

Exergy assessment and techno-economic optimization of bioethanol production routes

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Abstract:

Currently, electricity generation and second-generation ethanol production from lignocellulosic feedstocks represent technological alternatives in the sugar-energy sector. Nevertheless, the introduction of new production processes denotes a real challenge due to the complexity and diversity of the technological routes that can be evaluated. In addition, there are economic and environmental factors that must be considered during the development and consolidation of these new configurations. Accordingly, this paper presents a methodology to perform the exergy and exergo-environmental analysis, evaluation and ranking of sugarcane biorefinery scenarios. Hence, operating technical data of each configurations were adopted as well as the environmental issues of using these systems. The proposed models assessed the Conventional (*Route 1*), Biochemical (*Route 2*) and Thermochemical (*Route 3*) pathways using simulation programs and mathematical tools to simulate the ethanol production and electricity generation. Furthermore, the process integration and different uses for the excess bagasse were studied with various pretreatment methods aiming the optimizing and ranking of routes. The results indicated optimal settings that allowed the routes ranking in terms of the *renewability exergy index* “ λ ”. In this way, the optimized conventional route presented the maximum exergy efficiency of the processes, therefore the lowest average unitary exergy cost of the evaluated platforms. While the biochemical pathway (*Route 2*) was the system that promoted an increase of 28.58 % and 82.87% in the ethanol production, when compared to *Route 1* and *Route 3*, respectively. In addition, the thermochemical pathway (*Route 3*) presented the configuration with the highest power generation rate exceeding (214.98 kWh/TC). Concerning, the environmental impact results, it was found that the most sustainable configuration was the *Route 2*, which presented the lowest overall CO₂ emissions rates (131.45 gCO₂/MJ products).

Keywords:

Lignocellulosic Biomass, Exergy Analysis, Exergo-Environmental Performance, Biorefineries, Ethanol Conversion Pathways.

1. Introduction

Currently, second-generation biofuel production from lignocellulosic materials is a research topic of interest around the world. These works focus on determining what could be the biofuel participation in the energy matrix, process efficiency, productivity, environmental impact [1] and their biotransformation into value-added products based on the technological production routes [2].

1.1. Sugarcane-based biorefineries

In this framework, biomass conversion systems have to be developed using advanced conversion pathways to compete with hydrocarbon-based fuels. For the particular case of ethanol and electricity production, lignocellulosic biomass represents an attractive biomass feedstock, mainly agricultural and forest residues, like sugarcane bagasse, which are nowadays accessible in large volumes (*i.e. approximately 280 kg of bagasse with 50% humidity per ton of sugarcane*) and burnt in boilers for steam and electricity generation.

Lignocellulosic materials could be converted into ethanol through the biochemical configuration, which includes pretreatment methods followed by hydrolysis step of cellulose and hemicellulose into sugars and their subsequent fermentation. Alternatively, the thermochemical pathway could also be adapted to ethanol production, in which biomass gasification provides a potential technology to obtain a variety of biofuels. Figure 1 shows the selected routes for ethanol and electricity production in this study.

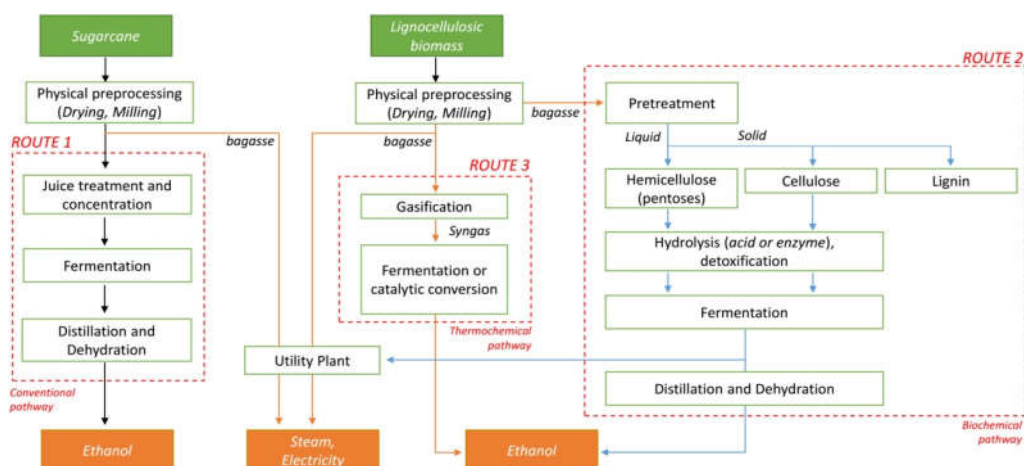


Figure 1. Pathways for bioethanol and electricity production from lignocellulosic biomass.

Another aspect to be highlighted in the bioenergy field is the application of systematic process design methodology looking for optimal configurations, increase efficiency and ranking the different pathways [3], [4], [5]. In this work, three technological pathways for ethanol production and electricity generation were assessed. Route 1 involved the conventional configuration, Route 2 represented the biochemical system and Route 3 simulated the thermochemical platform into the sugarcane biorefinery Brazilian context.

1.2. Thermochemical conversion of biomass

When lignocellulosic materials are exposed to heat (normally above 300°C), an irreversible chemical change occurs and the biomass is transformed into various solid, liquid, or gaseous components. The range of products produced will depend on the temperature of the process, the rate at which the biomass is exposed to this temperature, and the gasifying medium (*oxygen or air*). The main thermochemical conversion processes are *torrefaction pyrolysis/charcoal production, gasification and combustion*. Torrefaction and pyrolysis are oxygen-free conversion systems, while gasification and combustion approaches require the use of an oxidant. Gasification uses oxidants in small amounts, while combustion uses stoichiometric or excess amounts of air [6].

Some applications in this pathway included the thermodynamic evaluation, exergy analysis and advanced gasification of energy systems [7], [8], [9].

1.3. Biochemical conversion of biomass

Biological conversion methods include the use of several microorganisms to convert biomass organic resources into various high-energy gaseous or liquid fuels. The two most important biological conversion processes are fermentation and anaerobic digestion processes. Fermentation is the conversion of sugars from crops into alcohol, while anaerobic digestion converted the biomass into methane gas (*biogas*) and carbon monoxide by the action of anaerobic microorganisms [6].

Applications in the biochemical field involved the integrated first- and second-generation processes for ethanol production from sugarcane to boost and to consolidate biorefineries configurations and the optimization strategy aimed at renewable carbon valorization [1], [10], [11], [12].

2. Description of Processes

2.1. ROUTE 1-Conventional platform

The ethanol production process from sugarcane develop in this work considers the autonomous distillery technology available in Brazil, such as sugarcane dry cleaning, concentration in multi-effect evaporation systems, sugarcane juice sterilization and ethanol dehydration via *monoethylene glycol* (MEG). A brief explanation of these steps is given below.

Cleaning of sugarcane and extraction of sugars: Sugarcane goes through a cleaning stage to remove the contaminants brought during harvest. This feedstock is prepared for extraction through shredders and juice is then extracted by mills. The juice extraction separates the sucrose-containing juice from the bagasse [13]. Bagasse is used as fuel in a cogeneration (COGEN) unit, while the juice is directed to the treatment process. In the simulations, it was adopted a dry cleaning system.

Juice treatment: The juice from extraction system contains a significant quantity of small pieces of bagasse, suspended matter and non-sugar impurities. Thus, it was adopted that juice passes through a physical treatment consisting of filters and cyclones for removing solids and insoluble contaminants. Soluble impurities were removed at the chemical treatment stage by chemical reactants, being juice heating necessary for the purification reactions [14]. It was simulated that the juice undergoes a flash tank, before entering the clarifier.

Juice concentration, sterilization and cooling: The treated juice should be concentrated to reach an appropriate sugar concentration (approx. 17%) for the fermentation process [13]. Thus, the concentration of treated juice occurs in a multiple effect evaporation-MEE system. Exhaust steam from the COGEN unit was employed as an energy source for the 1st effect. MEE works with reducing pressure, owing to a vacuum imposed on the last effect, producing the necessary temperature difference between the heating vapour and the juice along the consecutive effects. Afterwards the must preparation, the sterilization stage was performed by a HTST (*High Temperature Short Time*) treatment, with heating to 130°C, followed by fast cooling down to the fermentation temperature [13].

Fermentation: This stage was simulated founded on the Melle-Boinot process. Ethanol recovery in the fermentation gas was performed by absorption column. After fermentation, the yeast were separated, treated and recycled to the process. Simulation of the fermentation process was performed based on [13], [14], [15].

Distillation: Initially, the wine is heated to a suitable temperature before entering the 1st distillation column. Later, hydrated ethanol (93.7% wt. of ethanol) is obtained as a result of stripping and rectification stages. In the distillation process, a large amount of vinasse is generated (approx. 0.02% wt. of ethanol), which is handled as effluent [10], [11].

Dehydration: The dehydration stage is required to remove the remaining water and produce anhydrous ethanol. In this work, a process of extractive distillation with MEG was studied. Simulation of the distillation and dehydration steps was performed based on Dias et al.,[16].

Cogeneration system: The bagasse with 50% (w/w) of moisture content obtained after sugar extraction was adopted as a fuel. It was adopted a steam-cycle operating with live steam at 480 C and 67 bar using a backpressure steam turbine to power generation. Moreover, the combustion reactions in the boiler section indicated by NREL [17] and Dias [18] were considered.

An autonomous distillery with processing capacity of 500 TC/hour was selected as it represents the processing capacity of a standard mill capacity, 2,000,000 TC/year in São Paulo State, Brazil. Table 1 shows the equipment specifications for each operation unit of the 1G ethanol processes. Figure 2 shows a schematic diagram for the conventional production route of ethanol and electricity.

Table 1. Main parameters adopted for simulating 1G ethanol production.

Parameter	Value	Unit
<i>Sugarcane cleaning, preparation and juice extraction</i>		
Efficiency of soil removal in cleaning operation	70	%
Efficiency of sugar extraction	96	%
Bagasse moisture content	50	% w.b.
<i>Juice treatment</i>		
Heating temperature of juice treatment	105	°C
Filter cake moisture content	70	%
CaO consumption	0.5	kg/t cane
<i>Juice concentration (evaporation system)</i>		
Pressure 1st effect	1.69	bar
Pressure 2nd effect	1.31	bar
Pressure 3rd effect	0.93	bar
Pressure 4th effect	0.54	bar
Pressure 5th effect	0.16	bar
Brix content in final must	19	%
<i>Fermentation</i>		
Conversion yield from sugars to ethanol	89	%
Sulphuric acid for yeast treatment	5	kg/m ³ _{etOH}
Yeast concentration in fermentation reactor	25	v/v%
<i>Distillation and rectification</i>		
Stages in rectification section (<i>Col. A1</i>)	8	
Stages in stripping section (<i>Col. A</i>)	19	
Stages in phlegm rectification (<i>Col.B-B1</i>)	45	
Stages in top concentrator (<i>Col. D</i>)	6	
Ethanol content in vinasse and phlegmasse	0.02	%
<i>Dehydration (monoethylene glycol - MEG)</i>		
Extractive column pressure	1.01	bar
Recovery column pressure	0.2	bar
Ethanol content in anhydrous ethanol	99.3	wt %
<i>Cogeneration Unit</i>		
Boiler pressure (<i>Superheated steam</i>)	67	bar
Boiler temperature (<i>Superheated steam</i>)	480	C
Isentropic efficiency of electricity generation (<i>ST</i>)	80	%

Table 2. Parameters for simulating the enzymatic hydrolysis process-Route2.

Parameter	Value	Unit
Enzymatic hydrolysis		
Reactor solids load	10	%
Reactor temperature	50	C
Enzyme loading (<i>Cellulase</i>)	15	FPU/g
Cellulose–glucose conversion	92	%
Hemicellulose–xylose conversion	35.7	%
Glucose–ethanol conversion (Fermentation)	92	%
Solid content in concentrate hydrolysate	17	%

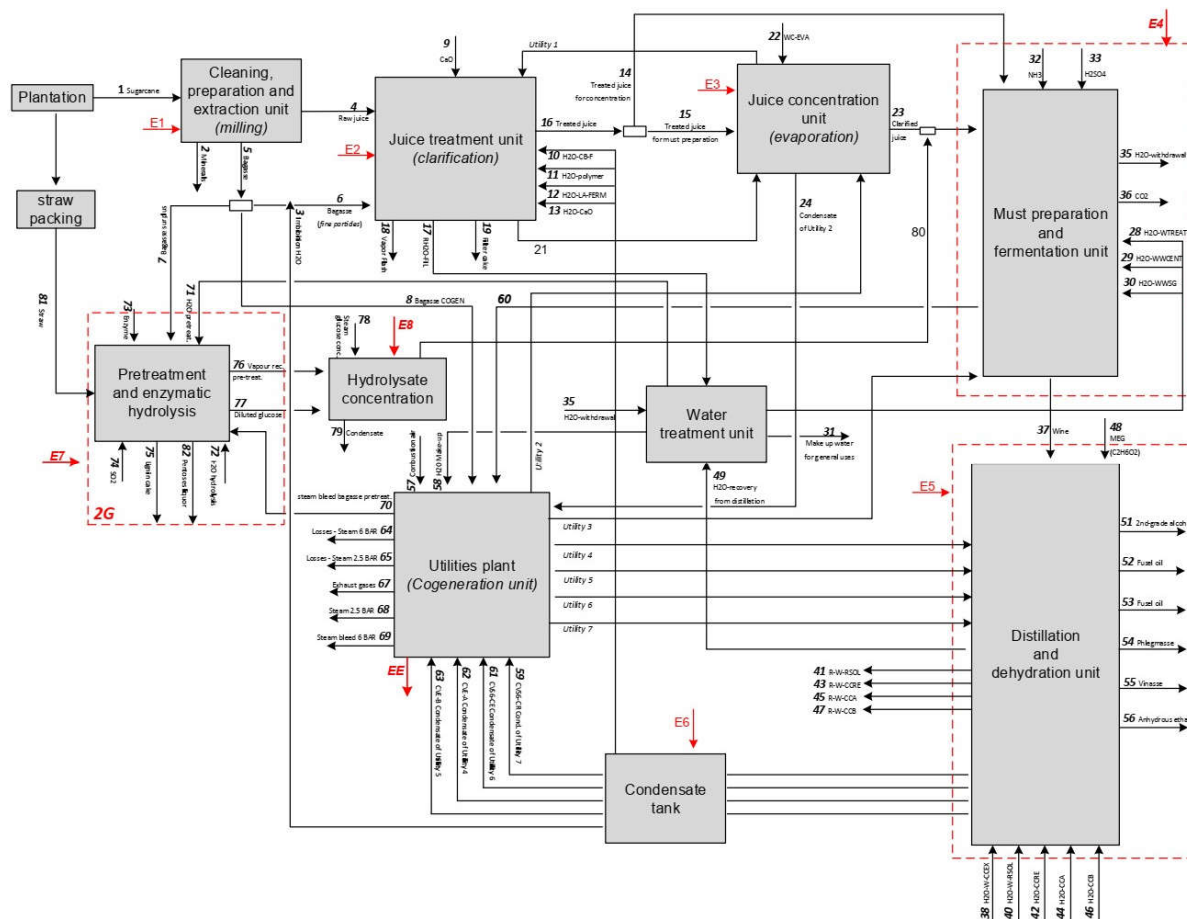


Figure 3. Flowsheet of the 2G ethanol production via biochemical.

2.3. ROUTE 3-Thermochemical platform

The simulation processes was develop using hierarchy units in Aspen Plus® and comprises many sections, which include bagasse gasification, syngas preparation (cleaning) and power generation. A brief description of these steps is given below.

Bagasse gasification: The sugarcane bagasse is feed in an atmospheric fluidized bed biomass gasifier. The equipment is represented as follows: Biomass decomposition, volatile reactions, char gasification, and gas-solid separation.

The first step is the biomass decomposition. In this stage, the material is converted into its constituting components such as *carbon (c)*, *hydrogen (h)*, *oxygen (o)*, *nitrogen (n)*, *sulfur (s)*, *chlorine (cl)* and *ash* through a yield reactor (RYIELD).

Then, the previously obtained stream goes through a separation column unit; at this step, the pyrolysis process occurs. A separation column model was utilized before the Gibbs reactor to split the volatile materials and solids to carry out the volatile reactions.

In the following step, char gasification, the gasifying medium (*air and steam*) is provided to guarantee optimal gasification operational conditions. The char particles resulting from the devolatilization step consist of the remaining carbon fraction and ash. Lastly, the cyclone model represents the gas/solid separation stage at the riser outlet. The top outlet stream (SYNGAS) is composed of all the gases from the Gibbs reactor and the bottom outlet solid stream SOLID represents the output from the ashes (ASH).

In the gasification process simulation were considered the following assumptions **i).** Steady-state and isothermal; **ii).** Devolatilization (*volatile combustion*) process is adopted to be instantaneous and to take place at the bed bottom; **iii).** Char and volatiles are formed in the pyrolysis process. The volatiles include non-condensable (*i.e.* H_2 , CO , CO_2 , CH_4 , C_2H_2), condensable volatiles (tar), and water [21]; **iv).** Char only contains carbon and ash [22].

Syngas preparation (cleaning): Several impurities in produced gas, such as tars, ammonia (NH_3), hydrogen sulfide (H_2S), nitrogen oxides (NO_x), sulfur oxides (SO_x), alkalis, and particulates, cause problems in downstream applications. This analysis has concentrated on removing tar contaminants from syngas. Hence, it was adopted the cleaning of gasification gas using cyclones to divide the solids and condensation flows for separation of liquids like tar and water.

Power generation: Compressed syngas is combusted in a gas turbine (GT) with compressed air. Later, the combustion exhaust is directed to the GT to generate electricity. The amount of air is calculated and the temperature of the exhaust from the GT burner is $580^\circ C$. The following characteristics were taken into consideration in the model: **i).** Steady-state operation; **ii).** Compressor pressure ratio adopted was 16; **iii).** Discharge pressure was 1 atm; **iv).** Polytropic efficiency of the compressor, gas and steam turbine were 80% and **v).** Polytropic efficiency of the pump was 80%.

In the hierarchy block (*Combined Heat and Power-CHP Unit*) develop in Aspen Plus[®] simulator for the combined cycle the syngas obtained in the gasification process is used as fuel. In addition, the air and syngas streams are compressed according to the specified pressure ratio and mixed in an RStoic reactor, where combustion reactions take place, at constant pressure.

Lastly, the outlet gases from the heat exchange with a stream of compressed liquid water, which then leaves as steam at the specified temperature. A heat exchanger is used to condense the water that will be pumped back and begin another cycle.

The schematic sketch of the thermochemical route integrated to the conventional bioethanol process can be found in Figure 4.

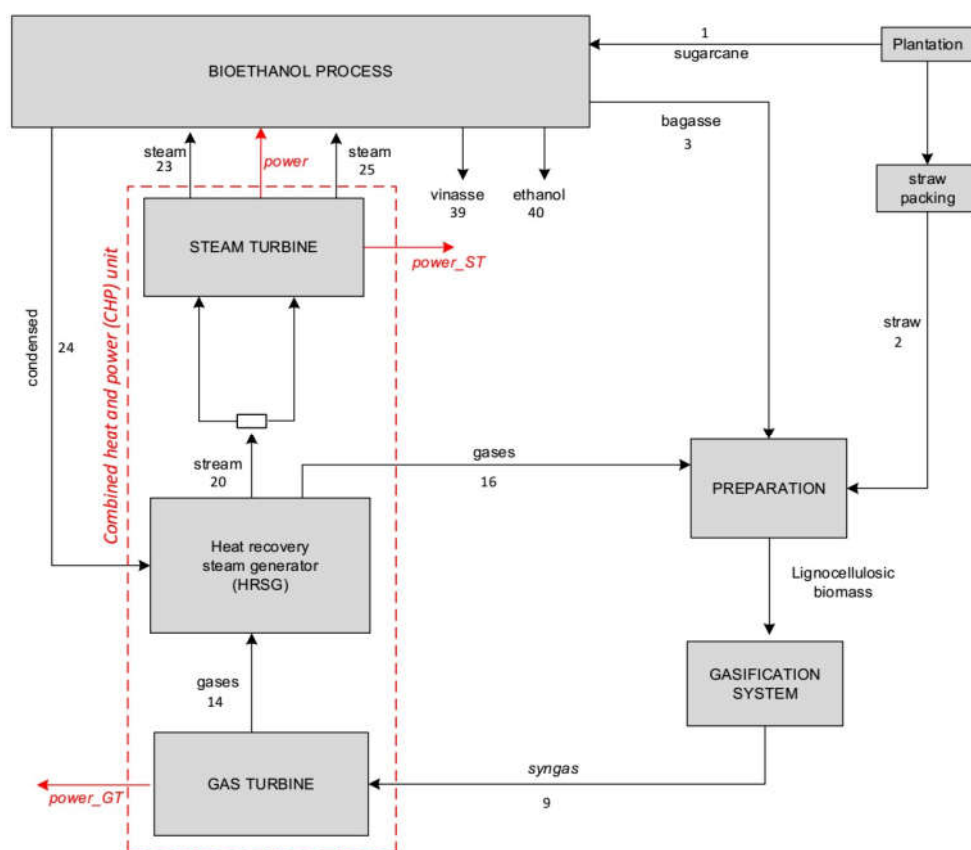


Figure 4. Flowsheet of the Route 3.

3. Methodology

3.1. Process Design of Sugarcane Biorefineries

The methodology has been divided in several steps. The first part deals with the process modeling and analysis, which includes mass, energy and exergy balances of each configuration. These balances would be established by theoretical and empirical correlations to decide the thermodynamic properties models of each system, utilizing the process simulation software Aspen Plus® [23], widely applied in the chemical and petrochemical industries. The process parameters evaluated were using literature data for Brazilian sugarcane mills.

After that, exergy efficiencies, irreversibility rates and the exergy use/exported per unit of products, as well as the environmental metrics related with the conversion processes were considered like indicators, allowing a systematic comparison of each biorefineries configurations. In this step, the use of EES® software (*Engineering Equation Solver*) was relevant for calculating the properties of liquids and gases, as it already includes a well-developed library of chemical compound properties. Moreover, it was developed for the simultaneous resolution of equation systems, and routines were implemented to calculate the values of these indicators

The energy integration step was performed according to the pinch analysis approach. Heat recovery potential between hot source and cold process streams is achieved in a heat cascade problem resolution. The optimal utility integration is obtained when the combined production of ethanol, electricity and heat are maximized, which minimizes the operating cost by solving the heat cascade problem employing a MILP (*mixed integer linear programming*) technique [24]. The MILP problem is solved utilizing the GLPK software package and *glpsol* solver embedded in the OSMOSE platform, as described by MIAN et al.[25] and Albarelli et al.[26].

3.2. Process Simulation: Property method and composition

The components properties of the lignocellulosic biomass were obtained from the biofuel databank developed by NREL [17]. Hence, biomass and ash adopted in the Aspen Plus[®] simulator were added as non-conventional (NC) components, and the global stream class is MIXCINC (*with substreams MIXED, Conventional Inert Solid-CISOLID and NC*), usually employed when both conventional and non-conventional solid are existing in the feedstock stream. Table 3 shows the feeding composition adopted in this study.

Table 3. Raw material composition.

Formula	Components	Molecular weights	wt%, wet basis		
		(kg/kmol)	SUGARCANE	CISOLID	MIXED
C ₆ H ₁₀ O ₅	Cellulose	162.14	5.95	43.46	
C ₅ H ₈ O ₄	Hemicellulose	132.12	3.52	25.71	
C _{7.3} H _{13.9} O _{1.3}	Lignin	122.49	3.19	23.30	
C ₁₂ H ₂₂ O ₁₁	Sucrose	342.29	13.92		16.13
C ₆ H ₁₂ O ₆	Glucose	180.16	0.60		0.70
K ₂ O	Minerals	94.2	0.20		0.23
KCl	Potassium chloride	74.55	1.17		1.36
C ₆ H ₆ O ₆	Aconitic acid	174.1	0.6		0.70
H ₂ O	Water	18.015	69.82		80.89
SiO ₂	Silicon dioxide (SOIL)	60.08	1.03	7.52	

Adapted from Dias [18], Palacios-Bereche [27].

In addition, different property packages were used within the simulator to more accurately represent chemical component behaviors in specific routes. In the 1G ethanol process simulation, the property method adopted was NRTL (*Non-Random Two-Liquid*), for calculation of activity coefficients of the liquid phase, while ideal behavior was presumed for the vapor phase in most of the simulations [23].

In the 2G ethanol process (*Biochemical Route*), the thermodynamic method considered was UNIQUAC (*short for UNiversal QUAsiChemical*) for liquid phase and RK Redlich–Kwong equation of state for vapor phase. Besides, the main property used in the *Thermochemical Route* was Peng–Robinson equation of state with Boston–Mathias (PR-BM) alpha function for calculations involving gases.

Regarding the cogeneration system, the thermodynamic method RKS-BM (RKS Redlich–Kwong–Soave and BM Boston–Mathias) was adopted, which is adequate for high-temperature gases [23]. For the steam flows, steam tables (*STEAMNBS model*) were employed, once these characterise pure water and steam properties for a wide range of temperatures and pressures.

3.3. Exergy Assessment

The exergy approach, which combined the First and Second Law of Thermodynamics was applied to assess the performance of the integrated 1st and 2nd generation bioethanol process. Exergy represented the maximum work that could be obtained by means of reversible processes from a thermodynamic system that interacts with the components of the environment until the dead state equilibrium is attained [28]. Exergy analysis offers an effective way for evaluating the quantity and quality resource, as it denotes the maximum of the quantity of a particular resource that could be converted into work, given the prevailing environmental conditions.

In this work, the chemical (b_{CH}) and physical (b_{PH}) exergies are measured due to the physico-chemical processes involved. Thus, the b_{PH} was determinate according to (1).

$$B_{PH} = H - H_0 - T_0(S - S_0) \quad (1)$$

Where H is the enthalpy flow rate at P, T (kW), S represent the entropy rate/flow rate at P, T (kW/K), T_0 is the Temperature at the reference state (K), H_0 denote the Enthalpy flow rate at P_0, T_0 (kW) and S_0 is the Entropy rate/flow rate at P_0, T_0 (kW/K).

On the other hand, chemical exergy denote the energy available to do work when the substance undergoes a reversible process from the restricted reference state (25 °C, 1 atm) to a thermodynamically dead state in which the system achieve a complete thermodynamic equilibrium (*thermal, pressure, and chemical*) [28]. Chemical exergy is the most important contribution to its exergy value for the majority of natural resources including lignocellulosic materials. Conceptually, b_{CH} quantifies the value of a chemical substance, or compound, as measured against a selected reference environment [29]. Equation (2) defines the chemical exergy:

$$B_{ch} = n_{mix} \left[\sum_i x_i b_i^{ch} + R_u T_0 \sum_i x_i \ln Y_i x_i \right] \quad (2)$$

Where n_{mix} is the total amount of moles of all constituents in a mixture, x_i is the mole fraction of component i in the mixture. In this study, the influence of Y was evaluated for each compound permitting to observe that it provides values close to one. For this reason, Y was considered equal to one, an ideal solution, in mixtures for chemical exergy calculations. The term b_i^{ch} is the standard chemical exergy. The b_{CH} for various compounds are found in the [28] and [30].

The exergy efficiency expressions adopted in the ethanol production and electricity generation routes are given in Equations (3), (4), and (5) for the utilities plant (*cogeneration unit*), the global exergy efficiency (*expression Index 1*), and the global exergy efficiency (*expression Index 2*), respectively.

$$\eta_{cogen} = \frac{B_{electricity} + B_{steam} - B_{consumption}}{B_{bagasse} + B_{water} + B_{condensed}} \quad (3)$$

$$\eta_{global_1} = \frac{B_{ethanol} + B_{electricity}}{B_{cane} + B_{straw}} \quad (4)$$

$$\eta_{global_2} = \frac{B_{ethanol} + B_{electricity} + B_{by-products}}{B_{cane} + B_{straw} - B_{bagasse}} \quad (5)$$

3.4. Exergo–environmental analysis

Exergy analysis methods can be applied to detect the processes inefficiencies looking for enhancing the efficiency of the carbon based fossil and renewable energy-resource use, for quantification of the destruction locations, types and magnitudes of wastes and losses. To enhance the interconnection of the exergy and the environmental analysis, renewable share and exergy efficiency are suggested, in a contribution to sustainability via the exergo–environmental analysis.

The environmental impact of a particular technology or product should be viewed over the full life, relating all environmental inputs (*resource intake*) and outputs (*emissions*) to one functional unit:

the product or service under consideration. In this framework, exergo–environmental analysis is different in nature: it is much more resource and product, and hence also efficiency, oriented [31].

3.4.1. Renewability exergy index for bioethanol production routes

In this study, the exergo–environmental discussion regarding the renewability for the bioethanol production and electricity generation routes was conducted by the *renewability exergy index* λ [32]. Reversible processes represent process that having occurred can be reversed to the initial system and surroundings states. This concept could contribute in the analysis of the renewability of energy conversion processes to develop in a rational basis by using thermodynamic parameters [33].

Based on these aspects, one can define a renewability exergy index that consider the exergy associated to the useful products ($B_{\text{products/by-products}}$) of a given energy conversion process, the destroyed exergy or total process irreversibility ($B_{\text{destroyed}}$), the exergy associated to the fossil fuels (B_{fossil}) required, the needed exergy to disposal the wastes, and the exergy related with emissions, residues and not treated wastes, as presented in (6):

$$\lambda = \frac{\Sigma B_{\text{products/byproducts}}}{B_{\text{fossil}} + B_{\text{destroyed}} + B_{\text{deactivation}} + B_{\text{disposal}} + \Sigma B_{\text{emissions/residues}}} \quad (6)$$

According to [32], depending on the value of the renewability exergy index, it indicates that: *i*). Processes with $0 \leq \lambda < 1$ are environmentally unfavourable; *ii*). For internal and externally reversible processes with non-renewable inputs, $\lambda = 1$; *iii*). If $\lambda > 1$, the process is environmentally favorable, and additionally, increasing λ suggests that the process is more environmentally friendly; *iv*). When $\lambda \rightarrow \infty$, it means that the process is reversible with renewable inputs and no wastes are generated.

When λ renewability index is higher than 1, the exergy of the products could be used to "restore" the environment to the conditions prior to the occurrence of the process and still obtain a positive flow of exergy to another use.

It is emphasized that the index has a strong relationship with the control volume (VC) analyzed, due to the number of energy conversion processes being involved. Thus, when the adopted VC is expanded, the value of the λ index is decreased as a function of the irreversibility rates and the contribution of non-renewable (fossil) inputs to the process. For this reason, the compatibility of the control volumes is a key issue when different systems are compared to prevent distortions into the analysis.

3.4.2. Average unitary exergy cost (AUEC)

Exergetic cost is a conservative value accounting for the external exergy that is necessary to render an exergy stream available within a specific productive process [34]. The average unit exergy costs are a measure of the cumulative irreversibility and exergy consumption, which occur during the upstream processes to form a given exergy flow. Thus, higher irreversibilities translate into a higher unit exergy costs.

3.5. Process integration assumptions

The value of $\Delta T_{\text{min,ref}}$ represents a compromise between the heat exchangers' surface area required to satisfy the energy target, which affects the investment cost, and the heat that is recovered from the process, influencing in the energy conversion efficiency.

Another aspect to be highlighted is that the heat transfer between streams is assured by considering an appropriate ΔT_{min} . Equation (7) shows the relationship between $\Delta T_{\text{min}/2}$, assigned to each stream (*j*), and the corresponding heat transfer coefficient (α).

$$\Delta T_{min,j}/2 = \Delta T_{min,ref}/2 \cdot \left(\frac{\alpha_{ref}}{\alpha_j} \right)^b \quad (7)$$

Where α_{ref} and $\Delta T_{min,ref}$ are, respectively, the heat transfer coefficient and minimum approach temperature of a reference heat exchanger [35]. The minimum approach temperature difference (ΔT_{min}) selected for the process streams was 10°C, except for streams of the evaporation system, where 4°C was adopted. The existence of a *Multiple Effect Evaporator (MEE)* in the system represents a conceptual problem for the construction of the CC and the GCC, because the minimum target utility is greatly affected by the arrangement and operation conditions. The thermal integration procedure was carried out applying the iterative steps described on Palacios-Bereche et al. [13].

3.6. Techno-economic assessment

For the techno-economic assessment, capital investment (CAPEX) and operational expenses (OPEX) were estimate for each biorefinery configuration. The assessment is focus on a cash flow analysis related to the investment associated with the industrial plants. These plants were calculated using the database for equipment costs and capacities of the process simulation results, as well as on its main cash inflows (*revenues*) and outflows (*expenses*) founded on the average market prices from historical data for ethanol and electricity in Brazil.

Hence, to determinate the total investment cost, the process equipment are adjusted using correlations from literature Turton [36]; Ulrich and Vasudevan [37] to detail the specific process pressures size, purchase cost, and material. Then, the total investment is calculated using multiplication factors to consider indirect expenses like installation costs, contingencies, and auxiliary facilities. All costs were updated to 2016 by employing the *Marshall and Swift Index* (1536).

3.7. Environmental performance

In this work, the environmental impacts were accounted in the biorefineries configurations using the Life Cycle Assessment (LCA) approach cradle-to-gate. Life cycle inventory (LCI) and life cycle impact assessment (LCIA) have been already integrated into the energy systems modelling of the OSMOSE platform [38]. The ecoinvent database V3.1 was used for this purpose. This methodology is commonly applied in the bioenergy sector [39–43].

The impact assessment method selected the Brazilian case-Activity ‘*cane sugar production with ethanol by-product*’, which was proposed by the Intergovernmental Panel on Climate Change (IPCC). Thus, the Global Warming Potential (GWP) 100 years is chosen as environmental performance indicator. LCA results are obtained by multiplying life cycle inventory flows with the appropriate characterization factor for each inventory flow.

Furthermore, material flows are modelled to determine the overall CO₂ emissions of the technological pathways. Therefore, direct emissions are associated with each flow a corresponding elementary flow, through the ecoinvent database available in SimaPro[®] software. Different LCA methods (*e.g.* *IMPACT 2002+*, *IPCC 2007*) and indexes could be utilized for the impact assessment.

Another aspect to be highlighted is that the global analysis of the technological routes uses the carbon dioxide equivalents emissions as an indicator; it provides the relation between the net-CO₂ emissions from the processes operation and the exergy of the products for each configuration. Hence, it is denominated *specific CO₂ equivalent emissions in exergetic base* (CO₂ EE), as given in (8).

$$CO_{2EE} = \frac{\text{Global } CO_{2\text{equivalent emissions}}}{B_{\text{products}}} \quad (8)$$

4. Results

4.1. Techno-economic optimization

In this section, it is presented the process integration for technological routes targeting the *Maximum Energy Recovery or Minimum Energy Requirement (MER)*. It represents the best possible energy recovery in a heat exchanger network (HEN) for a particular ΔT_{min} . In this work, the technological were evaluated using the OSMOSE-LUA platform.

4.1.1. Process Integration for the proposed Sugarcane Biorefineries

The hot and cold streams are used to build the heat cascade, which is represented graphically by the process composite curves (CC) and grand composite curves (GCC), in terms of temperature profile and enthalpy (heat load), as reported in Fig. 5 to Fig. 7. Firstly, Figure 5 shown the CC and the GCC for the conventional biorefinery of first-generation ethanol process.

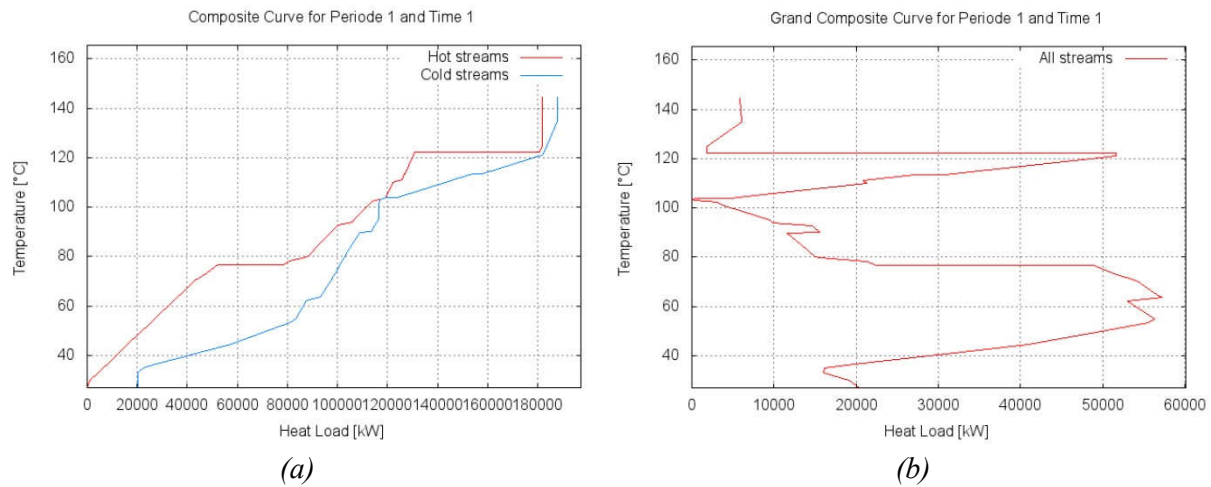


Figure 5. Composite (a) and grand composite (b) curves for Route 1.

Later, Figure 6 presented the CC (a) and GCC (b) for the 2G biochemical configuration.

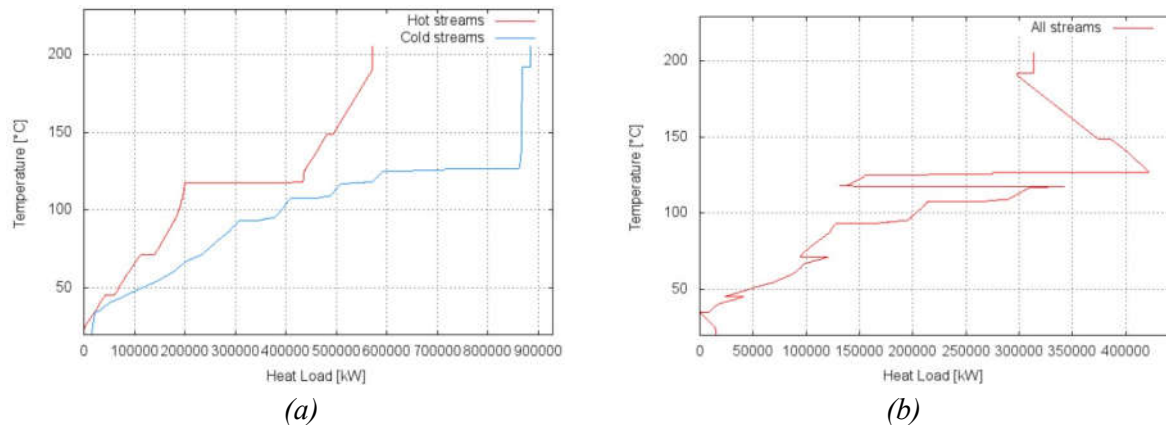


Figure 6. Composite (a) and grand composite (b) curves for Route 2.

The hot composite curve is obtained by lumping the heat from different hot streams in the same temperature interval and therefore represents the heat available from the process. Equivalently, the cold composite curve is composed by all the cold streams and therefore represents the heat requirement.

Heat exchange can occur only if the temperature difference between the composite curves is greater than the set ΔT_{\min} . The grand composite curve displays the net heat exchanged per temperature interval and is obtained by subtracting the hot composite curve from the cold composite curve. This graphical representation is especially useful to display the integration of certain units, and in particular the steam network, with the rest of the process. Lastly, the MER for Route 3 is shown in Figure 7.

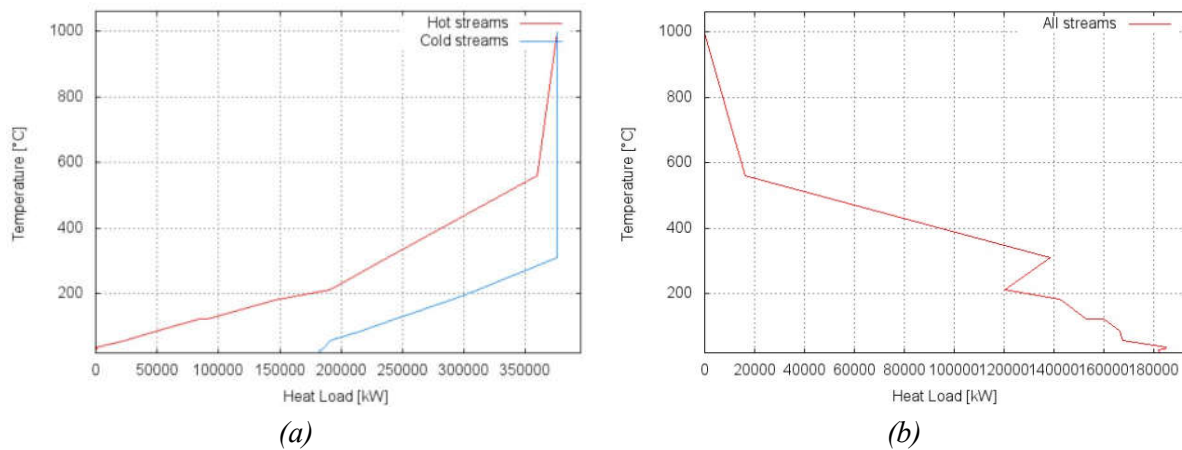


Figure 7. Composite (a) and grand composite (b) curves for Route 3.

4.2. Exergo–environmental analysis

4.2.1. Renewability exergy index for bioethanol production routes

This index was applied with *two (2) variations* for each configuration. Firstly, it was considered the exergy of the products (ethanol and electricity) and by-products separately with respect to products that could be obtained through the residues processing, denominated *Index 1*. These by-products vary according to the route evaluated (Table 4 only for *Index 1*). Afterwards, it was adopting the exergy of the products and by-products together in the numerator, defined as *Index 2*, as presented in Figure 8.

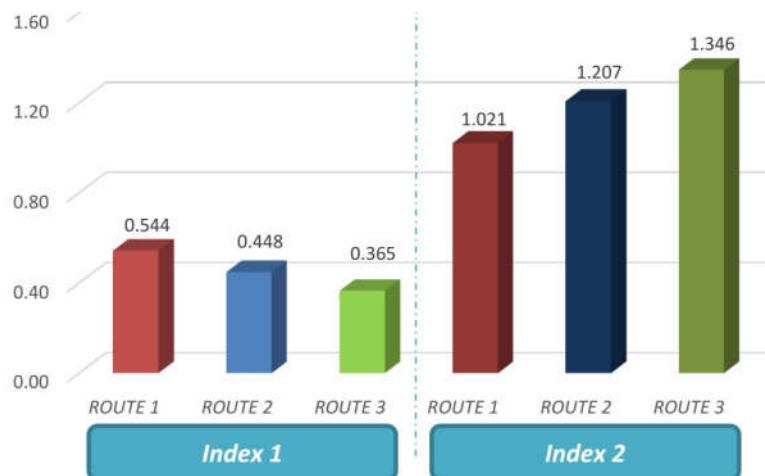


Figure 8. Renewability exergy index of the technological routes.

Table 4. Exergy flows associated with the renewability index.

Parameter	ROUTE 1	ROUTE 2	ROUTE 3
<i>B [kW]</i>			
<i>B chemical inputs (Fossil)</i>			
Calcium Oxide (CaO)	138	138	138
MEG (C ₂ H ₆ O ₂)	20	58	20
Nutrients (NH ₃)	794	794	794
Sulfuric acid (H ₂ SO ₄)	100	97	100
Sulphur dioxide (SO ₂)	0	1468	0
<i>B fossil</i>	<i>1051</i>	<i>2554</i>	<i>1051</i>
<i>B products</i>			
B ethanol	265.485	341.338	186.669
B surplus electricity	35.803	26.072	122.539
<i>B products</i>	<i>301.288</i>	<i>367.410</i>	<i>309.208</i>
<i>B by-products and residues</i>			
Surplus bagasse	74.815	165.653	306.072
Filter cake	20.492	24.227	16.306
Vinasse	35.628	38.779	31.677
Pentose liquor	0	53.023	0
<i>B by-products and residues</i>	<i>130.935</i>	<i>281.682</i>	<i>354.055</i>
<i>B emissions</i>			
CO ₂ (Fermentation unit)	5390	5621	5120
Gases (Distillation and dehydration unit)	889	1278	759
Flue gas (Cogeneration unit)	24.536	26.120	45.036
<i>B emissions</i>	<i>29.926</i>	<i>33.020</i>	<i>50.915</i>
Irreversibility			
<i>B destroyed</i>	<i>392.288</i>	<i>502.140</i>	<i>440.892</i>

In addition, Table 4 summarizes the different parts the renewability index λ to indicate their contribution by component. It should be noted that the irreversibility determined for each route refer to the total destroyed exergy, involving also the contributions of the cogeneration process. It must be underlined that when this approach is used, two values of the exergy efficiency appear, stating the relationship between technological routes renewability and exergetic performance.

Figure 8 depicts the *Index 1* and *Index 2* employed in the global exergy efficiency calculation using the Equation (9) and (10), respectively.

It is observed that the renewability exergy index (λ) for the evaluated routes was environmentally unfavorable, *Index 1*, indicating that the exergy of the products cannot be used to restore the environment to the prior conditions to the occurrence of the process, mainly due to the total irreversibility found in the ethanol production and electricity generation processes. While applying *Index 2*, the renewability indicator λ was environmentally favorable as a result of the residues exergetic valorization and their potential as by-product.

The results obtained for the renewability index (λ) were compared with the values reported by Pellegrini; Oliveira Jr, [44] and Velásquez et al. [33]. Therefore, when comparing with the simulation of the traditional mill analyzed by Pellegrini; Oliveira Jr [44] and with the configuration adopted by Velásquez et al. [33] for the *Route 1*, a lower value of the λ indicator is obtained. This is probably due to differences in the definition adopted for the chemical inputs (B_{fossil}), emissions ($B_{emissions}$) and the exergy of products/by-products ($B_{products/by-products}$).

However, the results obtained involving the *Route 2* of this research depict similar values of that reported in Velásquez et al. [33] for the analysis of the lignocellulosic materials conversion (pulp + fruit), in the framework of the biofuels production impact assessment.

Index 1 for the *Route 3* presented divergent results when compared to the metric obtained in the analysis of the BIGCC system, conducted by Pellegrini [45]. This is mainly due to differences in milling capacity and the implementation of the gasification process using both sugarcane bagasse and straw as energy sources.

Consequently, through the application of the indicators CO₂ equivalent index in exergetic base and renewability exergy index, the exergy concept is used as an environmental indicator to quantify the processes irreversibilities and to determine the presence of traces left in the surroundings (*environmental impact*). A comparison between the λ indicator and the global exergy efficiency of the technological routes is presented in Figure 9 (*Index 1*) and Figure 10 (*Index 2*).

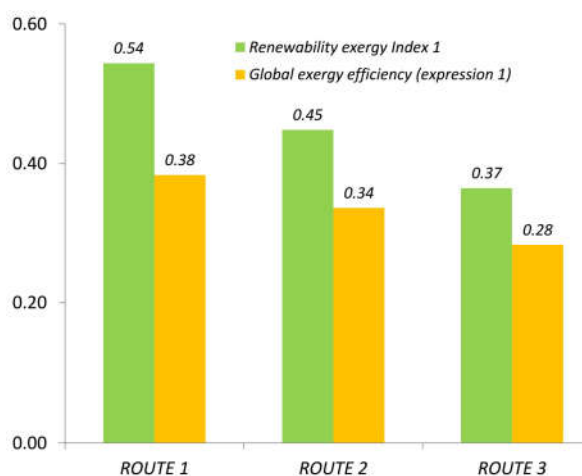


Figure 9. Comparison between renewability exergy Index 1 and global exergy efficiency.

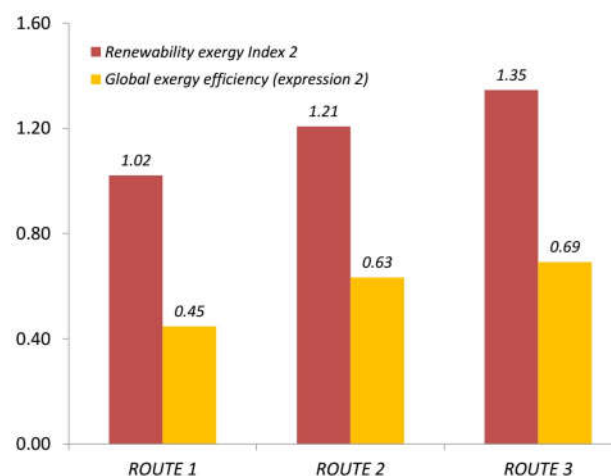


Figure 10. Comparison between renewability exergy Index 2 and global exergy efficiency.

4.3. Techno-economic assessment

After the energy integration analysis implemented in the MILP formulation, the minimum energy required and the optimum processes integration of the systems were evaluated. From the inputs and outputs of each unit (*mass and energy balances*) and the thermodynamic models adopted in the simulation, the processes were completely defined. Thus, these parameters were used to determinate the configurations performance according to technical, environmental and economic criteria, previously established.

Table 5 presents the optimization results of the conventional, biochemical and thermochemical routes analyzed. It is important to notice the values of the total cost of investment include the operating cost (OPEX) and capital expenditure (CAPEX) of each biorefinery plant.

Table 5. Techno-economic assessment.

Case Studies		Estimated Total cost (MUS\$)	Annualized Capital Cost (MUS\$/y)
Route 1	Conventional	239.1	28.0
Route 2	Biochemical	343.3	40.3
Route 3	Thermochemical	334.2	39.2

(MUS\$ = Million Dollars)

According to this table, Route 2 (*biochemical platform*) represents the best system in terms of environmental impact. However, a higher total cost of investment when compared to the thermochemical and conventional platform.

4.4. Global analysis of the technological configurations

In the overall performance of these technological routes for ethanol production and power generation, the CO₂ equivalent emissions were evaluated, by means of the relation between the estimate global CO₂ emissions emitted in the atmosphere due to its operation and the exergy of the products for each configuration, denominated CO₂ equivalent index in exergetic base. Subsequently, the surplus electricity available for sale to the grid was analyzed and finally the ethanol production rate of these systems was considered as shown in Figure 11.

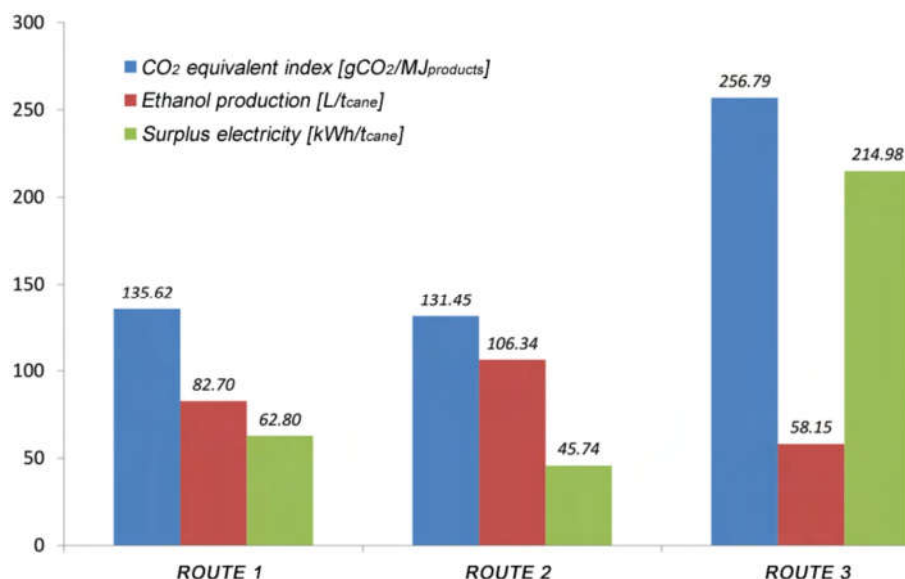


Figure 11. Global analysis of the evaluated technological routes.

It is worth mentioning that the highest electricity generation was obtained in *Route 3*, involving the thermochemical conversion process (biomass gasification). However, a higher CO₂ emissions rate was also observed in this configuration in contrast to the other studied routes.

On the other hand, it must be underlined that *Route 2* achieved the highest productivity in terms of ethanol production, as well as the lower CO₂ equivalent rate (CO_{2e}) among all the technological configurations.

It should be noted that CO₂ emissions account for the emissions related to both ethanol production and power generation as products. Thus, the CO₂ equivalent index was applied considering only ethanol as product (to compare the results with other authors), obtaining 148.26 gCO_{2e}/MJ (*Route 1*), 154.48 gCO_{2e}/MJ (*Route 2*) and 333.19 gCO_{2e}/MJ (*Route 3*). For instance, the ethanol production when compared with the scenarios evaluated by Milanez et al. [46], involving 1G and 1G-2G integrated plants were reported 84.9 l/t cane and 108 l/t cane, respectively. Albarelli et al. [14] presents results for the process simulation of the conventional ethanol production (*autonomous distillery*) and the 2G ethanol via biochemical configuration, involving steam explosion as pre-treatment and enzymatic hydrolysis. Their results were also similar to those obtained in this study, being 81.9 l/t cane and 93.6 l/t cane, respectively. In order to synthesize the main results of this work and to lead to the configurations ranking, the parameters considered in the assessment of these biomass conversion technologies are shown in Table 6. This table summarizes the renewability exergy index λ results for the two variations (*Index 1*) and (*Index 2*).

Table 6. Ranking configurations.

Case Studies	ROUTE 1	ROUTE 2	ROUTE 3
Parameters			
Global CO ₂ emissions ($gCO_2/MJ_{products}$)	135.6	131.4	256.8
Environmental Impact ($kgCO_{2e}/TC$)	276.1	258.0	414.1
Ethanol production (L/TC)	82.7	106.3	58.1
Surplus electricity (kWh/TC)	62.8	45.7	214.9
Exergy efficiency (<i>Index 1</i>)	38.38	33.67	28.34
Renewability exergy indicator (<i>Index 1</i>)	0.54	0.45	0.37
Average unitary exergy cost (<i>Index 1</i>)	2.60	2.97	3.52
Exergy efficiency (<i>Index 2</i>)	44.67	63.29	69.15
Renewability exergy indicator (<i>Index 2</i>)	1.02	1.21	1.35
Average unitary exergy cost (<i>Index 2</i>)	2.24	1.58	1.45

For the purpose of the global technological assessment, the exergy efficiency expression (*Index 1*) was adopted, once the proposed simulations were aiming to obtain bioethanol and electricity as products. It is observed that the optimized conventional scenario (*Route 1*) presented the best indicator in terms of the exergy efficiency. Therefore, its average unitary exergy cost was the smallest among the evaluated platforms.

While the biochemical route presented the most important system regarding the bioethanol production, due to the integration of 1G with the 2G bioethanol technology. In this respect, it must be underlined that this pathway has the lowest global CO₂ emission rates, being the configuration with the best performance related to the environmental impact.

In addition, the thermochemical route presented the most relevant configuration when power generation (*surplus electricity*) was the target, at the cost of reaching the greatest environmental impact of the technological routes.

Furthermore, the exergy efficiency (*Index 2*) was applied for comparing the renewability and exergy efficiency variations, when using the inherent residues in the energy conversion process of these routes. These are also confronted as by-products, aiming their processing and consequent valorization. An opposite behavior was found when utilizing the exergy efficiency integrated into the *Index 2*. It is noted that the *Route 3* would be the most relevant configuration regarding the efficiency and the average unitary exergy cost, among the systems studies.

5. Conclusions

According to the results related to the exergy efficiency of the processes, it is verified that the chemical reactions involved in the hydrolysis, fermentation and combustion systems represent the principal destroyed exergy (irreversibility rate) in the ethanol production and electricity generation using sugarcane bagasse and straw as an energy input in the COGEN unit.

In the global assessment of the technological routes, the optimized conventional route (*Route 1*) showed the highest exergy efficiency. Therefore, the lowest average unitary exergy cost, as a consequence of the steam consumption reduction and the energy integration procedure, allowed that more bagasse was addressed for other conversion purposes.

In terms of the process integration analysis, the second-generation ethanol production (*Route 2*) via enzymatic hydrolysis, linked to the conventional process, allowed to reach the highest rate of ethanol production. However, the economic analysis has shown that the 2G process (biochemical platform) has the highest capital cost due to the enzymes cost compared to the other technological routes. It was also situated as the most sustainable configuration due to present the lowest overall CO₂ emissions rates (131.45 gCO₂/MJ products). The integration of the second-generation to the conventional process of ethanol production was also improved by thermal integration.

Consequently, better use of energy was accomplished, allowing higher exergy efficiency in *Route 2* over the other configurations.

Lastly, it is worth noting that the overall evaluation of the thermochemical route (*Route 3*) was the highest rate with reference to the surplus power generation, achieving 214.98 kWh/TC, at the cost of the greatest environmental impact of the technological pathways.

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Nomenclature

B^{\cdot}	Exergy flow rate (kW)
b	Specific exergy (kJ/kg)
b_{ch}	Standard chemical exergy (kJ/kg)
CAPEX	Total capital expenditure
$CO_2 EE$	Specific CO_2 equivalent emissions (<i>exergetic base</i>)
CV	Control volume
etOH	Ethanol
EOS	Equation of state
h	Specific enthalpy (kJ/kg)
NRTL	Non-random two-liquid
\dot{m}	mass flow rate, (kg/s)
LHV	Lower heating value (kJ/kg)
P	Pressure (kPa, bar)
Q^{\cdot}	Heat rate (kW)
s	Specific entropy (kJ/kg K)
ST	Steam turbine
t	temperature, ($^{\circ}C$, K)
TC	Ton of sugarcane
W^{\cdot}	Power, (kW)
x	Mole or mass fraction

Greek symbols

η	efficiency
λ	Renewability exergy index

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