Modeling, Simulation and Optimization in Energy Systems. 2009;2:61.

[32] Torres C, Valero A, Rangel V, Zaleta A. On the cost formation process of the residues. Energy. 2008;33(2):144 – 152. 19th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impactof Energy Systems.

[33] Pellegrini LF, de Oliveira Junior S. Combined production of sugar, ethanol and electricity: Thermoeconomic and environmental analysis and optimization. Energy. 2011;36(6):3704 – 3715.

[34] Palacios-Bereche R, Mosqueira-Salazar KJ, Modesto M, Ensinas AV, Nebra SA, Serra LM, et al. Exergetic analysis of the integrated first- and second-generation ethanol production from sugarcane. Energy. 2013;62:46–61.