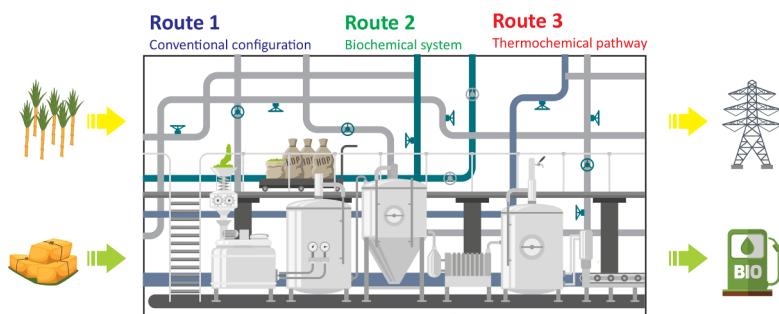


Full Length Article

Exergy assessment and techno-economic optimization of bioethanol production routes

Pablo A. Silva Ortiz^{a,*}, François Maréchal^b, Silvio de Oliveira Junior^a^a Mechanical Engineering Department, Polytechnic School, University of São Paulo, Brazil^b Industrial Process and Energy Systems Engineering, École Polytechnique Fédérale de Lausanne, Switzerland

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Lignocellulosic biomass
Exergy analysis
Exergo-environmental performance
Sugarcane biorefineries
Ethanol conversion pathways

ABSTRACT

Currently, electricity generation and second-generation ethanol production from lignocellulosic feedstocks represent technological alternatives in the bioenergy sector. Nevertheless, the introduction of new production processes denotes a real challenge due to the complexity and diversity of the pathways 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, and ranking of sugarcane-based biorefineries. 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 surplus bagasse were studied, aiming at 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 context, the biochemical pathway (*Route 2*) presented the maximum exergy efficiency, therefore the lowest average unitary exergy cost of the evaluated platforms. This system that promoted an increase of 22% and 45% in the ethanol production, when compared to *Route 1* and *Route 3*, respectively. Besides, the thermochemical pathway (*Route 3*) presented the configuration with the highest power generation rate. Concerning the environmental impact results, it was found that the most sustainable configuration was *Route 2*, which presented the lowest overall CO₂ emissions rates (131.45 gCO₂/MJ products).

* Corresponding author at: Av. Prof. Luciano Gualberto, 1289 Cidade Universitária, CEP:05508-900 São Paulo, SP, Brazil. Tel.: +55 11 3091 9668; fax: +55 11 3813 1886.

E-mail addresses: pasilvaortiz@usp.br (P.A. Silva Ortiz), francois.marechal@epfl.ch (F. Maréchal), soj@usp.br (S. de Oliveira Junior).

Nomenclature			
B	Exergy flow rate (kW)	P	Pressure (kPa, bar)
b	Specific exergy (kJ/kg)	Q	Heat rate (kW)
b_ch	Standard chemical exergy (kJ/kg)	s	Specific entropy (kJ/kg K)
CAPEX	Total capital expenditure	ST	Steam turbine
CO ₂ EE	Specific CO ₂ equivalent emissions (exergetic base)	t	temperature, (°C, K)
CV	Control volume	TC	Ton of sugarcane
etOH	Ethanol	W	Power, (kW)
EOS	Equation of state	x	Mole or mass fraction
h	Specific enthalpy (kJ/kg)		
NRTL	Non-random two-liquid		
m	mass flow rate, (kg/s)		
LHV	Lower heating value (kJ/kg)		
Greek symbols			
η	efficiency		
λ	Renewability exergy index		

1. Introduction

Nowadays, second-generation biofuel production from lignocellulosic materials is a research topic of interest around the world. These works focus on determining what could be biofuel participation in the energy matrix, process efficiency, productivity, environmental impact [1], and their transformation 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 pre-treatment 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. In this study, Fig. 1 shows the selected routes for ethanol and electricity production.

It is worth mentioning that in the bioenergy field, the application of systematic process design methodology looking for optimal configurations, increase efficiency, and ranking the different routes. For example, Bechara et al. [3] developed a methodology for ethanol and power production combined distillery and cogeneration units. The methodology involves process simulation, heat integration and thermo-economic evaluation, bi-objective multi-variable evolutionary optimization, and process selection. The objective functions of the biorefineries were exergy efficiency and capital cost, whereas the selection criterion is the maximization of the Net Present Value. Gassner and Maréchal [4] carried out a methodology for the optimal conceptual design of thermochemical fuel production processes from biomass. A decomposed modelling approach involving energy flow, energy integration, and economic models is combined with a multi-objective optimisation strategy. The methodology was applied to the process design of the synthetic natural gas (SNG) production from lignocellulosic materials. Lastly, Gassner and Maréchal [5] investigates how to overcome this limitation by thermochemically converting the residues (lignin compounds) to increase the total energy yield by a combined generation of several fuels and power. The authors show that the fuel yield can be more than doubled to reach total energy and exergy efficiencies of up

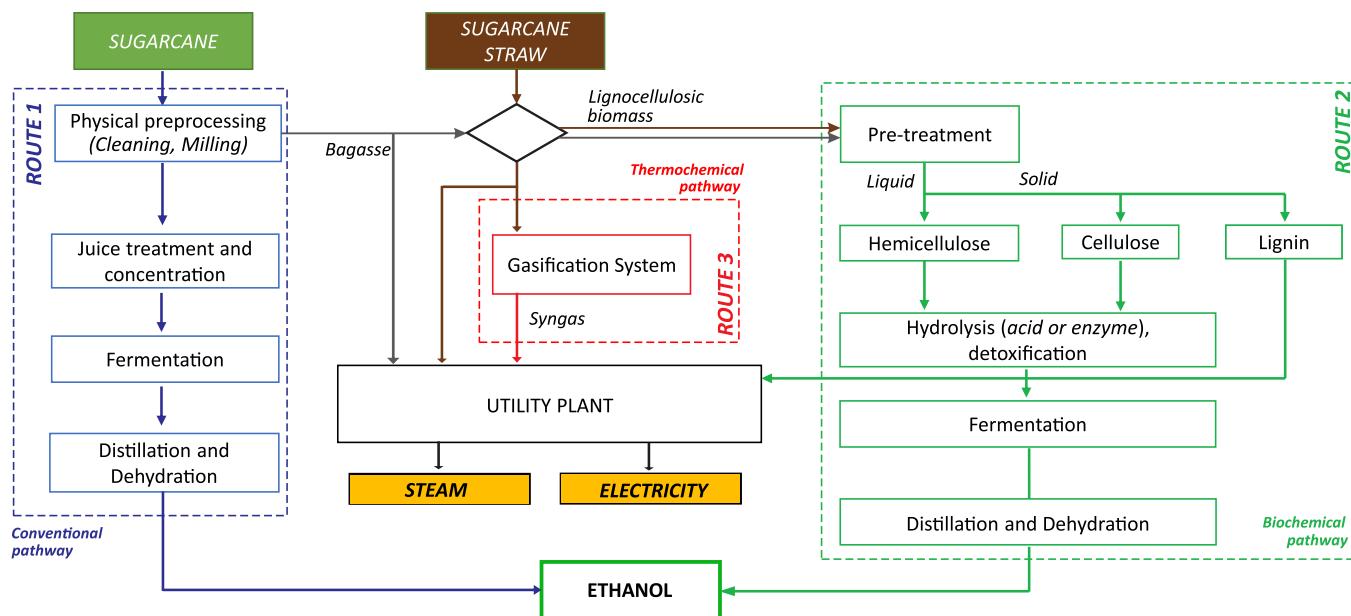


Fig. 1. Simplified overview of pathways for ethanol and electricity production.

72% and 78%, respectively. From a methodological point of view, it was demonstrated that the combination of process integration and exergy recovery techniques in a site-scale approach is key for tapping the full potential of the limited biogenic resources in the biorefineries. 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 a 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. For instance, Piekarczyk et al. [7] investigated the global effects of natural resources management concerns to the second-generation biofuels using the thermo-ecological cost. Thus, Fischer-Tropsch (FT) and Substitute Natural Gas (synthesis of biofuels) were analysed through the thermo-ecological methodology. Ptasinski et al. [8] compared the biomass gasification process using the exergy-based efficiencies as a conversion indicator of different types of raw materials (wood, vegetable oil, sludge, and manure) against gasification of coal. Souza-Santos et al. [9] presented additional improvements on the strategy of the Fuel-Slurry Integrated Gasifier/Gas Turbine (FSIG/GT) concept for electric power generation applied to the case study of sugarcane bagasse. The authors demonstrated the possibility of achieving higher overall power generation efficiency, which surpasses the efficiencies reached by other strategies such as high-pressure Rankine, BIGCC systems, and combined cycles using pressurized-chamber boilers. Cruz et al. [10] carried out the thermodynamic performance through an exergy analysis of the lignocellulosic biomass gasification followed by the FT synthesis, which is becoming a promising route to produce synthetic biofuels and electricity.

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 valorisation [1]. For example, Albarelli et al. [11] simulated a biorefinery plant producing ethanol from sugarcane juice and second-generation ethanol using bagasse fine fraction (*P-fraction*). Liquid hot water and steam explosion methods were selected as pre-treatment technologies. The processes were thermal and water integrated and compared to a biorefinery producing ethanol from juice and sugarcane bagasse. The authors demonstrated that after thermal and water integration, the evaluated processes were self-sufficient in energy demand, being able to export

the surplus electricity. Palacios-Bereche et al. [12] carried out an exergetic analysis of the enzymatic hydrolysis of sugarcane bagasse integrated into the conventional process of ethanol production. Process simulations were performed to evaluate mass and energy balances, adopting steam explosion as pre-treatment technology of sugarcane bagasse, and an integrated cogeneration system. Bonomi et al. [13] presented a framework for assessing the technical and sustainability impacts of existing biorefineries and provides a possible roadmap for the development of novel biorefineries. The case study used is the Brazilian sugarcane biorefinery. Thus, the authors explore the main issues regarding biorefinery assessment, including feedstock production and transportation modelling, biofuels and green chemistry products.

1.4. Process design and techno-economic assessments of sugarcane-based biorefineries

The techno-economic performance of biofuel production and electric power generation from biomass have been explored in order to support the stakeholders in decision-making processes. In this context, the techno-economic analysis for producing liquid fuels from forest residues was determined by Carrasco et al. [14] from a combination of laboratory experiments and simulation of the pyrolysis process. The simulated plant for a feed rate of 2000 dry metric tons per day includes feedstock sizing and drying, pyrolysis, hydrogen production, and hydro-treatment of pyrolysis oils.

The main finding shows that the biomass is converted into bio-oil (61% yield), char (24%), and gases (15%) in the pyrolysis reactor, with an energy demand of 17%. Besides, the total capital investment for a grass-roots plant was estimated to be US\$427 million with an annual operational cost of US\$154 million. Shemfe et al. [15] discussed the effect of key process and economic parameters on product value and the impact of electric power generation equipment on capital cost and energy efficiency for the fast pyrolysis and bio-oil hydroprocessing technologies. In this work, a process model of 72 MT/day pinewood fast pyrolysis and bio-oil hydroprocessing plant was explored using Aspen Plus® simulator and Aspen Process Economic Analyser® for equipment sizing and cost estimation.

Furthermore, Albrecht et al. [16] proposed a standardized methodology for techno-economic analysis of fuel production processes and exemplarily applied on sustainable fuels from Fischer-Tropsch synthesis. The methodology consists of three main steps: (i) literature survey on available production designs, (ii) flowsheet simulation, and (iii) techno-economic assessment with the TEPET (Techno-Economic Process Evaluation Tool) software. Results show a level of detail and key assumptions in terms of economic factors, and market prices focus on best practices from the chemical industry. Lastly, Silva et al. [17] investigated the sustainability of the first-generation ethanol production process using a water steam condensed stream reuse approach. Three case studies were investigated i). Distillation with use of a reboiler as a heat source, ii). Conventional direct steam injection distillation, and iii). Distillation with mechanical vapour recompression. The results showed that the use of closed circuits and water reuse streams provided an overall consumption of 673 l water/t of cane in the mill. Furthermore, the techno-economic analysis shows that Case I achieved a net revenue of US\$ 115 million, which was approximately 9% and 12% higher than achieved for Cases II and III, respectively. Therefore, the authors demonstrated that it is beneficial to employ a reboiler as a heat source in distillation systems compared to conventional systems employed in ethanol production.

Even though several studies have addressed the thermodynamic assessment from the first and second law standpoint, there is not a systematic methodology reported to understand the renewability of sugarcane biorefinery platforms into the Brazilian context that take into account heat integration, exergy-based GHG emissions, exergy analysis, average unitary exergy cost and the specific net production cost of products. Hence, three technological pathways for ethanol production

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

Parameter	Value	Unit
Sugarcane cleaning, preparation and juice extraction		
Efficiency of soil removal in cleaning operation	70	%
Efficiency of sugar extraction	96	%
Bagasse moisture content	50	% w.b.
Juice treatment		
Heating temperature of juice treatment	105	°C
Filter cake moisture content	70	%
CaO consumption	0.5	kg/t cane
Juice concentration (evaporation system)		
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 the final must	19	%
Fermentation		
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%
Distillation and rectification		
Stages in rectification section (Col. A1)	8	
Stages in stripping section (Col. A)	19	
Stages in phlegm rectification (Col.B-B1)	45	
Stages in top concentrator (Col. D)	6	
Ethanol content in vinasse and phlegmasse	0.02	%
Dehydration (monoethylene glycol – MEG)		
Extractive column pressure	1.01	bar
Recovery column pressure	0.2	bar
Ethanol content in anhydrous ethanol	99.3	wt %
Cogeneration Unit		
Boiler pressure (<i>Superheated steam</i>)	67	bar
Boiler temperature (<i>Superheated steam</i>)	480	°C
Isentropic efficiency of electricity generation (ST)	80	%

and electricity generation here analysed: (*Route 1*) base-case: traditional ethanol plant; (*Route 2*) biochemical system increased ethanol production by introducing the pre-treatment and hydrolysis processes; and (*Route 3*) thermochemical plant focus on the surplus electricity. The global assessment of these systems was based on complementary methods, *i.e.*, Techno-economic analysis and optimization, Exergy assessment and Exergo-environmental analysis. Furthermore, the comparison metrics used were: Estimated total cost, Annualized capital cost, Specific net production cost of the products, Exergy efficiency, Average unitary exergy cost, Specific CO₂-equivalent emissions in exergetic base, and Renewability exergy index, respectively.

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.

2.1.1. 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 [18].

Bagasse is used as fuel in cogeneration (COGEN) unit, while the juice is directed to the treatment process. In the simulations, it was adopted a dry cleaning system.

2.1.2. Juice treatment

The juice from the 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 [19]. It was simulated that the juice undergoes a flash tank, before entering the clarifier.

2.1.3. Juice concentration, sterilization, and cooling

The treated juice should be concentrated to reach an appropriate sugar concentration (approx. 17%) for the fermentation process [18]. 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 vapor and the juice along with the consecutive effects. Afterward, the most preparation and the sterilization stage was performed by an HTST (*High-Temperature Short Time*) treatment, with heating to 130 °C, followed by fast cooling down to the fermentation temperature [18].

2.1.4. Fermentation

This stage was simulated founded on the *Melle-Boinot* process. Ethanol recovery in the fermentation gas was performed by the absorption column. After fermentation, the yeast was separated, treated and recycled to the process. The simulation of the fermentation process was performed based on [18–20].

2.1.5. 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 [11,12].

2.1.6. 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. [21].

2.1.7. 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 [22] and Dias [23] were considered.

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

2.2. ROUTE 2-biochemical platform

This route integrated first and second generation to produce ethanol and to generate electricity. It was also simulated using the commercial flow sheeting Aspen Plus® simulator considering, sugarcane dry

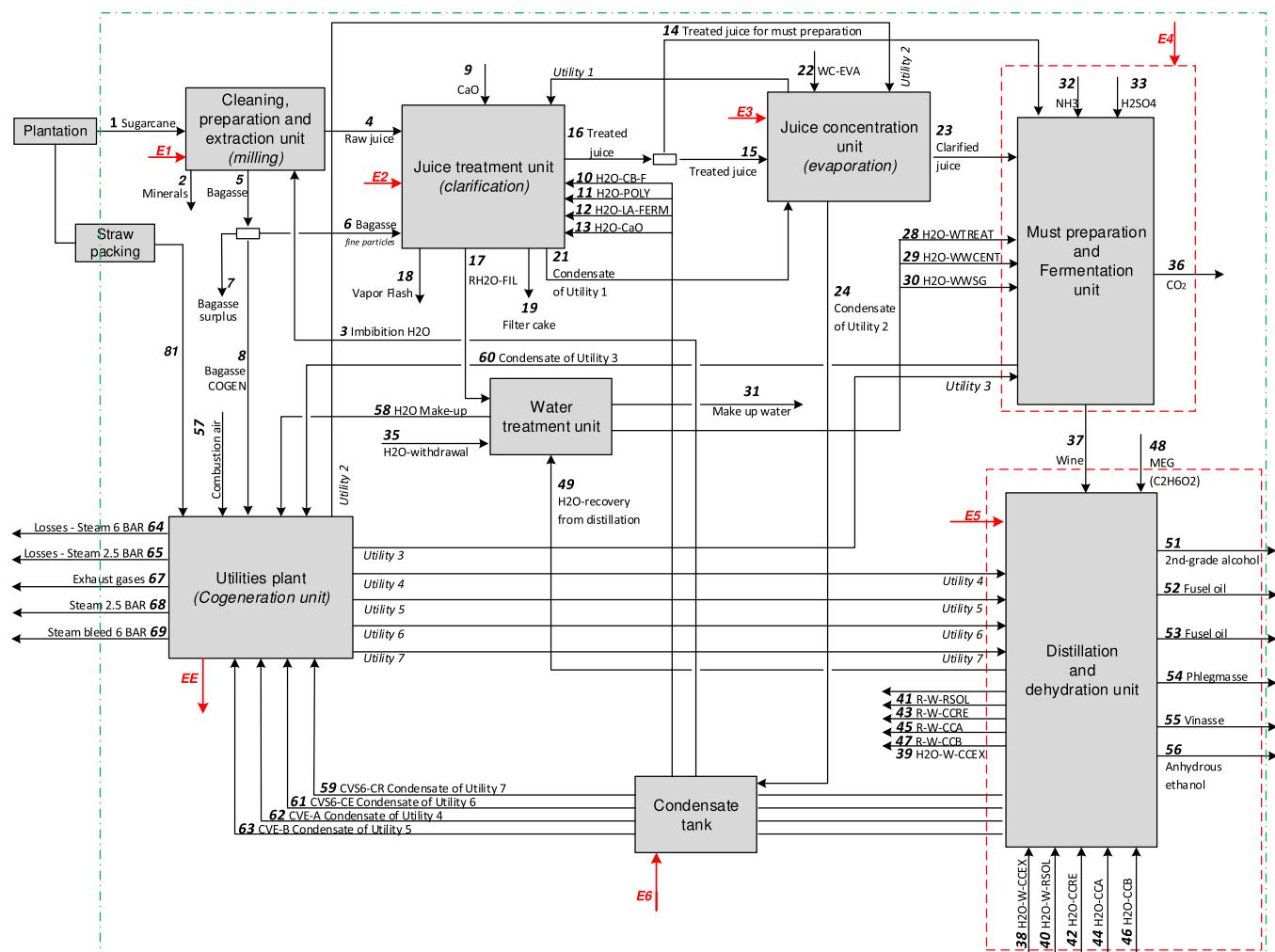


Fig. 2. A schematic diagram of Route 1.

cleaning, concentration in multi-effect evaporators, sterilization of the sugarcane juice, ethanol dehydration utilizing MEG and the employ of sugarcane bagasse for saccharification via steam explosion pre-treatment and enzymatic hydrolysis steps.

In the second-generation ethanol production, sugarcane bagasse and straw (lignocellulose feedstock) could be used as raw materials for ethanol production through pre-treatment and hydrolysis processes. Steam explosion technology was adopted as the pre-treatment method, in which high-pressure steam rapidly heats biomass to promote hemi-cellulose hydrolysis, followed by rapid pressure release. Reaction time, temperature, particle size, and moisture content are considered the critical issues in this biomass pre-treatment process. Specifications used for simulation of the pre-treatment step are found in Silva and De Oliveira [24].

In the pre-treatment process, a fraction of hemicellulose (xylan) is transformed into xylose and xylose oligomers. A diffuser is used to separate a liquid stream of the pre-treated material, C5 liquor. The solid fraction of the pre-treated material is directed to the enzymatic hydrolysis reactor. Table 2 indicates the key parameters adopted in the enzymatic hydrolysis step for the integrated 1G and 2G ethanol configuration. In addition, the reactions considered in the sub-system of the enzymatic hydrolysis process for the second-generation ethanol production are shown in Silva and De Oliveira [25] and Silva et al. [26]. More details of the 2G process descriptions can be found elsewhere [13,23].

For Route 2, bagasse was considered as the fuel of the cogeneration system. The process scheme of second-ethanol production via the

biochemical pathway is given in Fig. 3. Furthermore, it was adopted sugarcane straw and lignin cake as a complementary energy input in the model of the cogeneration system to help cover the energy demands of the overall process.

The total amount of straw produced at the field is assumed to be equal to 140 dry kg straw per tonne of sugarcane stalks [27]. In this work, it was assumed to be recovered and used 90 kg of straw/tonne of cane on a dry basis in the industrial plant; the remaining is left in the field for agricultural purposes. Furthermore, it was carried out a sensitivity analysis in order to explore the impact of the straw consumption on the proposed routes. Hence, additional scenarios were evaluated using 30%, 50%, 65% and 100% of the straw already available in sugarcane fields, as given in Section 4.

Table 2
Parameters for simulating the enzymatic hydrolysis process.

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	%

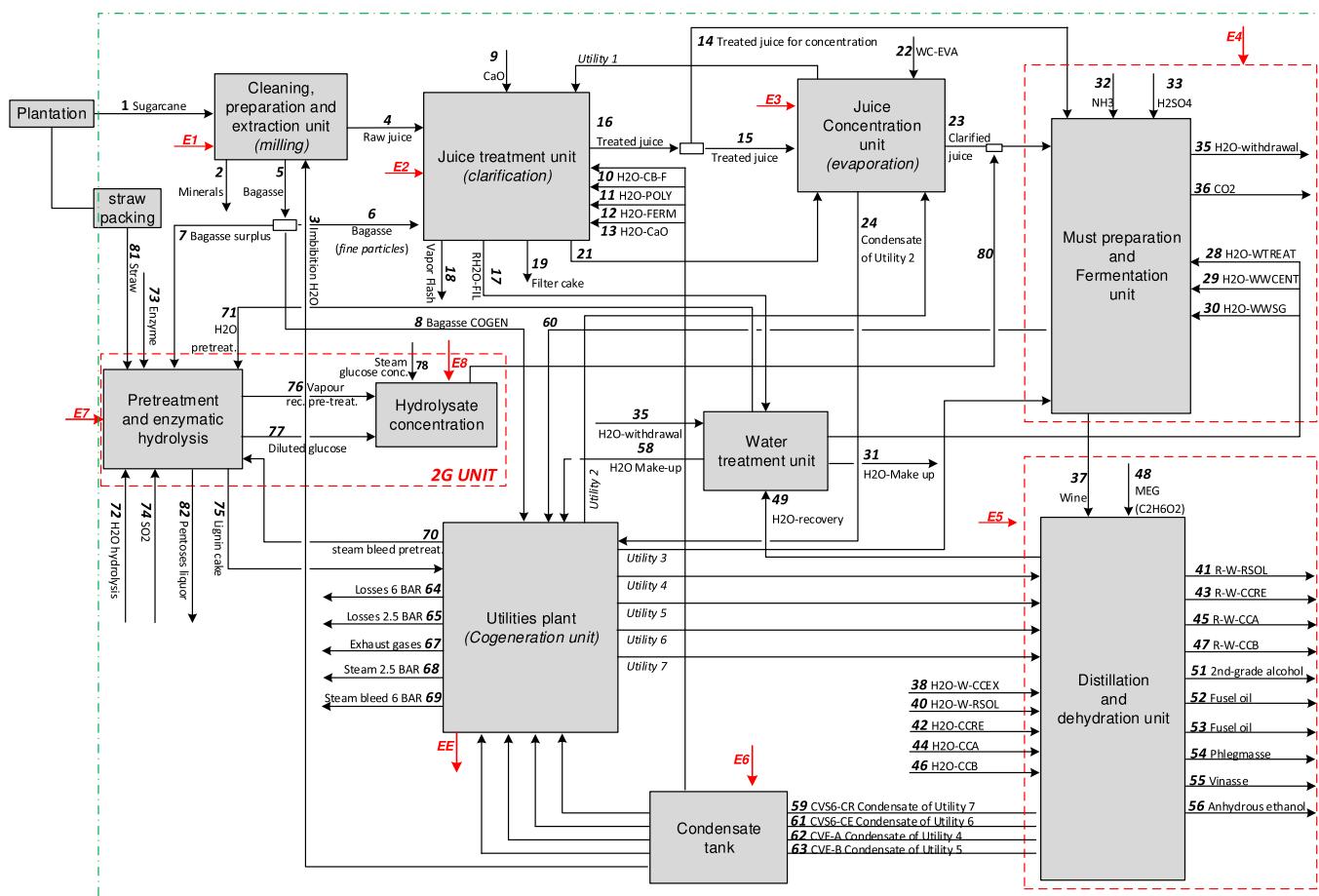


Fig. 3. Flowsheet of the 2G ethanol production via biochemical route.

2.3. ROUTE 3-Thermochemical platform

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

2.3.1. 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 was 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 includes non-condensable (*i.e.*, H₂, CO, CO₂, CH₄, C₂H₂), condensable volatiles (tar), and water [28]; *iv)*. Char only contains carbon and ash [29].

2.3.2. Syngas preparation (*cleaning*)

Several impurities in produced gas, such as tars, ammonia (NH₃), hydrogen sulfide (H₂S), 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.

2.3.3. Combined heat and power (CHP)

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 °C. The following characteristics were taken into consideration in the model: *i)*. Steady-state operation; *ii)*. The compressor pressure ratio adopted was 16; *iii)*. Discharge pressure was 1 atm; *iv)*. Polytropic efficiency of the compressor, gas, and the steam turbine was 80% and *v)*. The polytropic efficiency of the pump was 80%. In the hierarchy block (*CHP Unit*) developed in the 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 into the conventional bioethanol process can be found in Fig. 4.

3. Methodology

3.1. Process design of sugarcane biorefineries

The methodology has been divided into several steps. The first part deals with the process modelling 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® [30], 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 to 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 the 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

Table 3
Raw material composition.

Formula	Components	Molecular weights (kg/kmol)	wt%, wet basis		
			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	–

minimizes the operating cost by solving the heat cascade problem employing a MILP (*mixed integer linear programming*) technique [31]. The MILP problem is solved utilizing the GLPK software package and *glpsol* solver embedded in the OSMOSE platform, as described by MIAN et al. [32] and Albarelli et al. [33].

3.2. Process simulation: Property method and composition

The component's properties of the lignocellulosic biomass were obtained from the biofuel databank developed by NREL [22]. 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 sub-streams 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 assumed in this study

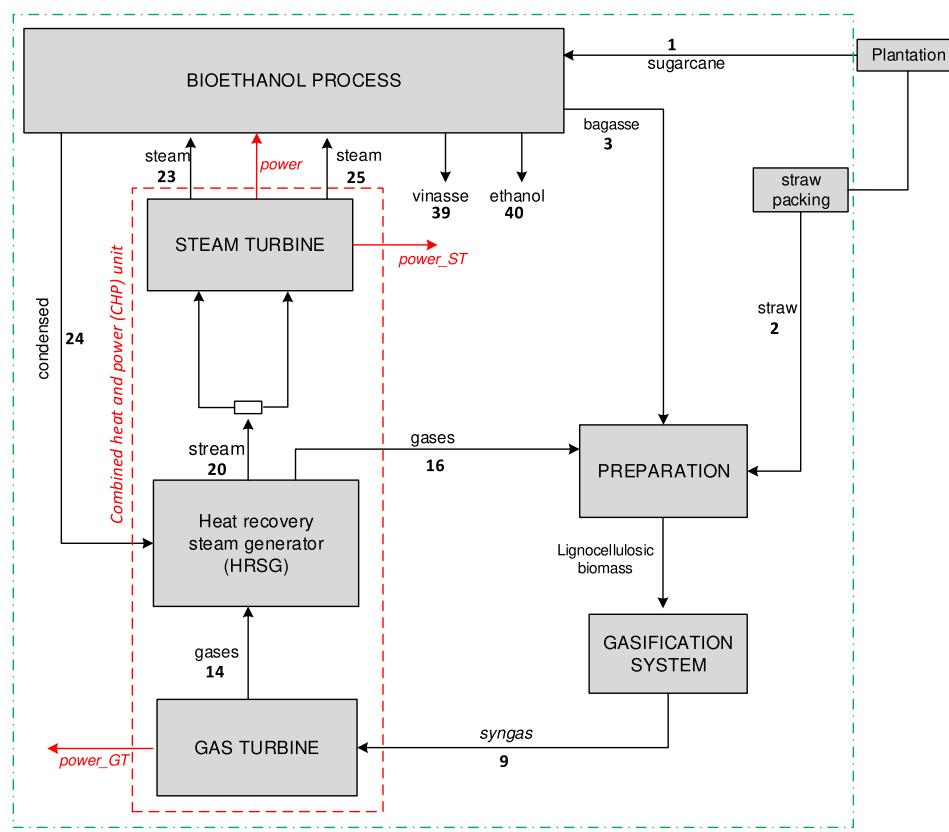


Fig. 4. Flowsheet of the Route 3.

adapted from Dias [23], Palacios-Bereche [34].

Besides, different property packages were used within the simulator to represent chemical component behaviors in specific routes more accurately. 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 behaviour was presumed for the vapour phase in most of the simulations [30].

In the *Biochemical Route*, the thermodynamic method considered was UNIQUAC (*short for UNIversal QUAsiChemical*) for the liquid phase and RK Redlich-Kwong equation of state for vapour 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 [30]. For the steam flows, steam tables (*STEAMNBS model*) were employed, once these characterize pure water and steam properties for a wide range of temperatures and pressures.

3.3. Exergy assessment

The exergy method, which combined the First and Second Law of Thermodynamics was applied to assess the performance of the biorefinery configurations for ethanol process. Exergy represented the maximum work that could be obtained employing reversible processes from a thermodynamic system that interacts with the components of the environment until the dead state equilibrium is attained [35].

Exergy analysis offers an effective way of evaluating the quantity and quality resource, as it evidences the maximum quantity of a particular resource that could be converted into work, given the prevailing environmental conditions. In this sense, the exergy method quantifies the irreversibilities (measure of the inefficiency) and allows to identify the equipment/process in which are produced.

The expressions for calculating the exergy associated with the different streams of the biorefinery configurations are measured based on the chemical (b_{CH}) and physical (b_{PH}) of the 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 represents the entropy flow rate at P, T (kW/K), T_0 is the temperature at the reference state (K), H_o denotes the enthalpy flow rate at P_o , T_o (kW) and S_o is the entropy flow rate at P_o, T_o (kW/K).

Table 4
Exergy efficiency definitions for representative units.

Sub-system	Exergy efficiency expressions	Eqs.
Cleaning, preparation and extraction unit (milling)	$\eta_{milling} = \frac{B_{juice} + B_{bagasse}}{B_{cane} + B_{water_imb} + B_{e_preprep} + B_{e_milling}}$	(3)
Juice treatment unit (clarification)	$\eta_{clarification} = \frac{B_{clarified_juice}}{B_{juice} + B_{bagasse} + B_{water} + B_{CaO} + B_{e_trat}}$	(4)
Juice concentration unit (evaporation)	$\eta_{clarification} = \frac{B_{Brix_final_must} + B_{condensed}}{B_{clarified_juice} + B_{utility}2.5 + B_{cond1.69} + B_{e_evap}}$	(5)
Utility plant (Cogeneration unit)	$\eta_{cogen} = \frac{B_{electricity} + B_{steam} - B_{consumption}}{B_{bagasse} + B_{water} + B_{condensed}}$	(6)
Must preparation and fermentation unit	$\eta_{prep_ferm} = \frac{B_{wine}}{B_{Brix_finalmust} + B_{water} + B_{utility}6 + B_{NH3} + B_{H2SO4} + B_{e_ferm}}$	(7)
Distillation and dehydration unit	$\eta_{dist_dehyd} = \frac{B_{ethanol}}{B_{wine} + B_{water} + B_{utilities} + B_{MEG} + B_{e_ferm}}$	(8)
Overall process Global exergy efficiency (expression Index 1)	$\eta_{global_1} = \frac{B_{ethanol} + B_{electricity}}{B_{cane} + B_{straw}}$	(9)
Global exergy efficiency (expression Index 2)	$\eta_{global_2} = \frac{B_{ethanol} + B_{electricity} + B_{by_produtos}}{B_{cane} + B_{straw} - B_{bagasse}}$	(10)
Ethanol process ¹	$\eta_B = \frac{B_{ethanol} + B_{bagasse}}{\sum B_{resources} + B_{consumption} + B_{steam} + B_{fossil}}$	(11)
Unit exergy cost, c	$c = \frac{1}{\eta_B}$	(12)

¹ $B_{resources}$ represents the exergy of the feedstocks, whereas B_{fossil} denotes the exergy associated with the chemical and biochemical components given in Table 6.

One particularly essential aspect in the exergy analysis refers to the chemical exergy calculation, which denotes 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 achieves a complete thermodynamic equilibrium (*thermal, pressure, and chemical*) [35]. Conceptually, chemical exergy is the most significant contribution to its exergy value for the majority of natural resources including lignocellulosic materials. Due to b_{CH} quantifies the value of a chemical substance, or compound, as measured against a selected reference environment [36]. Eq. (2) defines the chemical exergy for its calculation.

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

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. Besides, the term b_i^{ch} is the standard chemical exergy. In this work, the b_{CH} for the selected compounds used in the exergy analysis are found in [26].

3.3.1. Exergy efficiency definitions

Table 4 depicts the exergy efficiency definitions of the main stages adopted in the ethanol production and electricity generation routes. Thus, the expressions to quantify the exergy performance of energy conversion processes of each subsystem are given in Equations (3) to (8), serving as the basis for exergy analysis of processes. Besides, the different ways of defining efficiency of the overall process for the global exergy efficiency (*expression Index 1*), the global exergy efficiency (*expression Index 2*), the ethanol process, and the unit exergy cost c are specified from Equations (9) to (12), respectively.

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. It is explored the sustainability contribution of the systems through the link between the exergy and the environmental analysis to enhance

renewable share and exergy efficiency performance 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 [37].

3.4.1. Renewability exergy index for bioethanol production routes

The exergo-environmental discussion regarding the renewability for the ethanol production and electricity generation routes was conducted by the *renewability exergy index* λ [38]. Reversible processes represent a process that has occurred can be reversed to the initial system and surroundings states. This concept could contribute to the analysis of the renewability of energy conversion processes to develop in a rational basis by using thermodynamic parameters [39].

Based on these aspects, the renewability exergy index considers the exergy associated to the useful products ($B_{products/by-products}$) of a given energy conversion process, the total process irreversibility ($B_{destroyed}$), the exergy associated to the fossil fuels (B_{fossil}), the needed exergy to disposal the wastes, and the exergy related with emissions, residues and not treated wastes, as presented in Eq. (13):

$$\lambda = \frac{\sum B_{products/byproducts}}{B_{fossil} + B_{destroyed} + B_{deactivation} + B_{disposal} + \sum B_{emissions/residues}} \quad (13)$$

The value of the renewability exergy index (λ) indicates if the processes are environmentally favourable or unfavourable. Fig. 5 synthesizes the main cases related to the interpretation of the renewability exergy index [38]. If λ is higher than 1, the exergy of the products could be used to "restore" the environment to the conditions before the occurrence of the process and still obtain a positive flow of exergy to another use. It is emphasized that the renewability exergy index has a strong relationship with the control volume (VC) analysed, due to the number of energy conversion processes being involved. Thus, when the adopted VC is expanded, the λ value decreased as a function of the irreversibility rates and the contribution of non-renewable (fossil) inputs to the process. For that reason, the compatibility of the control volumes is a crucial issue when different systems are compared to prevent distortions in the assessment.

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 production process [34]. The average unit exergy costs (AUEC) metric is 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 higher unit exergy costs.

$$AUEC_{process} = \frac{c_{ethanol} * B_{ethanol} + c_{electricity} * B_{electricity}}{B_{ethanol} + B_{electricity}} \quad (14)$$

It is noted that the exergy cost allows a closer view of the contribution of each product to plant efficiency, allowing for the allocation of losses between products based on a thermodynamic premise as given Eq. (14). In this expression, the unit exergy cost c (kJ/kJ) of the ethanol and the electricity production is calculated as the inverse of the exergy efficiency of the ethanol process and cogeneration unit, respectively (Table 4).

3.5. Process integration assumptions

The value of $\Delta T_{min,ref}$ 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 the energy conversion efficiency.

Another aspect to be highlighted is that the heat transfer between streams is assured by considering an appropriate ΔT_{min} . Eq. (15) shows the relationship between $\Delta T_{min}/2$, assigned to each stream (j), and the corresponding heat transfer coefficient (α).

$$\Delta T_{min,j/r} = \Delta T_{min,ref}/2 \cdot \left(\frac{\alpha_{ref}}{\alpha_j} \right)^b \quad (15)$$

where α_{ref} and $\Delta T_{min,ref}$ are, respectively, the heat transfer coefficient and minimum approach temperature of a reference heat exchanger [40]. 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 by Palacios-Bereche et al. [18].

3.6. Techno-economic assessment

For the techno-economic assessment, capital investment (CAPEX) was estimated for each biorefinery configuration. The assessment is focused on the investment associated with industrial plants. These plants were calculated using the database for equipment costs and capacities of the process simulation results of the ethanol production and electricity generation in Brazil. Hence, to determinate the total investment cost, the process equipment is adjusted using correlations from literature Turton [41]; Ulrich and Vasudevan [42] 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. The method usually used to update historical cost data makes use of published cost indices. All costs were updated to 2018 by employing the

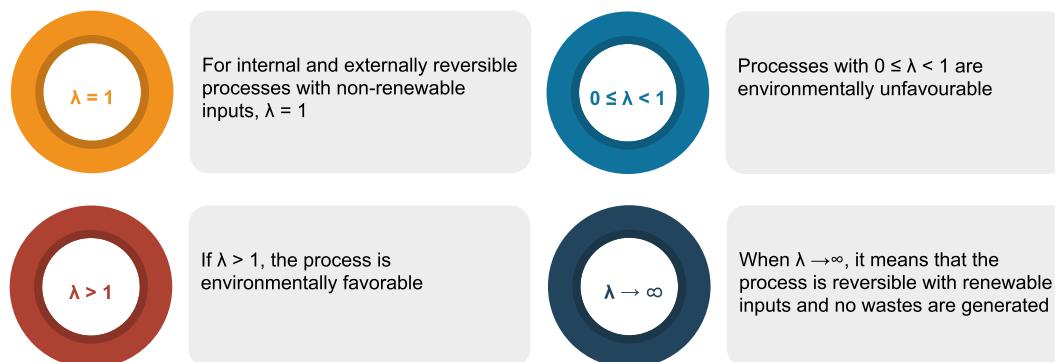


Fig. 5. Renewability exergy index.

Chemical Engineering Plant Cost Index-CEPCI (603.10). The cost indexes related present costs to past costs and are based on data for labor, material and energy costs, according to Eq. (16) [43].

$$\text{Cost in year A} = \text{Cost in year B} \frac{\text{Cost in year A}}{\text{Cost in year B}} \quad (16)$$

It is important to notice that most plant and equipment cost data is given on a U.S. Gulf Coast (USGC) or Northwest Europe (NWE) basis, as these are historically the main centres of the chemical industry, for which the most data are available. In this work, it was selected USGC basis and corrected using a location factor (LFA) as indicated in Equation (17).

$$\text{Cost of plant in location A} = \text{Cost of plant on USGC} \cdot \text{LFA} \quad (17)$$

The location factor for Brazil based on 2003 data was 1.14 [43]. It was updated by dividing by the ratio U.S. dollar/local currency (Brazilian Reais, BLR) in 2003 and multiplying by the ratio U.S. dollar/local currency (Brazilian Reais, BLR) in the year of interest (2018).

Furthermore, capital costs were expressed on an annual basis. Thus, it is assumed that the capital has been borrowed over a fixed period (20 years, usually for large projects) at a fixed rate of interest (10%), in which case the capital cost could be annualized according to Equation (18) [44].

$$\text{Annualized capital cost} = \text{Capital cost} \frac{i(1+i)^n}{(1+i)^n - 1} \quad (18)$$

where i represents the fractional interest rate per year and n depicts the number of years.

3.7. Exergy-based CO₂ equivalent emissions performance

The environmental impacts were accounted in the biorefineries configurations using the Life Cycle Assessment (LCA) method. Life cycle inventory (LCI) and life cycle impact assessment (LCIA) has been already integrated into the energy systems modelling of the OSMOSE platform [45]. The ecoinvent database V 3.1 was used for this purpose. This methodology is commonly applied in the bioenergy sector [46–50].

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). Consequently, the Global Warming Potential (GWP) 100 years is chosen as an environmental performance indicator. LCA results are obtained by multiplying life cycle inventory flows with the appropriate characterization factor for each inventory flow.

Table 5 reports the life cycle inventory (LCI) data adopted in the analysis. LCI data for the sugarcane production was developed mainly by Brazilian Bioethanol Science and Technology Laboratory (CTBE).

Table 5
Life cycle inventory data.

Compounds	GHG (kgCO ₂ /x)	Units	Comments
Sugarcane (SC)	0.034	kg SC	Including transportation, without trash burning, with sugar yield of our process
SC straw	0.010	kg SC straw	Using the yield of sugars, of SC straw/SC
Electricity	0.250	kwh	Electricity, GLO/kWh ¹
H ₃ PO ₄	1.423	kg H ₃ PO ₄	Commercial phosphoric acid used has a concentration of 85% by mass
CaO	0.150	kg CaO	Lime
H ₂ SO ₄	0.124	kg H ₂ SO ₄	Sulphuric acid
NH ₄ OH	2.089	kg NH ₄ OH	Ammonia, liquid at regional storehouse/kg/RER ²
C ₃ H ₆ O	2.220	kg C ₃ H ₆ O	Acetone
C ₅ H ₈ O ₂	5.730	kg C ₅ H ₈ O ₂	Furfural
Enzyme	4.090	kg Enzyme	Enzyme cocktail (CH _{1.57} N _{0.29} O _{0.31} S _{0.007})
NaOH	1.096	kg NaOH	Analyzing 1 kg ‘Sodium hydroxide, 50% in H ₂ O, production mix at plant/RER ³ ,
SO ₂	0.440	kg SO ₂	Sulphur dioxide, liquid, SO ₂
C ₂ H ₄ O ₂	1.403	kg C ₂ H ₄ O ₂	Acetic acid via methanol carbonylation

Adapted from [13,54,55]. ¹Based on the Brazilian electricity mix. ²RER: Europe (geographical location). ³GLO: global (geographical location).

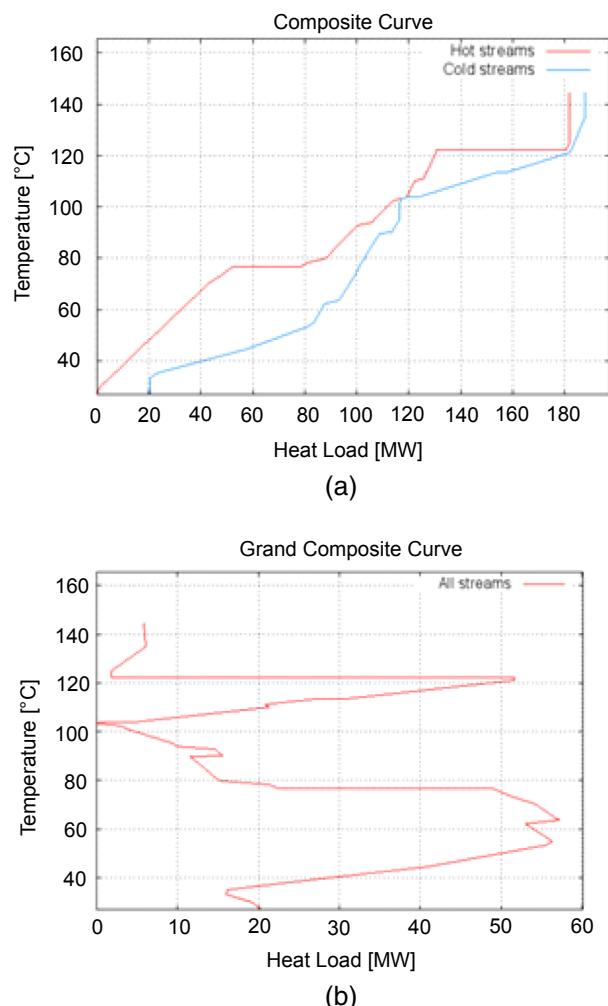


Fig. 6. Composite (a) and grand composite (b) curves for Route 1.

Details on the methodological approach of the model and the assumptions considered for the definition of the inventory can be found elsewhere [13].

Consequently, the balance of each unit operation block displays the CO₂ equivalents of the combined feed streams, combined product streams, and net production in the simulation results. In the case of the comparison of ethanol-producing scenarios, boundaries were set from cradle-to-gate and the functional unit defined as one litter of ethanol.

In this respect, it must be underlined that the global analysis of the

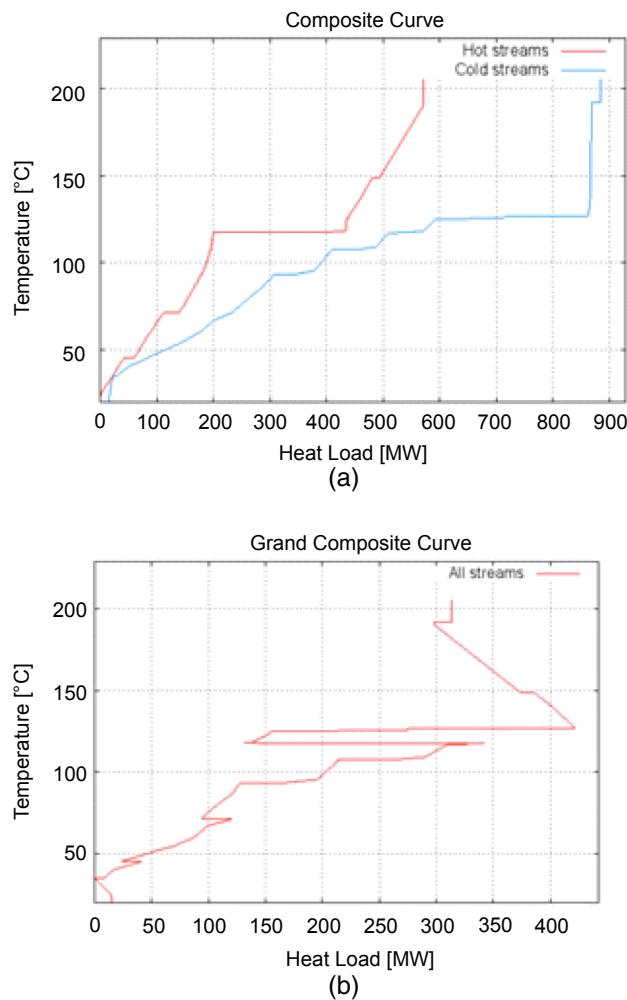


Fig. 7. Composite (a) and grand composite (b) curves for Route 2.

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 Eq. (19).

$$CO_{2EE} = \frac{\text{Global CO}_2\text{ equivalent emissions}}{B_{\text{products}}} \quad (19)$$

4. Results

4.1. Techno-economic optimization

The process integration strategy for technological routes targeting the *Maximum Energy Recovery or Minimum Energy Requirement (MER)* is presented. It denotes the best possible energy recovery in a heat exchanger network (HEN) for a particular ΔT_{min}. In this work, the technological routes were evaluated using the OSMOSE computer platform [45].

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 Figs. 6–8. Initially, Fig. 6 shown the CC and the GCC for the conventional biorefinery of the first-generation ethanol process. Later, Fig. 7 presented the CC (a) and GCC (b) for the

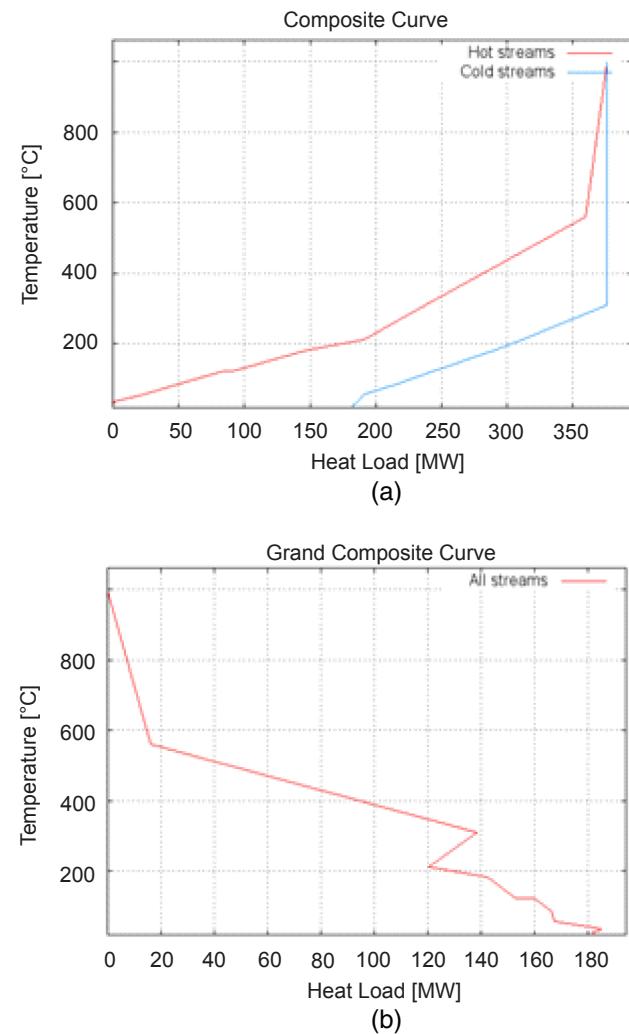


Fig. 8. Composite (a) and grand composite (b) curves for Route 3.

2G biochemical configuration. 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 of 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 Fig. 8.

4.2. Exergy assessment of the proposed technological routes

By clearly establishing the different biorefinery systems according to their exergy flows/content, it is possible to quantify the imperfections in the technological processes conversion and to indicate those points on which improvements must be carried out. Thus, the exergy analysis results of the technological pathways for ethanol production and electricity are given in this section.

4.2.1. ROUTE 1-Conventional biorefinery

Fig. 9 indicates the exergy efficiency at the different stages of the Route 1. In addition, Fig. 10 exhibits the exergy destruction rate of this

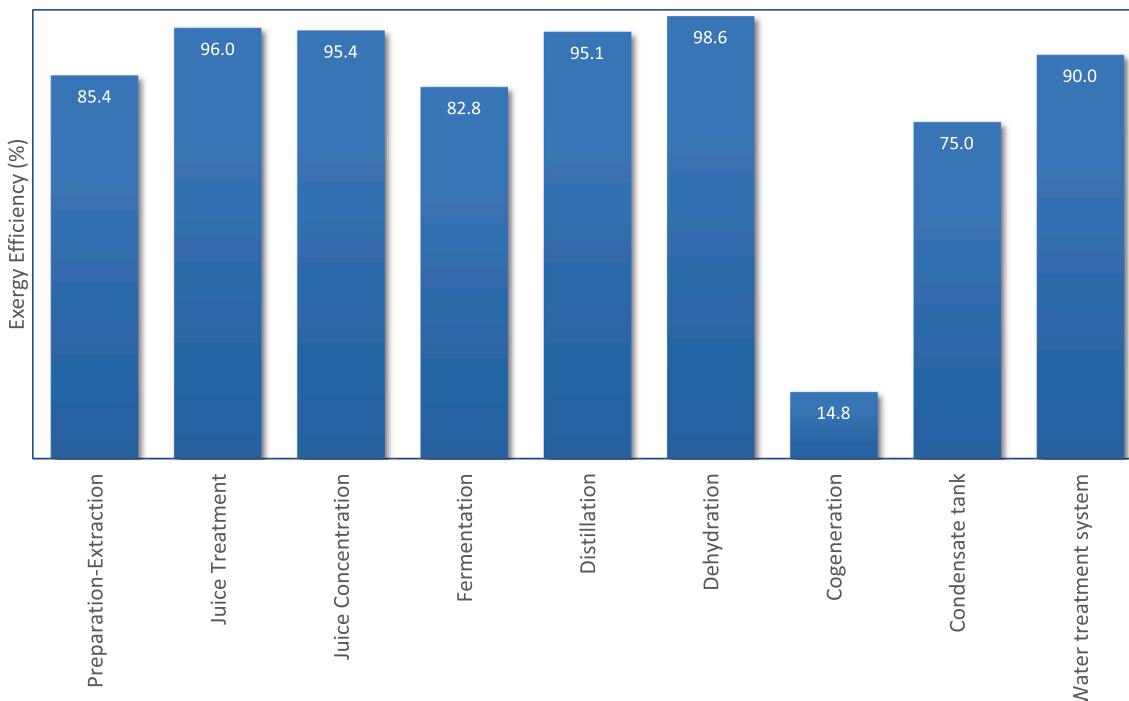


Fig. 9. Exergy efficiency by subsystem of Route 1.

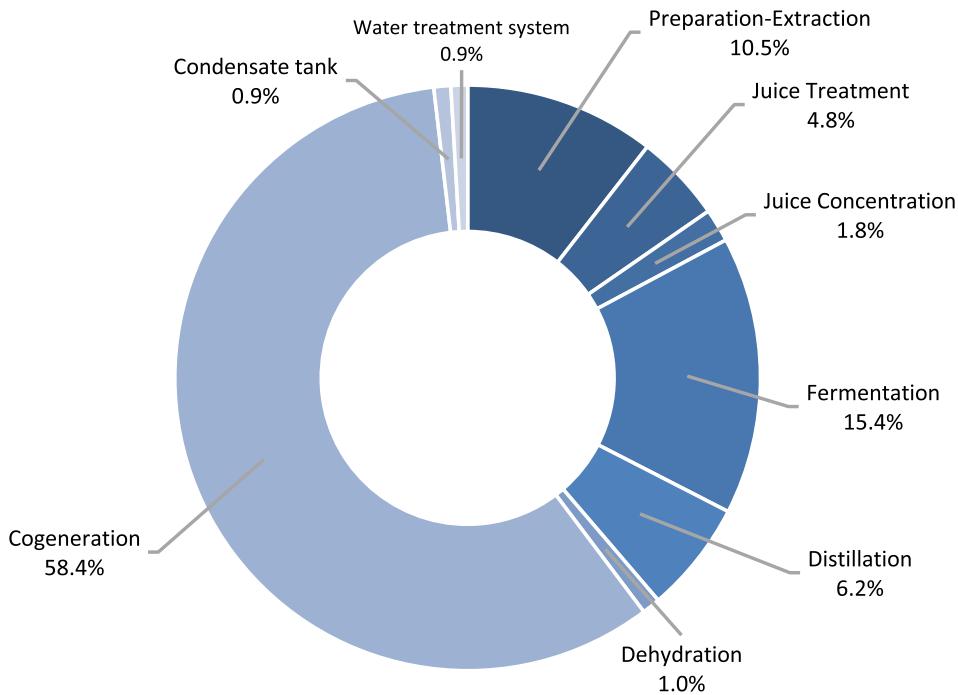


Fig. 10. Process irreversibility share in Route 1.

configuration. In terms of the irreversibility per litter of ethanol produced [kWh/l], it was obtained: Cleaning, preparation and extraction (*milling unit*) 1.522, Juice treatment (*clarification unit*) 0.701, Juice concentration (*evaporation unit*) 0.266, Must preparation and fermentation 2.223, Distillation 0.894, Dehydration 0.145, Cogeneration 8.450, Condensate tank 0.135 and water treatment system 0.133. The exergy balance for this technological route is given in Table A.1.

4.2.2. ROUTE 2-Biochemical platform

Fig. 11 provides the exergy efficiency results for Route 2. Fig. 12 presents the process irreversibility in this platform. With respect to the destroyed exergy per litter of ethanol produced [kWh/l] in each subsystem of this route, it was found: Cleaning, preparation and extraction (*milling unit*) 1.120, Juice treatment (*clarification unit*) 0.513, Juice concentration (*evaporation unit*) 0.179, Must preparation and

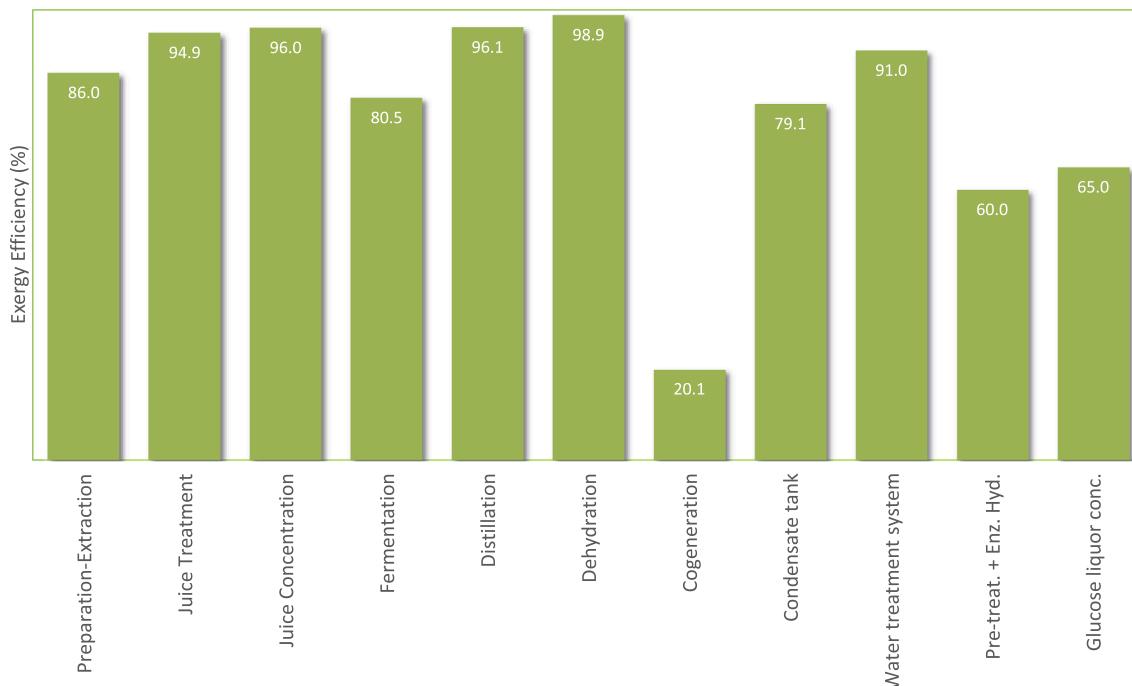


Fig. 11. Exergy efficiency by subsystem of Route 2.

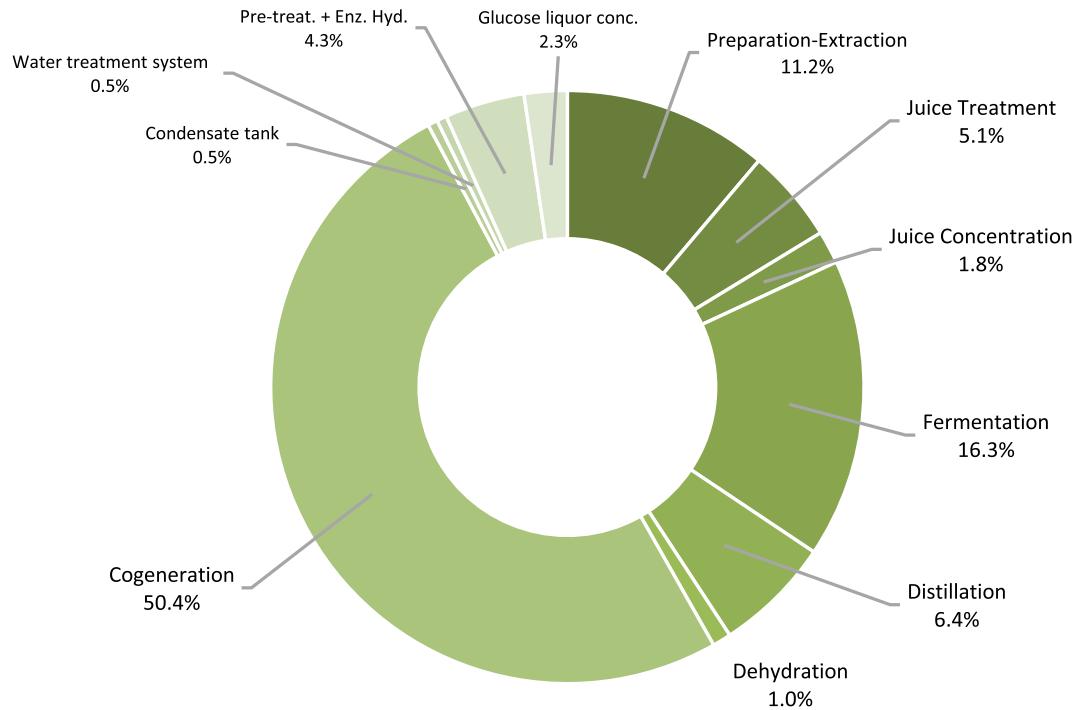


Fig. 12. Process irreversibility share in Route 2.

fermentation 1.635, Distillation 0.641 and Dehydration 0.101, Cogeneration 5.056, Condensate tank 0.054, Water treatment system 0.055, Pre-treatment (*steam explosion*) and Enzymatic hydrolysis 0.436, and Glucose liquor concentration 0.235. Lastly, it is noted that the milling capacity in the plant when considered the use of straw reaches 570 tons of biomass per hour. The exergy balance for this technological pathway is given in Table A.2.

4.2.3. ROUTE 3-Thermochemical platform: Ethanol production and electricity

Fig. 13 illustrates the exergy efficiency of the Route 3 involving the bioethanol production integrated to the thermochemical platform. Fig. 14 provides the exergy destruction rate per stage in this configuration. In this route, the irreversibility per litter of ethanol produced [kWh/l], it was obtained: Preparation-Extraction 2.021, Juice Treatment 0.908, Juice Concentration 0.331, Fermentation 2.653, Distillation 1.185, dehydration 0.184, Cogeneration 10.437, Condensate tank

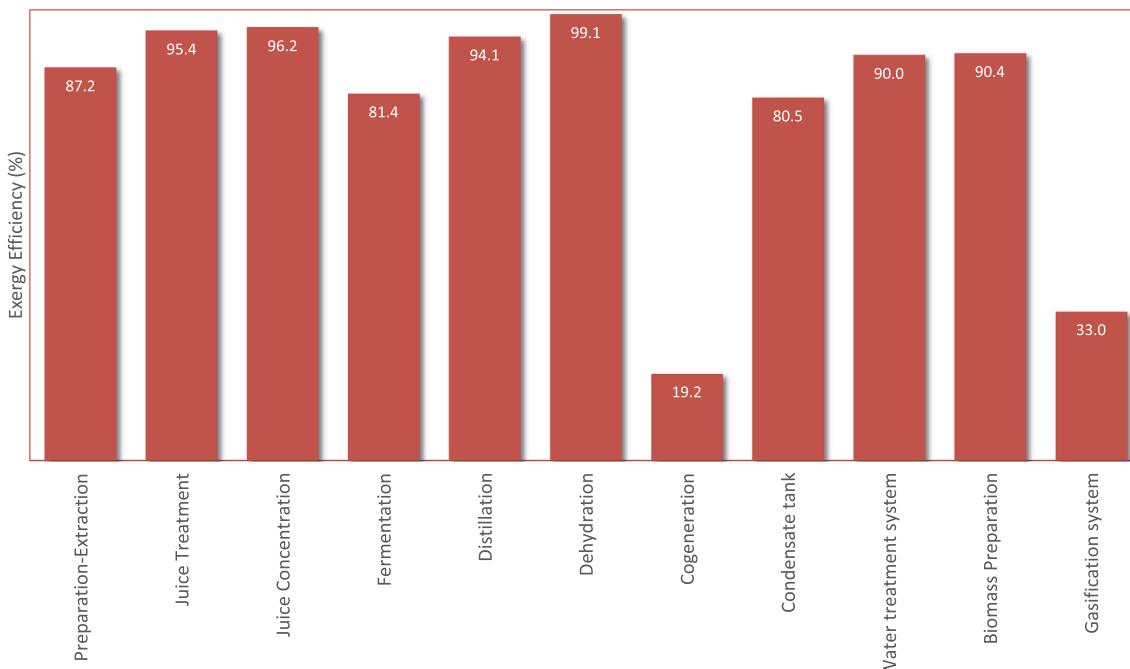


Fig. 13. Exergy efficiency by subsystem of Route 3.

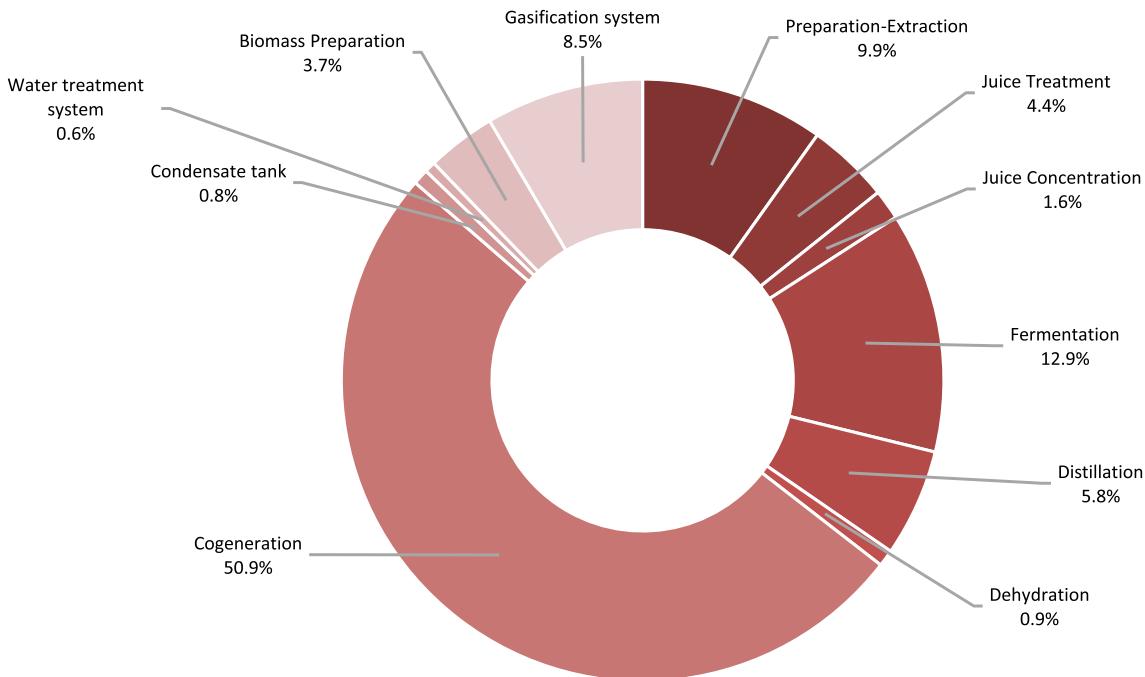


Fig. 14. Process irreversibility share in Route 3.

0.173, Water treatment system 0.121, Biomass Preparation 0.760, and Gasification system 1.738. The properties of the key streams for this technological configuration are shown in Table A.3.

4.3. Exergo-environmental analysis

4.3.1. Renewability exergy index for bioethanol production routes

The λ_{index} was applied with two (2) variations for each pathway. Firstly, it was considered the exergy of the products (ethanol and

electricity) and by-products separately concerning products that could be obtained through the residues processing, denominated *Index 1*. These by-products vary according to the pathway assessed (Table 6). Afterward, λ included the exergy of the products and by-products together in the numerator, defined as *Index 2*, as presented in Fig. 15.

Table 5 summarizes the different parts of the *Renewability Exergy Index* (λ) to indicate their contribution by component. It should be noted that the irreversibility determined for each route refers to the total destroyed exergy, involving also the contributions of the

Table 6
Exergy flow rates and rates associated with the renewability index.

Parameter	ROUTE 1	ROUTE 2	ROUTE 3
<i>Exergy of the chemical and biochemical inputs</i>			
MEG – Monoetilenoglicol ($C_2H_6O_2$)	12	16	12
Sulfuric acid (H_2SO_4)	100	100	100
Nutrients (NH_3)	794	794	794
Sulphur dioxide (SO_2)	0	1468	0
Calcium Oxide (CaO)	137.6	137.6	137.6
Enzymes ¹ ($CH_{1.57}N_{0.29}O_{0.31}S_{0.007}$)	0	14,238	0
Yeast ² ($CH_{1.8}O_{0.9}N_{0.14}$)	39,732	39,732	39,732
ΣB_{fossil} inputs (kW)	40,763	56,468	40,763
<i>Exergy of the products</i>			
Surplus Electricity	35,803	26,072	116,539
AE – anhydrous ethanol	264,060	339,506	185,667
$\Sigma B_{products}$ (kW)	299,863	365,578	302,206
<i>Exergy of the by-products/residues</i>			
Filter cake	9,491	11,221	10,724
Lignin cake	0	69,133	0
Vinasé	60,883	78,278	42,808
Pentoses liquor	0	12,880	0
$\Sigma B_{by-products}$ (kW)	70,374	171,511	53,532
<i>Exergy of the CO₂ emissions</i>			
$\Sigma B_{emissions}$ (kW)	24,536	26,120	32,036
<i>Irreversibilities</i>			
$\Sigma B_{destroyed}$ (kW)	598,701	532,987	596,358

¹ Enzymes composition was assumed as indicated per NREL [22].

² The yeast component was created based on the chemical formula specified by Eijsberg [56].

Table 7
Techno-economic assessment.

Case Studies		Estimated	Annualized
		total cost (MUS\$)	capital cost (MUS\$/y)
Route 1	Conventional	349.56	41
Route 2	Biochemical	501.90	59
Route 3	Thermochemical	488.60	57
(MUS\$ = Million Dollars)			

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. Fig. 15 depicts the Index 1 and Index 2 employed in the global exergy efficiency calculated using the Eqs. (9) and (10), respectively.

It is observed that the λ_{index} for the evaluated routes was environmentally unfavourable, 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 favourable for the biochemical pathway (Route 2) as a result of the residue's exergetic valorisation and their potential as a by-product (Fig. 17).

The results obtained for the λ_{index} were compared with the values reported by Pellegrini and Oliveira Jr. [51], and Velásquez et al. [39]. Therefore, when comparing with the simulation of the traditional mill analysed by Pellegrini and Oliveira Jr. [51] and with the configuration adopted by Velásquez et al. [39] for the Route 1, a lower value of the λ indicator is attained. 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. [39] for the analysis of the lignocellulosic material's conversion (pulp + fruit), in the framework of the biofuels production impact assessment.

Consequently, through the application of the indicators CO₂ equivalent in energetic 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 Fig. 16 (Index 1) and Fig. 17 (Index 2).

4.4. 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

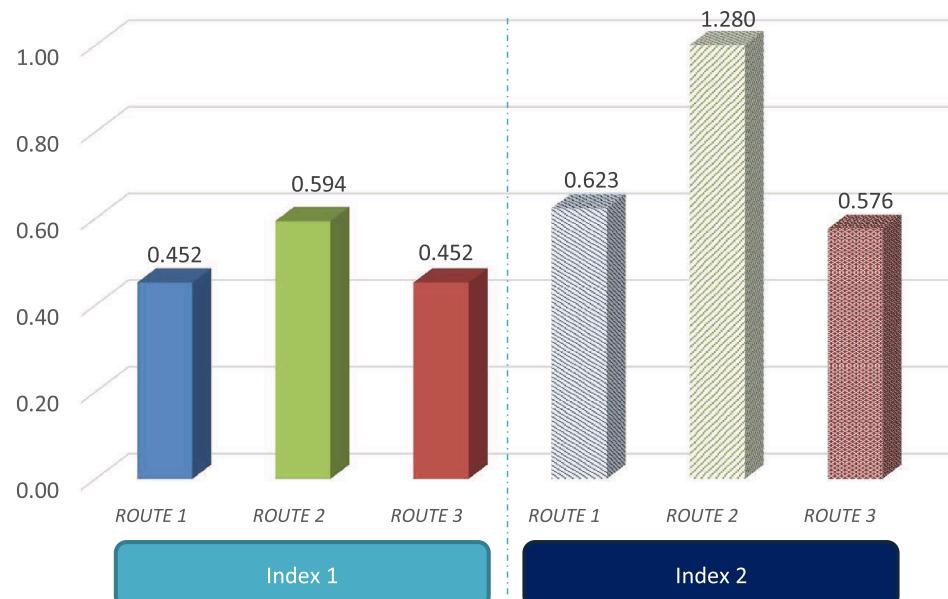


Fig. 15. Renewability exergy index of the technological routes.

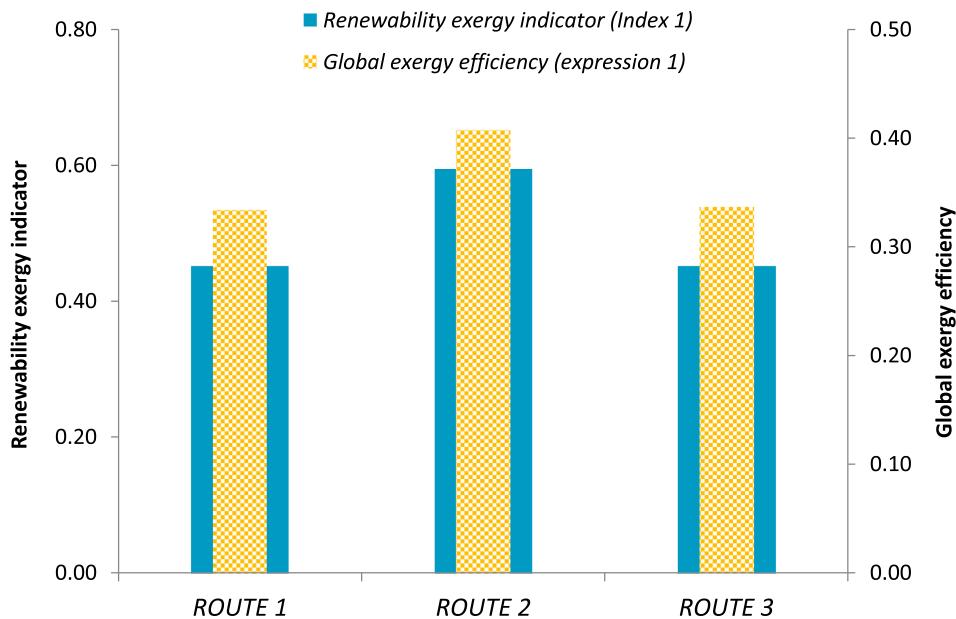


Fig. 16. Comparison between renewability exergy *Index 1* and global exergy efficiency.

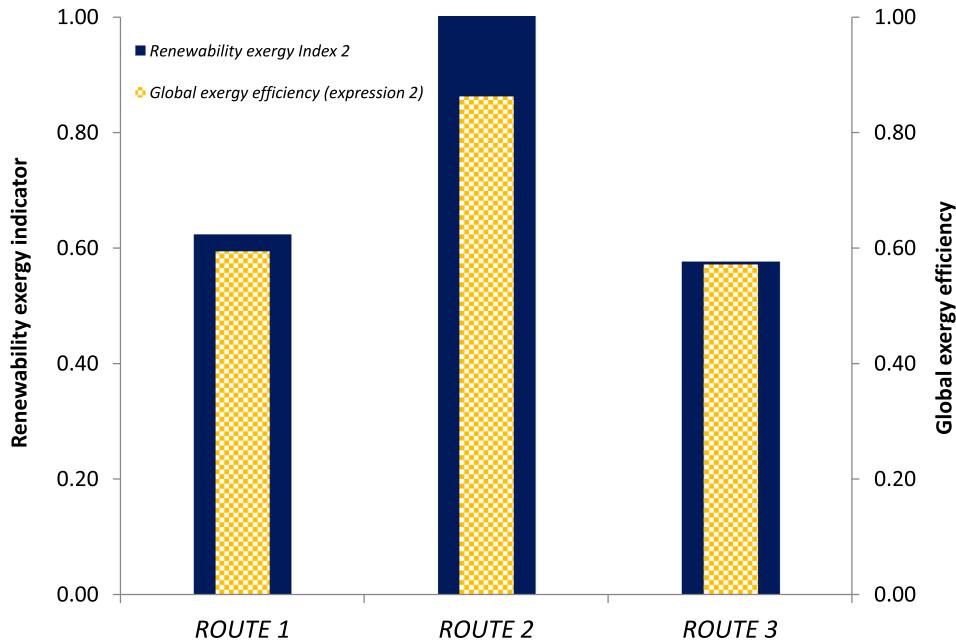


Fig. 17. Comparison between renewability exergy *Index 2* and global exergy efficiency.

models adopted in the simulation, the processes were defined entirely.

Thus, these parameters were used to determinate the performance of the configurations according to technical, environmental and economic criteria previously established. Table 6 presents the optimization results of the conventional (*Route 1*), biochemical (*Route 2*), and thermochemical (*Route 3*) sugarcane-based biorefineries analysed. According to this table, *Route 2* (biochemical platform) represents the higher total cost of investment when compared to the thermochemical and conventional platforms. It is emphasized that the cogeneration system denotes a larger percentage of the cost formation breakdown for the configurations, as shown in Fig. 18.

4.5. Global analysis of the technological configurations

Initially, the average unitary exergy costs (AUEC) involved in selected technological pathways are presented to compare the performance efficiency for each process. Thus, the AUEC value of the overall process, ethanol process, and cogeneration system for the biorefinery routes is given in Fig. 19. Later, Fig. 20 illustrated the comparison of the performance efficiencies for the selected configurations.

On the other hand, the sensitivity analysis of straw consumption using 30%, 50%, 65%, and 100% of the straw already available in sugarcane fields was carried out for each technological route, as given in Fig. 21, in which it is contrast the exergy efficiency against the AUEC of

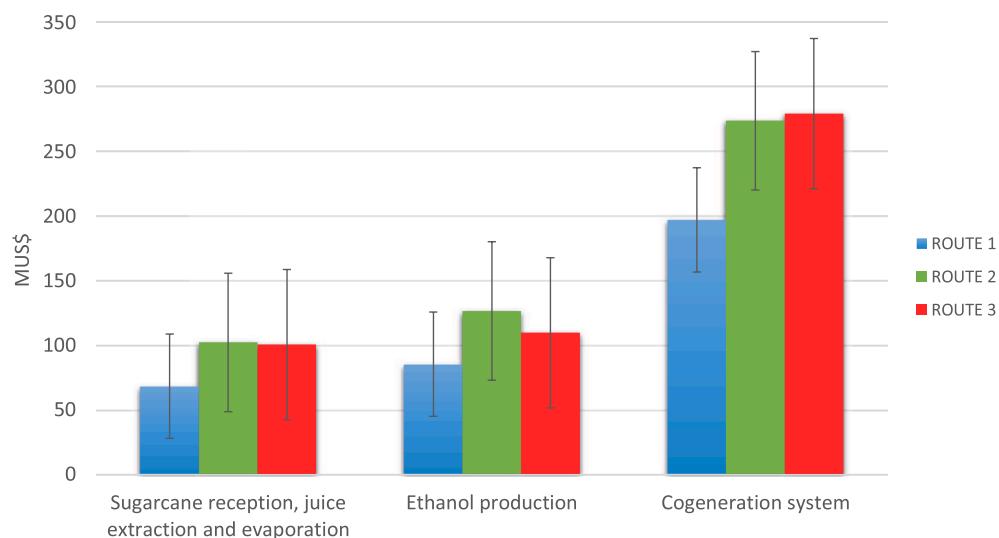


Fig. 18. The estimated capital requirement of different components by the technological routes.

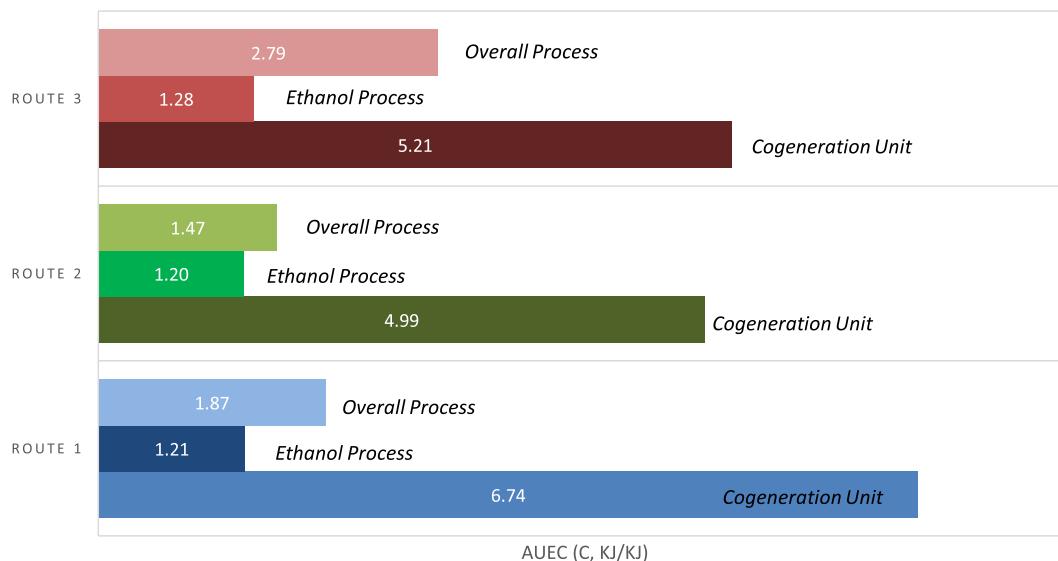


Fig. 19. Average unitary exergy cost of the technological routes.

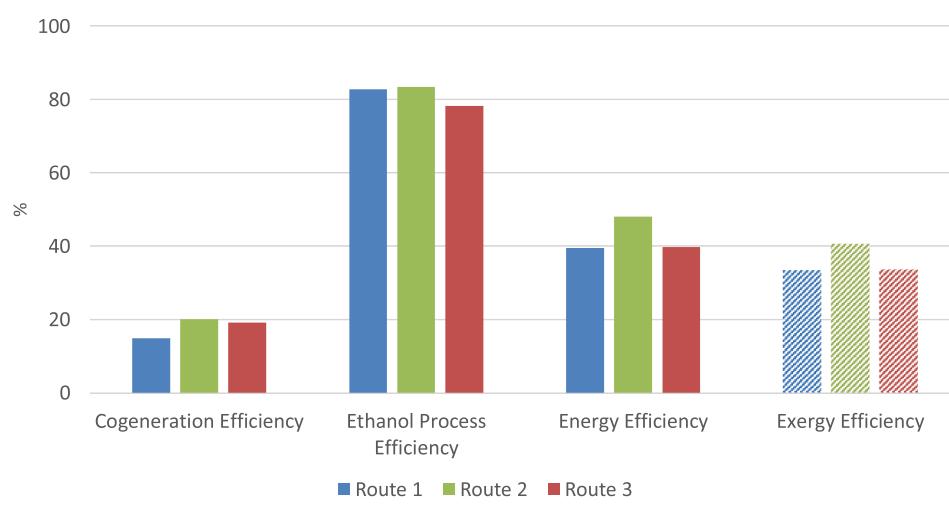


Fig. 20. Performance efficiency for each configuration.

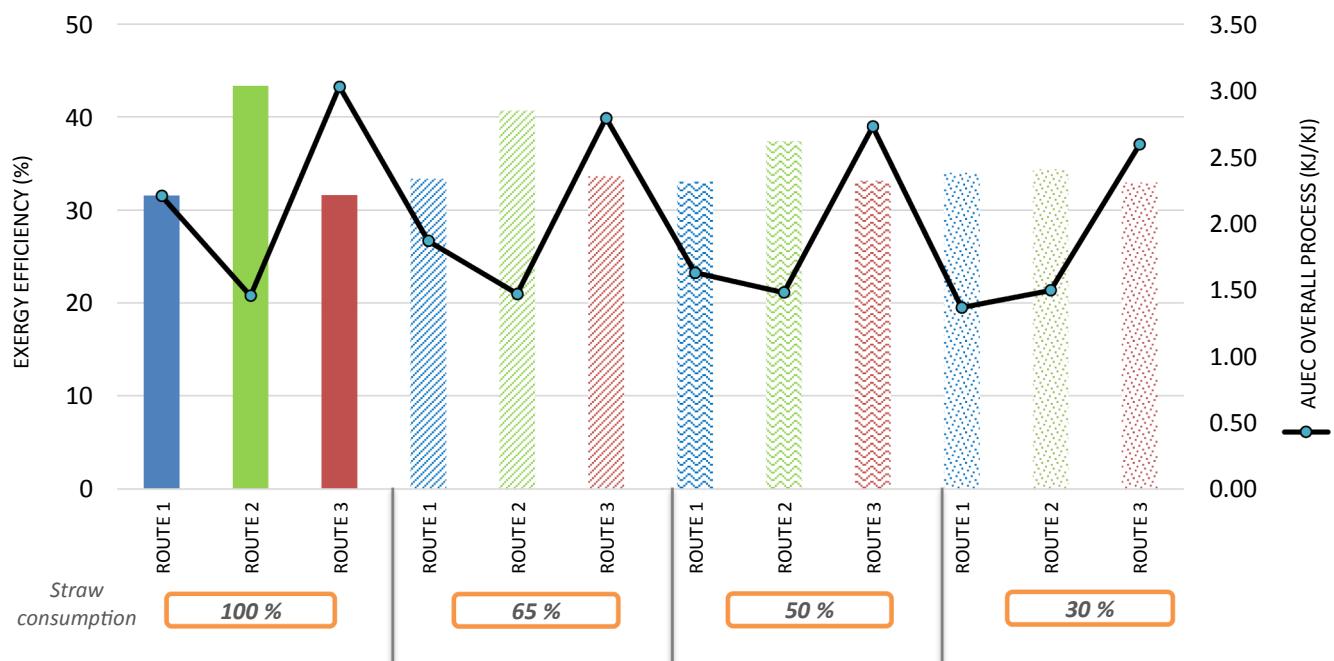


Fig. 21. Sensitivity analysis of the straw consumption.

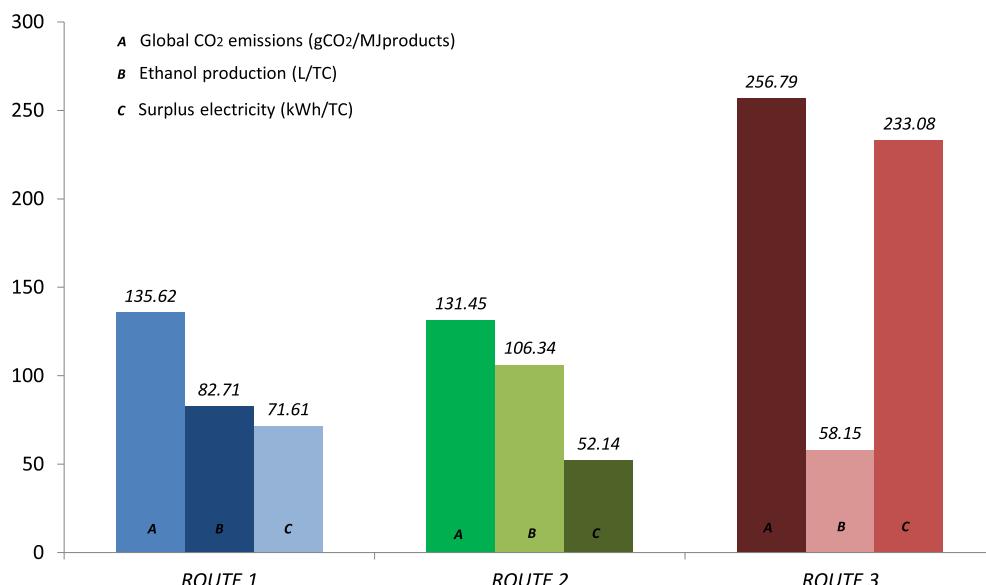


Fig. 22. Global analysis of the evaluated technological routes.

Table 8
Ranking of the sugarcane-based systems.

Parameters	Route 1	Route 2	Route 3
Global CO ₂ emissions (gCO ₂ /MJ _{products})	135.62	131.45	256.79
Ethanol production (L/t cane)	82.71	106.34	58.15
Surplus electricity (kWh/t cane)	71.61	52.14	233.08
Specific net production cost of ethanol (US\$/L)	0.248	0.277	0.493
Specific net production cost of electricity (US \$/kWh)	0.327	0.644	0.133
Average unitary exergy cost (kJ/kJ)	1.87	1.47	2.79
Exergy efficiency (Index 1)	33.37	40.68	33.63
Renewability exergy indicator (Index 1)	0.45	0.59	0.45
Exergy efficiency (Index 2)	59.39	86.16	57.10
Renewability exergy indicator (Index 2)	0.62	1.28	0.58

the systems. It is noted that the 90 kg straw/tonne cane was adopted as reference value for the case studies. Besides, all the parameters considered in the additional scenarios are shown in Table A.4.

The results have shown that when considering this lignocellulosic feedstock available in sugarcane fields, additional electricity could be exported to the Brazilian grid. For instance, it compared the conventional versus the thermochemical routes when using the straw (90 and 140 kg straw/tonne cane) is obtained a potential 28% and 10% of surplus electricity, respectively. For Route 2, the straw was mainly addressed to the production of ethanol. Hence, it was estimated an additional ethanol production of 16%.

In the overall performance of these technological routes for ethanol production and power generation, the specific CO₂ equivalent emissions were evaluated through the relation between the estimate global

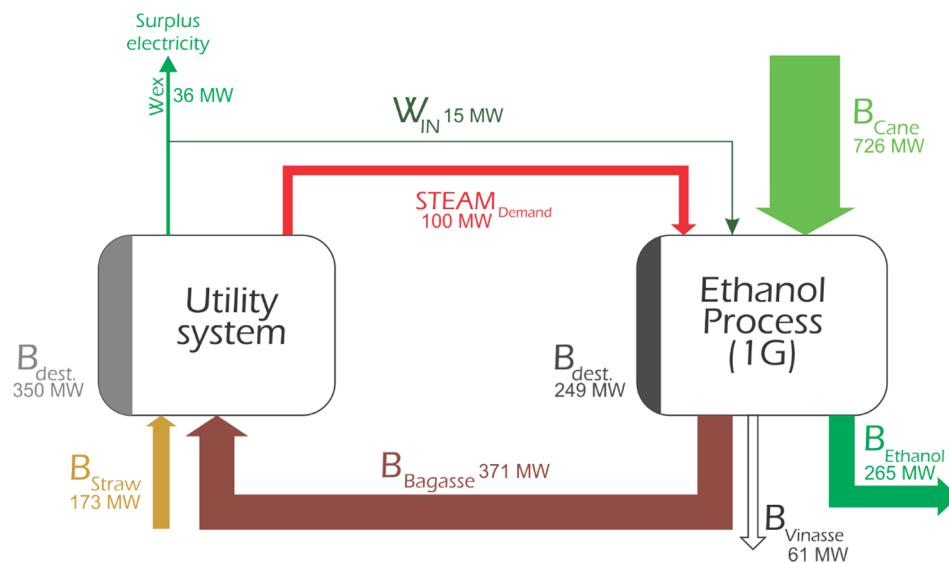


Fig. 23. Grassmann diagram of the conventional configuration.

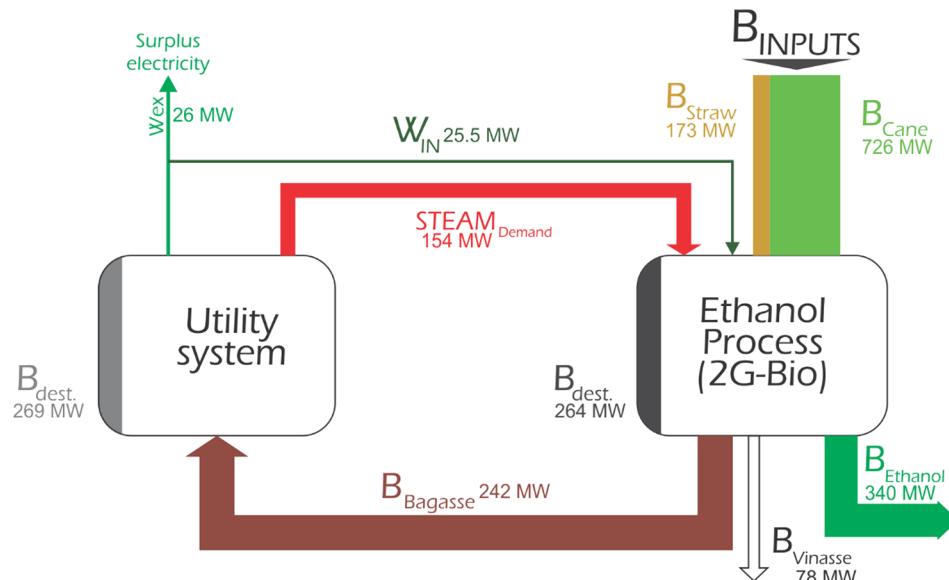


Fig. 24. Grassmann diagram of the biochemical pathway.

CO_2 emissions emitted in the atmosphere due to its operation and the exergy of the products for each configuration ($\text{CO}_{2\text{EE}}$). Subsequently, the global analysis was analysed based on the ethanol production rate, the surplus electricity available for sale to the grid, and carbon dioxide equivalent index in exergetic of these systems, as shown in Fig. 22.

From this multi-dimensional perspective, the main research findings show that the highest electricity generation was obtained in Route 3, involving the thermochemical conversion process (*biomass gasification*) since the lignocellulosic biomass was addressed to power generation. However, a higher $\text{CO}_{2\text{EE}}$ and lower ethanol yield values were also noted in this biorefinery system in contrast to the other studied routes. It must be underlined that Route 2 achieved the highest productivity in terms of ethanol production, as well as the lower CO_2 equivalent rate among all the technological configurations. It is noted that CO_2 emissions account for the emissions related to both ethanol production and power generation as products (Fig. 22). Furthermore, $\text{CO}_{2\text{EE}}$ was applied considering only ethanol as a product obtaining 148.26 g CO_2 /MJ

(Route 1), 154.48 g CO_2 /MJ (Route 2) and 333.19 g CO_2 /MJ (Route 3) in order to explore the individual contribution on the exergy-based specific CO_2 equivalent emissions performance. Thus, an increase of 8.5%, 15.9%, and 22.9% was obtained in this parameter, respectively. It is mainly due to the high biogenic carbon emissions involved in ethanol production.

For instance, the ethanol production, when compared with the scenarios evaluated by Milanez et al. [52], involving conventional plant and integrated biorefineries were reported 84.9 l/t cane and 108 l/t cane, respectively. Albarelli et al. [19] presents results for the process simulation of the *autonomous distillery* and the second-ethanol production via the biochemical pathway, using 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.

On the other hand, Modesto et al. [53] analysed several cogeneration systems such as Rankine cycles (with and without straw use) and

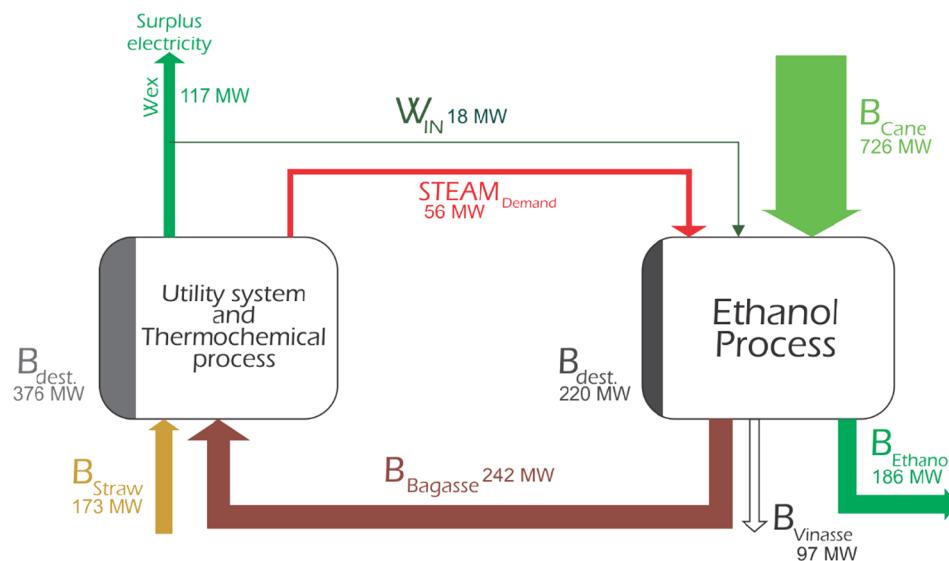


Fig. 25. Grassmann diagram of the thermochemical route.

BIGCC (85% of bagasse and 15% of straw) to assess the electricity generation of the sugarcane-based configurations obtaining 91.67 kWh/t cane, 129.3 kWh/t cane and 149 kWh/t cane.

In order to lead to the configurations ranking, the performance parameters considered in the assessment of these biomass conversion technologies are shown in Table 8. This table summarizes the renewability exergy index results for the two variations λ (Index 1) and (Index 2). Furthermore, the specific net production cost of ethanol (US\$/l) and electricity (US\$/kWh) were carried out to support the techno-economic assessment of the systems. The results of these performance parameters shown that Route 1 has the lowest net production cost of ethanol, and Route 3 offers the lowest net production cost of electricity, as a function of the Annualized Capital Cost (Table 7) and ethanol production and electricity generation rate achieved in the selected biorefineries.

For the global technological assessment, the exergy efficiency expression (Index 1) was adopted once the proposed simulations were aiming to obtained ethanol and electricity as products. It was founded that the biochemical scenario (Route 2) presented the best indicator in terms of exergy efficiency. Therefore, its average unitary exergy cost was the smallest among the evaluated processes. This platform given the most relevant results related to ethanol production, due to the integration of first with the second-ethanol 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. Besides, the thermochemical route presented the most relevant configuration when power generation (*surplus electricity*) was the target, at the cost of reaching the highest environmental impact of the routes.

Additionally, 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 valorisation.

Figs. 23–25 show the exergy flow diagram for each route. These graphical representations have the advantage that with a simple glance, it is possible to get information on the energy state of the components that constitute the system. In the beginning, Fig. 23 gives the simplified version of the Grassmann diagram focus on the conventional pathway. Fig. 24 represents the exergy flow diagram of the biochemical route (Route 2). Lastly, Fig. 25 offers the simplified Grassmann diagram in

order to visualized the exergy balance of the thermochemical configuration focus on the production of ethanol and electricity generation.

5. Conclusions

This work shows that the applied methodology could be used to improve the renewability of the ethanol production process and that feasible processes can be achieved by thermal integration. With this focus, particular emphasis was given to assess the potential valorisation of by-products. Since the renewability index criteria allow identifying the effect of useful exergy of the products and by-products involved in the systems. It was contrasted with the use of lignocellulosic materials as a complementary fuel for the cogeneration unit and second-generation ethanol process aiming to obtain competitive scenarios increasing the ethanol production and surplus electricity generation.

In terms of the exergy efficiency, 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 cogeneration unit. According to the process integration analysis, second-generation ethanol production (Route 2) allowed reaching the highest ethanol production rate. However, the economic analysis has shown that the biochemical platform has the highest estimated total cost compared to the other technological routes. It was also situated as the configuration with the lowest specific CO₂ emissions rate (131.45 gCO₂/MJ products).

Regarding the techno-economic assessment findings, it was determined that Route 1 provided advantages (lowest specific net production cost of ethanol) over the other pathways. Besides, it was set that Route 3 has the lowest specific net production cost of electricity of the selected systems. Nevertheless, when compared with the exergy-based results of the average unitary exergy cost of Route 2 reported the lowest value since the AUEC performance indicator computes on a rational basis, the contribution of the products.

The overall assessment of the thermochemical pathway (Route 3) shown the highest rate concerning the surplus power generation (233.08 kWh/t cane) at the cost of the most significant environmental impact (specific CO₂ emissions) of the routes.

Lastly, the ranking of the sugarcane-based pathways could support stakeholders in decision-making for the process design and early steps

of biorefinery configurations since it provided a multi-criteria perspective through a set of key performance indicators.

CRediT authorship contribution statement

Pablo A. Silva Ortiz: Conceptualization, Methodology, Validation, Writing - original draft. **François Maréchal:** Validation, Supervision, Project administration. **Silvio de Oliveira Junior:** Conceptualization, Methodology, Validation, Writing - original draft, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial

Appendix A

A.1. ROUTE 1-Conventional: 1G ethanol production (autonomous distillery) and electricity.

Table A1
Global analysis – Route 1.

Stream	T [°C]	P [bar]	m [kg/s]	Btot [kJ/kg]	Btot [kW]
1 – Sugarcane	25	1.013	138.9	5651	784,924
2 – Mineral impurities	25	1.013	1.73	2209	3822
3 – Imbibition water	50	1.013	41.67	54.11	2254
4 – Raw juice	30.08	1.013	140.4	2520	353,808
5 – Bagasse produced in extraction system	30.08	1.013	38.41	10,827	415,865
6 – Bagasse for filters (fine particles)	30.08	1.013	0.69	10,827	7471
7 – Bagasse surplus	30.08	1.013	6.91	10,827	74,862
8 – Bagasse for cogeneration	30.08	1.013	30.81	10,827	333,580
9 – Calcium oxide (CaO)	25	1.013	0.07	1965	137.6
15 – Treated juice for concentration	98.03	1.013	38.56	2444	94,241
14 – Treated juice for must preparation	98.03	1.013	102.9	2444	251,488
16 – Treated juice	98.03	1.013	141.5	2444	345,826
18 – Vapour Flash	99.12	0.97	1.65	50	82.5
19 – Filter cake	89.04	1.1	4.39	4668	20,493
23 – Clarified juice	95.65	6	111.8	3201	357,872
31 – Make up water for general uses	25	1.013	114.76	50	5738
32 – Ammonia (NH ₃)	25	1.013	0.04	19,841	794
33 – Sulphuric acid (H ₂ SO ₄)	29	1.013	0.06	1666	100
34 – Yeasts	29	1.013	2.29	5034	11,543
35 – Water withdrawal	25	1.013	147.2	50	7360
36 – Carbon dioxide (CO ₂)	31.66	1.013	8.88	607	5390
37 – Wine	31.22	1.363	145.2	2315	336,138
48 – Ethylene glycol MEG (C ₂ H ₆ O ₂)	80	1.013	0.001	19,463	19.5
49 – Water recovery from distillation	60	0.2	0.54	77.63	41.9
50 – GASES	34.05	1.34	0.32	2779	889.3
51 – Second-grade alcohol	34.05	1.34	0.18	24,771	4459
52 – Fusel oil (OL-FUS4)	90	1.16	0.01	5341	53.4
53 – Fusel oil (OL-FUS26)	82.24	1.16	0.02	22,613	452.3
54 – Phlegmasse	103.8	1.16	10.8	205.3	2217
55 – Vinas	75.29	1.39	124.4	286.4	35,628
56 – Anhydrous ethanol	35	1.013	8.96	29,630	265,485
67 – Exhaust gases	197.7	1.013	154.9	158.4	24,536
68 – Steam to the process at 2.5 bar	127.4	2.5	54.27	669	36,306
69 – Steam bleed to the process at 6 bar	158.8	6	11.96	796	9520
81 – Straw	25	1.013	12.5	13,845	173,060
E1 – Energy consumption-Extraction					1500
E2 – Energy consumption-Juice treatment					1200
E3 – Energy consumption-Juice concentration					1200
E4 – Energy consumption-Fermentation					900
E5 – Energy consumption-Distillation					900
E6 – Energy consumption-Condensate tank					300
Mechanical power demand of cane preparation and extraction system					8000

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge the São Paulo Research Foundation (FAPESP, Brazil) for grants 2012/23049-2 and 2014/26286-0. S. de Oliveira Jr. would like to thank the Brazilian National Council for Scientific and Technological Development (CNPq) for grant 304935/2016-6. Special thanks are given also to members of the Industrial Process and Energy Systems Engineering group (IPESE-EPFL) who provided much needed help and support.

A.2. ROUTE 2-Biochemical platform: 2G ethanol production and electricity.

Table A2

Global analysis – route 2.

Stream	T [°C]	P [bar]	M [kg/s]	B _{tot} [kJ/kg]	B _{tot} [kW]
1 – Sugarcane	25	1.013	138.9	5651	784,924
2 – Mineral impurities (dirt)	25	1.013	1.73	2209	3815
3 – Imbibition water	50	1.013	41.67	54.11	2254
4 – Raw juice	30.08	1.013	140.4	2520	353,865
5 – Bagasse produced in extraction system	30.08	1.013	38.41	10,827	415,865
6 – Bagasse for filters (fine particles)	30.08	1.013	0.71	10,827	7687
7 – Bagasse surplus for hydrolysis	30.08	1.013	15.3	10,827	165,653
8 – Bagasse for cogeneration	30.08	1.013	22.4	10,827	242,525
9 – Calcium oxide (CaO)	25	1.013	0.07	1965	137.5
10 – Water for yeast dilution	25	1.013	23.12	50	1155
11 – Water for polymer dilution	25	1.013	2.08	50	104.1
12 – Water for filter cake washing	80	1.5	4.17	59.96	250.03
13 – Water for clarification	25	1.013	1.08	50	54.12
16 – Treated juice	30	1.013	140	2444	342,160
19 – Filter cake	89.04	1.1	5.19	4668	24,227
32 – Ammonia (NH ₃)	25	1.013	0.04	19,841	793.64
33 – Sulphuric acid (H ₂ SO ₄)	29	1.013	0.06	1666	96.67
34 – Yeasts	29	1.013	2.29	5034	11,543
35 – Water withdrawal	25	1.013	157.2	50	7860
36 – Carbon dioxide (CO ₂)	31.66	1.013	9.26	607	5621
37 – Wine	31.22	1.363	158.7	2315	367,390
48 – Ethylene glycol MEG (C ₂ H ₆ O ₂)	80	1.013	0.001	19,463	58.4
49 – Water recovery from distillation	60	0.2	0.54	77.63	41.9
50 – GASES	34.05	1.34	0.46	2779	1278
51 – Second-grade alcohol	34.05	1.34	0.31	24,771	7679
54 – Phlegmasse	104	1.2	11.8	105.3	1242
55 – Vinasse	75	1.4	135.4	286.4	38,779
56 – Anhydrous ethanol	35	1.013	11.52	29,630	341,338
69 – Steam bleed to the process at 6 bar	158.8	6	13.8	796	10,985
70 – Steam bleed for bagasse pre-treatment	280	12.5	7.64	989	7556
71 – Water for pre-treated bagasse washing	30	1.013	123.4	50	6170
72 – Water for enzymatic hydrolysis	50	2.5	103	50	5150
73 – Enzyme	29	1.013	0.6	23,730	14,238
74 – Sulphur dioxide (SO ₂)	25	1.013	0.3	4892	1468
75 – Lignin cake	50	1.013	6.4	10,802	69,133
76 – Vapour recovered from bagasse pre-treatment	101	1.013	3.6	822	2959.2
77 – Diluted glucose liquor	50	1.013	105.7	480	50,736
78 – Steam for glucose liquor concentration	127	2.5	26	665	17,290
80 – Concentrated glucose liquor	56	0.2	13.8	3265	45,057
81 – Straw	25	1.013	12.5	13,845	173,060
82 – Pentoses liquor	37	1.013	98.63	537.6	53,023
E1 – Energy consumption-Extraction					1500
E2 – Energy consumption-Juice treatment					1200
E3 – Energy consumption-Juice concentration					1200
E4 – Energy consumption-Fermentation					900
E5 – Energy consumption-Distillation					900
E6 – Energy consumption-Condensate tank					300
E7 – Energy consumption-Enzymatic hydrolysis					9840
E8 – Energy consumption-Glucose liquor concentration					1215
Mechanical power demand of cane preparation and extraction system					8000

A.3. ROUTE 3-Thermochemical platform: Ethanol production, Synthesis gas and electricity

Table A3

Global analysis – Route 3.

Stream	T [°C]	P [bar]	m [kg/s]	Btot [kJ/kg]	Btot [kW]
1 – Sugarcane	25	1.013	138.9	5651	784,924
2 – Straw	25	1.013	12.5	13,845	173,060
3 – Bagasse	25	1.013	43.2	10,827	467,700
9 – Syngas	850	15.7	61.4	7939	487,450
14 – Gases	442	1.2	502.6	256	128,778
16 – Gases	190	1.1	502.6	89.6	45,033
20 – Steam at 67 bar	480	67	51.8	1431	74,158
23 – Steam at 2.5 bar	140	2.5	48.1	1228	59,067
24 – Condensed at 2.5 bar	125	2.5	45.8	1619	74,150
25 – Steam at 1.2 bar	140	1.2	2.1	2989	6277
39 – Vinasse	75	1.013	96.6	443	42,808
40 – Ethanol	35	1.013	6.30	29,630	186,669

A.4. Main parameters adopted in the sensitivity analysis of the straw consumption

Table A4

Sensitivity analysis of the straw consumption.

kg straw/TC	140			90			70			42			
	%	100	65	50	50	30	Route 1	Route 2	Route 3	Route 1	Route 2	Route 3	
Parameters	Units	Route 1	Route 2	Route 3	Route 1	Route 2	Route 3	Route 1	Route 2	Route 3	Route 1	Route 2	Route 3
Binputs	MW	995	995	995	899	899	860	860	860	806	806	806	
Bproducts	MW	314	431	314	300	366	302	284	322	285	274	277	266
Surplus Electricity	MW	50	26	129	36	26	117	20	26	100	10	26	80
Anhydrous ethanol	MW	264	405	186	264	340	186	264	296	186	264	251	186
Exergy Efficiency	%	31.56	43.35	31.61	33.37	40.68	33.63	33.05	37.39	33.15	34.00	34.37	32.96
COGEN Process Efficiency	%	14.83	18.12	18.58	14.84	20.06	19.20	13.70	20.95	18.08	13.35	22.35	16.88
AUEC COGEN Process	kJ/kJ	6.74	5.52	5.38	6.74	4.99	5.21	7.30	4.77	5.53	7.49	4.47	5.92
Ethanol Process Efficiency	%	74.19	83.86	71.65	82.83	83.44	78.28	83.79	84.16	81.57	88.37	84.25	86.36
AUEC Ethanol Process	kJ/kJ	1.35	1.19	1.40	1.21	1.20	1.28	1.19	1.19	1.23	1.13	1.19	1.16
AUEC OVERALL PROCESS	kJ/kJ	2.21	1.45	3.03	1.87	1.47	2.79	1.63	1.48	2.73	1.37	1.50	2.59

References

- [1] Dias MOS, Maciel Filho R, Mantelatto PE, Cavalett O, Rossell CEV, Bonomi A, et al. Sugarcane processing for ethanol and sugar in Brazil. Environmental Development 2015;1535:51. <https://doi.org/10.1016/j.envdev.2015.03.004>.
- [2] Bilal M, Asgher M, Iqbal HMN, Hu H, Zhang X. Biotransformation of lignocellulosic materials into value-added products—A review. Int J Biol Macromol 2017;98:447–58. <https://doi.org/10.1016/j.ijbiomac.2017.01.133>.
- [3] Bechara R, Gomez A, Saint-Antoine V, Schweitzer J-M, Maréchal F. Methodology for the optimal design of an integrated sugarcane distillery and cogeneration process for ethanol and power production. Energy 2016;117:540–9. <https://doi.org/10.1016/j.energy.2016.07.018>.
- [4] Gassner M, Maréchal F. Methodology for the optimal thermo-economic, multi-objective design of thermochemical fuel production from biomass. Comput Chem Eng 2009;33:769–81. <https://doi.org/10.1016/j.compchemeng.2008.09.017>.
- [5] Gassner M, Maréchal F. Increasing efficiency of fuel ethanol production from lignocellulosic biomass by process integration. Energy Fuels 2013;27:2107–15. <https://doi.org/10.1021/ef301952u>.
- [6] Capareda S. Introduction to Biomass Energy Conversions. CRC Press; 2013 <https://www.crcpress.com/Introduction-to-Biomass-Energy-Conversions/Capareda/p/book/9781466513334> (accessed February 2, 2019).
- [7] Piekarczyk W, Czarnowska L, Ptasiński K, Stanek W. Thermodynamic evaluation of biomass-to-biofuels production systems. Energy 2013;62:95–104. <https://doi.org/10.1016/j.energy.2013.06.072>.
- [8] Ptasiński KJ, Prins MJ, Pierik A. Exergetic evaluation of biomass gasification. Energy 2007;32:568–74. <https://doi.org/10.1016/j.energy.2006.06.024>.
- [9] de Souza-Santos ML, Bernal AFB, Rodriguez-Torres AF. New developments on fuel-slurry integrated gasifier/gas turbine (FSIG/GT) alternative for power generation applied to biomass configuration requiring no steam for gasification. Energy & Fuels 2015;29:3879–89. <https://doi.org/10.1021/acs.energyfuels.5b00775>.
- [10] Cruz PL, Iribarren D, Dufour J. Exergy analysis of alternative configurations of a system coproducing synthetic fuels and electricity via biomass gasification Fischer-Tropsch synthesis and a combined-cycle scheme. Fuel 2017;194:375–94. <https://doi.org/10.1016/j.fuel.2017.01.017>.
- [11] Albarelli JQ, Ensinais AV, Silva MA. A new proposal of cellulosic ethanol to boost sugarcane biorefineries: techno-economic evaluation. Int J Chem Eng 2014;2014. <https://doi.org/10.1155/2014/537408>.
- [12] Palacios-Bereche R, Mosquera-Salazar K, Modesto M, Ensinais A, Neira S, Serra L, et al. Exergetic analysis of the integrated first- and second-generation ethanol production from sugarcane. Energy 2013;62:46–61. <https://doi.org/10.1016/j.energy.2013.05.010>.
- [13] Bonomi A, Cavalett O, Cunha MP, Lima MA. Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization. Switzerland: Springer International Publishing; 2016. <https://www.springer.com/la/book/9783319260433>.
- [14] Carrasco JL, Gunukula S, Boateng AA, Mullen CA, DeSista WJ, Wheeler MC. Pyrolysis of forest residues: An approach to techno-economics for bio-fuel production. Fuel 2017;193:477–84. <https://doi.org/10.1016/j.fuel.2016.12.063>.
- [15] Shemfe MB, Gu S, Ranganathan P. Techno-economic performance analysis of bio-fuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading. Fuel 2015;143:361–72. <https://doi.org/10.1016/j.fuel.2014.11.078>.

- [16] Albrecht FG, König DH, Baucks N, Dietrich RU. A standardized methodology for the techno-economic evaluation of alternative fuels – A case study. *Fuel* 2017;194:511–26. <https://doi.org/10.1016/j.fuel.2016.12.003>.
- [17] Silva WC, Araújo ECC, Calmanovici CE, Bernardo A, Giulietti M. Environmental assessment of a standard distillery using aspen plus®: simulation and renewability analysis. *J Cleaner Prod* 2017;162:1442–54. <https://doi.org/10.1016/j.jclepro.2017.06.106>.
- [18] Palacios-Bereche R, Ensinas A, Modesto M, Nebra S. Double-effect distillation and thermal integration applied to the ethanol production process. *Energy* 2015;82:512–23. <https://doi.org/10.1016/j.energy.2015.01.062>.
- [19] Albarelli JQ, Ensinas AV, Silva MA. Product diversification to enhance economic viability of second generation ethanol production in Brazil: the case of the sugar and ethanol joint production. *Chem Eng Res Des* 2014;92:1470–81. <https://doi.org/10.1016/j.cherd.2013.11.016>.
- [20] Dias MOS. Simulação do processo de produção de etanol a partir do açúcar e do babaço, visando a integração do processo e a maximização da produção de energia e excedentes do babaço, Simulation of ethanol production processes from sugar and sugarcane bagasse, aiming process integration and maximization of energy and bagasse surplus; 2008. <http://repositorio.unicamp.br/jspui/handle/REPOUSIP/266223> (accessed October 9, 2018).
- [21] Dias MOS, Ensinas AV, Nebra SA, Maciel Filho R, Rossell CEV, Wolf Maciel MR. Production of bioethanol and other bio-based materials from sugarcane bagasse: Integration to conventional bioethanol production process. *Chem Eng Res Design* 2009;87:1206–16. <https://doi.org/10.1016/j.cherd.2009.06.020>.
- [22] Wooley RJ, Putsche V. Development of an Aspen Plus physical property database for biofuels components. Golden, Colorado, USA: National Renewable Energy Laboratory-NREL; 1996. <http://www.nrel.gov/docs/legosti/old/20685.pdf>.
- [23] Dia MOS. Desenvolvimento e otimização de processos de produção de etanol de primeira e segunda geração e eletricidade a partir da cana-de-açúcar, Development and optimization of first and second generation bioethanol and electricity production processes from sugarcane; 2011. <http://repositorio.unicamp.br/jspui/handle/REPOUSIP/266828> (accessed October 9, 2018).
- [24] Silva Ortiz P, de Oliveira S. Exergy analysis of pretreatment processes of bioethanol production based on sugarcane bagasse. *Energy* 2014;76:130–8. <https://doi.org/10.1016/j.energy.2014.04.090>.
- [25] Silva Ortiz P, Oliveira Junior S. Compared exergy analysis of sugarcane bagasse sequential hydrolysis and fermentation and simultaneous saccharification and fermentation. *Int J Exergy* 2016;19459. <https://doi.org/10.1504/IJEX.2016.075880>.
- [26] Silva Ortiz PA, Maciel Filho R, Posada J. Mass and heat integration in ethanol production mills for enhanced process efficiency and exergy-based renewability performance. *Processes* 2019. <https://doi.org/10.3390/pr7100670>.
- [27] Hassuan SJ, Leal MR, Macedo IC. Biomass Power Generation: Sugarcane Bagasse and Trash. Piracicaba: United Nations Development Programme (UNDP), Centro de Tecnologia Canavieira (CTC); 2005.
- [28] Gómez-Barea A, Leckner B. Modeling of biomass gasification in fluidized bed. *Prog Energy Combust Sci* 2010;36:444–509. <https://doi.org/10.1016/j.pecs.2009.12.002>.
- [29] Nikoo MB, Mahinpey N. Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS. *Biomass Bioenergy* 2008;32:1245–54. <https://doi.org/10.1016/j.biombioe.2008.02.020>.
- [30] Aspentech. Aspen physical property system. Physical property models, V8.6, 2014.
- [31] Marechal F, Kalitventzeff B. Targeting the minimum cost of energy requirements: a new graphical technique for evaluating the integration of utility systems. *Comput Chem Eng* 1996;20:S225–30. [https://doi.org/10.1016/0098-1354\(96\)00048-8](https://doi.org/10.1016/0098-1354(96)00048-8).
- [32] Mian A, Ensinas AV, Marechal F. Multi-objective optimization of SNG production from microalgae through hydrothermal gasification. *Comput Chem Eng* 2015;76:170–83. <https://doi.org/10.1016/j.compchemeng.2015.01.013>.
- [33] Albarelli JQ, Onorati S, Caliandro P, Peduzzi E, Meireles MAA, Marechal F, et al. Multi-objective optimization of a sugarcane biorefinery for integrated ethanol and methanol production. *Energy* 2017;138:1281–90. <https://doi.org/10.1016/j.energy.2015.06.104>.
- [34] Palacios Bereche R. Modelagem e integração energética do processo de produção de etanol a partir da biomassa de cana-de-açúcar, Modeling and energy integration of the ethanol production process from sugarcane biomass; 2011. <http://repositorio.unicamp.br/jspui/handle/REPOUSIP/265106> (accessed October 9, 2018).
- [35] Szargut J, Morris D, Steward F. *Exergy analysis of thermal, chemical, and metallurgical processes*. New York: Hemisphere Publishing Corporation; 1988.
- [36] Marais H, van Schoor G, Uren KR. The merits of exergy-based fault detection in petrochemical processes. *J Process Control* 2017. <https://doi.org/10.1016/j.jprocont.2017.11.005>.
- [37] Dewulf J, Van Langenhove H, Muys B, Bruers S, Bakshi BR, Grubb GF, et al. Exergy: its potential and limitations in environmental science and technology. *Environ Sci Technol* 2008;42:2221–32. <https://doi.org/10.1021/es071719a>.
- [38] de Oliveira Junior S. Exergy Analysis and Environmental Impact. In: de Oliveira Junior S, editor. *Exergy: Production, Cost and Renewability* London: Springer; 2013. p. 281–303. <https://doi.org/10.1007/978-1-4471-4165-9>.
- [39] Velásquez HI, De Oliveira S, Benjumea P, Pellegrini LF. Exergo-environmental evaluation of liquid biofuel production processes. *Energy* 2013;54:97–103. <https://doi.org/10.1016/j.energy.2013.03.037>.
- [40] Peduzzi E. *Biomass to Liquids: Thermo-economic analysis and multi-objective optimisation* [Ph.D. thesis]. École Polytechnique Fédérale de Lausanne (EPFL)2015. <http://infoscience.epfl.ch/record/204975>.
- [41] Turton R, Bailie R, Whiting W, Shaeiwitz J. *Analysis, synthesis, and design of chemical processes*. 3rd ed. Prentice Hall; 2009.
- [42] Ulrich G, Vasudevan P. *A guide to chemical engineering process design and economics*. 2nd Edition, CRC; 2003.
- [43] Sinnott R, Towler G. *Chemical Engineering Design*, 6th Edition-SI. Butterworth-Heinemann 2020. <https://doi.org/10.1016/B978-0-08-102599-4.00006-0>.
- [44] Smith R. *Chemical Process Design and Integration*. 2nd ed. Wiley; 2016.
- [45] 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. *Computer Aided Chemical Engineering* Elsevier; 2015. p. 587–92. <https://doi.org/10.1016/B978-0-444-63578-5.50093-1>.
- [46] Gerber L, Gassner M, Maréchal F. Systematic integration of LCA in process systems design: Application to combined fuel and electricity production from lignocellulosic biomass. *Comput Chem Eng* 2011;35:1265–80. <https://doi.org/10.1016/j.compchemeng.2010.11.012>.
- [47] Gerber L, Fazlollahi S, Maréchal F. A systematic methodology for the environmental design and synthesis of energy systems combining process integration Life Cycle Assessment and industrial ecology. *Comput Chem Eng* 2013;59:2–16. <https://doi.org/10.1016/j.compchemeng.2013.05.025>.
- [48] Cavaletti O, Cunha MP, Junqueira TL, Dias MOS, Jesus CDF, Mantelatto PE, et al. Environmental and economic assessment of bioethanol, sugar and bioelectricity. *Eng Trans* 2011;25:1007–12. <https://doi.org/10.3303/CET1125168>.
- [49] Cavaletti O, Junqueira TL, Dias MOS, Jesus CDF, Mantelatto PE, Cunha MP, et al. Environmental and economic assessment of sugarcane first generation biorefineries in Brazil. *Clean Technol Environ Policy* 2012;14:399–410. <https://doi.org/10.1007/s10098-011-0424-7>.
- [50] Chagas MF, Cavaletti O, Silva CR, Seabra JE, Bonomi A. Adaptação de Inventários de Ciclo de Vida da cadeia produtiva do etanol de cana-de-açúcar no Brasil. III Congresso Brasileiro Em Gestão Do Ciclo de Vida de Produtos e Serviços. Maringá-Brasil; 2012. <https://ainfo.cnptia.embrapa.br/digital/bitstream/item/155766/1/2016AA33.pdf>.
- [51] Pellegrini LF, de Oliveira Junior S. Combined production of sugar, ethanol and electricity: Thermoeconomic and environmental analysis and optimization. *Energy* 2011;36:3704–15. <https://doi.org/10.1016/j.energy.2010.08.011>.
- [52] Milanez AY, Nyko D, Valente MS, de Sousa LC, Bonomi A, Dayan C, et al. De promessa à realidade: como o etanol celulósico pode revolucionar a indústria da cana-de-açúcar uma avaliação do potencial competitivo e sugestões de política pública. *Biocombustíveis BNDES Setorial* 2015;41:237–94.
- [53] Modesto M, Aoki A, Lodi A, Pina E. Assessment of the potential to increase electricity generation from sugarcane straw in brazilian sugarcane cogeneration plants. *Chem Eng Trans* 2016;193–8. <https://doi.org/10.3303/CET1650033>.
- [54] Pereira LG, Dias MOS, Mariano AP, Maciel Filho R, Bonomi A. Economic and environmental assessment of n-butanol production in an integrated first and second generation sugarcane biorefinery: Fermentative versus catalytic routes. *Appl Energy* 2015;160:120–31. <https://doi.org/10.1016/j.apenergy.2015.09.063>.
- [55] Santos CL, Silva CC, Mussatto SI, Osseweijer P, van der Wielen LAM, Posada JA. Integrated 1st and 2nd generation sugarcane bio-refinery for jet fuel production in Brazil: techno-economic and greenhouse gas emissions assessment. *Renew Energy* 2018;129:733–47. <https://doi.org/10.1016/j.renene.2017.05.011>.
- [56] Eijsberg R. *The design and economic analysis of a modern bio-ethanol factory located in Brazil*. Delft: Delft University of Technology, Faculty of Applied Sciences; 2006.