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## Exergetic analysis of the integrated first- and second-generation ethanol production from sugarcane



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#### ABSTRACT

This study carried out an exergetic analysis of a proposed ethanol production scheme in which a new process — enzymatic hydrolysis of sugarcane bagasse — is integrated into the conventional process. Seven cases were evaluated, among them a conventional ethanol production plant without hydrolysis, a conventional plant combined with hydrolysis and hydrolysate concentration by evaporation, and a conventional plant combined with hydrolysis and hydrolysate concentration by the membrane system. Process simulations were performed to evaluate mass and energy balances, adopting the pre-treatment of sugarcane bagasse by steam explosion, and including an integrated cogeneration system. It was assumed that sugarcane trash and lignin cake, a hydrolysis residue, are available as supplementary fuel. The exergies of streams involved in the process were calculated, along with their exergetic cost. For the conventional process, in which ethanol and surplus electricity are the major products, a second-law efficiency of 28% was found. In the integrated process, with biogas as an additional product, a higher performance in resources management was achieved, with values in the range of 35–37%.

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#### 1. Introduction

The sugarcane industry is one of the most important economic sectors in Brazil, a position reached in large measure due to a high efficiency and competitiveness in the first-generation ethanol production process [1]. Nevertheless, the efficiency index and energy balance can still be improved if a second-generation process, such as enzymatic hydrolysis of sugarcane bagasse and trash, is integrated into the conventional process. However, from an energy point of view, the introduction of bagasse hydrolysis can be a real challenge, because bagasse, the raw material in the new process, is a fuel in the current one.

There are several studies in the literature evaluating the incorporation of bagasse hydrolysis into current distilleries. CGEE

(Center for Strategic Studies and Management in Science) [2] produced a prospective study evaluating the ethanol production increase by means of an enzymatic hydrolysis process in projected scenarios for the years 2015 and 2025. Dias et al. [3] studied the incorporation of the organosolv hydrolysis process with diluted acid into the current ethanol production process. Dias et al. [4] also studied the incorporation of the ethanol production by enzymatic hydrolysis into the conventional process adopting different pretreatments and producing biogas from pentose liquor. Walter and Ensinas [5] concluded a preliminary analysis of two technological routes for biofuel production from cellulosic materials (based on hydrolysis, and on gasification combined with the Fischer-Tropsch conversion processes). Macrelli et al. [6] carried out a technoeconomic evaluation of ethanol production by enzymatic hydrolysis taking into account the production of biogas from pentose liquor and its use in boilers as fuel. Furlan et al. [7] carried out the modelling and simulation of the integrated first- and secondgeneration ethanol production process including the optimization

However, the efficiency of an integrated process should be evaluated in terms of its sustainability and use of energy resources.

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	nclature	IU k	International unit unitary exergetic cost
$a_i$	activity	$L_i$	exergy losses (kW)
$E^c$	exergetic cost (kW)	$\overline{M}$	molar mass
Ε	exergy (kW)	P	product exergy (kW)
$D_i$	exergy destruction (kW)	S	entropy (kJ/kg-K)
e	specific exergy (kJ/kg)	T	temperature (°C)
$e^{PH}$	physical specific exergy of a stream (kJ/kg)	$y_i$	molar fraction
$e^{CH}$	chemical specific exergy of a stream (kJ/kg)	WTS	Water Treatment System
F	fuel exergy (kW)	$\epsilon$	exergetic efficiency
FPU	filter paper unit	$\tilde{arepsilon}_i^0$	chemical standard exergy of a pure component (kJ/kg)
h	enthalpy (kJ/kg)	•	

In this context, according to Ojeda et al. [8], exergy analysis serves as a unified and effective tool to evaluate global process efficiency, since it is a thermodynamic analysis technique based on the Second Law of Thermodynamics, capable of locating thermodynamic losses and identifying their causes and their impact on the natural environment. There are several studies in the literature applying exergy analysis to the ethanol production process by enzymatic hydrolysis [8–11], but none of them includes the concept of exergetic cost analysis.

Thus, the aim of this study is to carry out an exergetic analysis and an exergetic cost analysis of the ethanol production process by enzymatic hydrolysis of sugarcane bagasse integrated into the conventional process. Previous studies have shown that glucose hydrolysate, produced in the hydrolysis process, has a very low glucose content, the actual figure depending on the solids content in the hydrolysis reactors. For this reason, three levels of solids content in the hydrolysis reactor were simulated -5%, 8%, and 10% - in order to evaluate the impact on the process energy consumption. Furthermore, an alternative method based on membranes is proposed to concentrate the glucose liquor. Since pressure-driven membrane processes such as RO (reverse osmosis) and NF (nanofiltration) have the capability of removing water from aqueous solutions without phase change, membrane systems consume less energy than other separation techniques [12.13].

In exergetic analysis, techniques are developed with the aim of identifying and evaluating thermodynamic inefficiencies in terms of exergy destruction and loss. Calculation of the exergetic cost of the process streams and products completes the analysis [14]. On this basis, changes can be made to pieces of equipment and/or processes in order to improve efficiency.

The novelty of this work lies in the exergy and exergetic cost analysis performed by means of the Theory of Exergetic Cost applied to the overall process. Moreover, the unitary exergetic cost disaggregation provided by the Exergetic Cost Formation method gives a complete view of the impacts of each subsystem on the final product cost. This type of analysis allows an overall evaluation taking into account the utilities (i.e. steam and electricity) and the process itself. It is a very useful methodology when several products (electricity, ethanol, biogas) are obtained from a single raw material (sugarcane). Furthermore, these analyses provide an evaluation, from the point of view of the Second Law of Thermodynamics, of the advantages and disadvantages of membranes as a separation technique, and their impact on the exergetic costs of ethanol and electricity.

#### 2. Ethanol production process simulation

Several cases were evaluated in this study based on simulations developed in Refs. [15,16]. The simulations were modelled in Aspen

Plus<sup>®</sup>, based on data collected from the literature, as well as actual data for the conventional process, and experimental data for the second-generation process.

#### 2.1. Modelling and simulation

The model selected for property calculations depended on the operation. In the cogeneration system, for combustion gases the chosen method was the RKS-BM, which uses the Redlich—Kwong—Soave equation of state with the Boston Mathias function; this model is suitable for combustion calculations. For steams in the cogeneration system, the Steam Tables method of the Aspen Plus software was used.

For the sucrose—water solution (sugarcane juice), the UNIQUAC (UNIversal QUAsiChemical) model was selected, with the binary parameters of Starzak and Mathlouthi [17]. This model was deemed the most appropriate to represent the boiling point elevation. However, for enthalpy calculation, there were significant errors in comparison to equations from the literature based on experimental data (Kadlec et al.'s equation). For this reason, a subroutine was written in Fortran for the enthalpy calculation of juice according to the equations from the literature [16]. Finally, for ethanol mixtures in the distillation and dehydration steps, the UNIQUAC-RK model was selected.

Table 1 shows the components adopted in this study. Some of these are not found in the Aspen Plus® database; they were created, and their properties inserted into the software according to data from the literature [16,18]. The sugarcane composition adopted for this study is shown in Table 2. Cellulose, hemicellulose and lignin

**Table 1** Components used in simulation.

Database components	
Silicon dioxide	Calcium hydroxide
Water	Calcium phosphate
Sucrose	Ammonia
Glucose	Sulphuric acid
Potassium oxide	Glycerol
Aconitic acid	Acetic acid
Potassium chloride	Succinic acid
Carbon dioxide	Isoamyl alcohol
Carbon monoxide	Ethanol
Nitrogen	Xylose
Oxygen	Sulfur dioxide
Hydrogen	Sulfurous acid
Nitrogen oxide	Furfural
Phosphoric acid	Hydroxymethilfurfural
Created components	
Cellulose	Yeast
Hemicellulose	Cellulase enzyme
Lignin	-

 Table 2

 Sugarcane composition specified in simulation [16].

Component	% Mass
Sucrose	13.85
Fibres	13.15
Reducing sugars	0.59
Minerals	0.20
Other non-saccharides	1.79
Water	69.35
Soil	1.07

**Table 3**Description of the evaluated cases.

Case	Solid content in hydrolysis, %	Concentration of glucose hydrolysate	Description
Base Case	_	_	Conventional distillery without hydrolysis
EV5	5	Evaporation system	Hydrolysis process coupled with conventional distillery
EV8	8	Evaporation system	Hydrolysis process coupled with conventional distillery
EV10	10	Evaporation system	Hydrolysis process coupled with conventional distillery
ME5	5	Membrane system	Hydrolysis process coupled with conventional distillery
ME8	8	Membrane system	Hydrolysis process coupled with conventional distillery
ME10	10	Membrane system	Hydrolysis process coupled with conventional distillery

were selected to represent the fibre in sugarcane. Reducing sugars were simulated as glucose, minerals as  $K_2O$ , and other non-saccharides as aconitic acid and potassium chloride. The soil in sugarcane was simulated as  $SiO_2$ .

Regarding convergence in simulation, the Wegstein method was used by the simulator (default method in Aspen Plus<sup>®</sup>) to carry out mass and energy balances in each operation.

#### 2.2. Description of the processes

The Base Case represents the conventional anhydrous ethanol and electricity production process, namely, a distillery comprising the following elements: cane cleaning, preparation and extraction, cogeneration system, juice treatment, juice concentration, fermentation, distillation and dehydration.

In the simulation, cane dry cleaning, and a mill tandem extraction system were assumed. In the juice treatment, the following operations were adopted: screening, heating, liming, decantation, and mud filtration. The concentration of treated juice takes place in a multiple-effect evaporation system. In conventional autonomous distilleries, the must for ethanol production is prepared from sugarcane juice; for the fermentation process sugar concentration should not exceed 17%. Vapour bleedings with different pressures and temperatures resulting from the concentration process are used to cover heat demands in other parts of the plant. Must sterilization is carried out by an HTST-type treatment (High Temperature Short Time), with heating to 130 °C followed by fast cooling down to the fermentation temperature of 32 °C [3,16]. In this study, fermentation was based on the Melle-Boinot process (cell-recycle batch fermentation). At the end of the fermentation, the wine is centrifuged and most of the yeast is recovered. Following that, the wine is sent to distillation and rectification columns where hydrated ethanol (93.7% wt. of ethanol) and vinasse (0.02% wt. of ethanol) are separated. For ethanol dehydration, a process of extractive distillation with MEG (monoethylene glycol) was simulated. Anhydrous ethanol is obtained, with an ethanol content of 99.4% (mass basis).

The cogeneration system adopted in the simulation consists of a steam cycle with backpressure steam turbines, and live steam parameters of 67 bar and 480 °C. This is used to generate just the steam required for the process, leaving a surplus of bagasse that can be used in the enzymatic hydrolysis process.

Cases EV and ME consist of a conventional distillery coupled to a bagasse enzymatic hydrolysis process [16]. For the latter, a steam explosion pre-treatment is adopted, followed by a washing of pre-treated bagasse in order to remove soluble hemicellulose. This study assumed the addition of  $SO_2$  as a catalyst in the pre-treatment reactor at the rate of 2% w/w.

In the next step, water is added in order to adjust the concentration of water-insoluble solids in the hydrolysis reactor. In this study, three levels of solids content in the hydrolysis reactor were simulated: 5%, 8%, and 10%. A commercial enzyme mixture (activity 65 FPU/g and 17 IU/g of  $\beta$ -glucosidase), supplemented with a

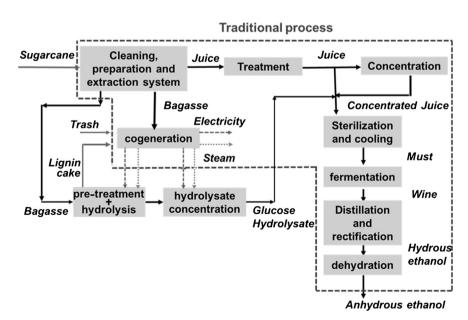


Fig. 1. Simplified block flow diagram of the integrated production of first- and second-generation ethanol from sugarcane.

commercial  $\beta$ -glucosidase preparation (376 IU/g of  $\beta$ -glucosidase) was adopted in this study, as per Ref. [19]. For the simulations, an average value of 0.114 g enzyme/g dry pre-treated pulp was adopted [19]. It was assumed that enzymes are purchased, i.e., they are an external input. The production of enzymes on site was not considered in this study due to a lack of information about its production process.

After the hydrolysis stage, the hydrolysate passes through a filter in order to separate the lignin cake (solid fraction) from the glucose liquor.

Before the glucose liquor can proceed to fermentation, it needs to be concentrated. For this, two alternatives were studied: a multiple-effect evaporation system (Case EV), and a membrane separation system (Case ME). Table 3 provides an overview of the cases evaluated in this study.

Sugarcane trash and lignin cake, a hydrolysis residue, are adopted as fuels in the cogeneration boiler to help cover energy demands of the overall process. Nevertheless, it is still necessary to burn part of the bagasse in the boilers to cover the energetic requirements of the integrated process. The amount of bagasse for

**Table 4** Equipment specifications in each operation process [16].

Parameter V	/alue
Sugarcane cleaning, preparation and juice extraction	
Efficiency of soil removal in cleaning operation, %	0
Efficiency of sugar extraction in extraction system, %	6.2
Imbibition water, kg/t cane	00
Moisture content in bagasse, %	0
Mineral content in raw juice, %	3.4
Juice treatment	
Heating temperature of juice treatment, °C	05
Sucrose content in filter cake, %	!
Moisture content in filter cake, %	0
CaO consumption, kg/t cane 0.	).5
Juice concentration	
Brix content in final must, %	9
Pressure 1st effect — Evaporation system, bar 1.	.69
Pressure 2nd effect — Evaporation system, bar 1.	.31
Pressure 3rd effect — Evaporation system, bar 0.	.93
Pressure 4th effect — Evaporation system, bar 0.	.54
Pressure 5th effect — Evaporation system, bar 0.	.16
Fermentation	
Conversion yield from sugars to ethanol, %	9
Fermentation temperature, °C 3-	4
Yeast concentration in fermentation reactor, v/v %	.5
Sulphuric acid for yeast treatment, kg/m <sup>3</sup> of ethanol 5	;
Distillation and rectification	
· · · · · · · · · · · · · · · · · · ·	8
Number of stages in rectification section (column A1) 8	;
Number of stages in top concentrator (column D) 6	5
Number of stages in phlegm rectification column (columns B–B1) 4:	15
	.02
Dehydration	
,	.01
	.20
	9.4
Cogeneration system	
Pressure of boiler live steam, bar	
	80
Isentropic efficiency of electricity generation in steam turbines, %	_
	7.6
	8.2
	0
	0
Boiler thermal efficiency, % (LHV base)	-
	6
system, kWh/t of cane	•
	2
	2.5
Process steam temperature, °C 1:	27.4

**Table 5**Main specifications in enzymatic hydrolysis process [16].

Hydrolysis process	
Pre-treatment reactor temperature, °C	190
Pre-treatment reactor pressure, bar	12.5
Pre-treatment reactor steam consumption, kg of steam/kg of raw material	0.55
Pressure at flash tank, bar	1.01
Efficiency of solids removal from solution in pentoses separation, %	90
Loss of soluble lignin in pentoses separation, %	6.3
Moisture content of cellu-lignin, %	60
Water for pentoses washing, l/kg of dry material	15
Hydrolysis reactor temperature, °C	50
Moisture content in lignin cake (before the dewatering), %	70
Solids content in concentrate hydrolysate, %	19
Energy consumption in trash shredder, kWh/t of trash	82.03
Energy consumption in cleaner station, kWh/t of trash	13.6
Energy consumption in bagasse feeder, kWh/t of bagasse	0.46
Energy consumption in xylose separator, kWh/t of material	2.3
Energy consumption in pentoses separator, kWh/m <sup>3</sup>	0.4
Energy consumption in lignin cake dewatering press, kWh/kg of	56.1
dry matter	

hydrolysis was calculated by iteration, because the increase in raw material for hydrolysis increases the plant steam consumption.

In addition, pentose liquor, a hydrolysis by-product, is taken to an UASB reactor (upflow anaerobic sludge blanket reactor) in order to produce biogas from the organic matter present in it.

A block flow diagram of the integrated first- and second-generation ethanol production from sugarcane is presented in Fig. 1. Table 4 shows equipment specifications in each operation of the conventional process (common to all cases), and Table 5 shows specifications for the enzymatic hydrolysis process (Cases EV and ME).

The basic characteristics of the modelled plant, common to all cases, are: mill capacity, 2,000,000 t cane/year; crushing rate, 500 t cane/h; season operation hours, 4000 h/year; and bagasse production, 277 kg/t cane. The main operational parameters applied to all cases are shown in Table 6.

Fig. 2 shows the flow sheet of the conventional ethanol production process in Aspen Plus<sup>®</sup>, and Fig. 3 shows the cogeneration system integrated with the enzymatic hydrolysis process. Fig. 4 shows the operations in the enzymatic hydrolysis process.

#### 3. Exergetic analysis

By means of the exergetic analysis, exergy destruction and losses in a system can be located and quantified. An exergetic

**Table 6**Main operational parameters for integrated first- and second-generation ethanol production.

Parameter	1st gen. 1st and 2nd generation						
	Base Case	EV5	EV8	EV10	ME5	ME8	ME10
Steam consumption (kg/t of cane)	500.9	793.2	754.7	742.3	689.8	690	690.2
Bagasse for enzymatic hydrolysis (kg/t of cane)	_	110.3	149.5	172.7	195.9	206.2	212.4
Sugarcane trash processed (kg/t of cane)	78	78	78	78	78	78	78
Self-consumption energy (kWh/t of cane)	12	38.7	38.1	38	53.1	45.1	42.2
Surplus energy (kWh/t of cane)	42.3	62.5	54.6	51.3	25.3	32.9	35.7
Anhydrous ethanol production (l/t of cane)	79	86.7	88.1	88.7	92.6	91.5	90.9

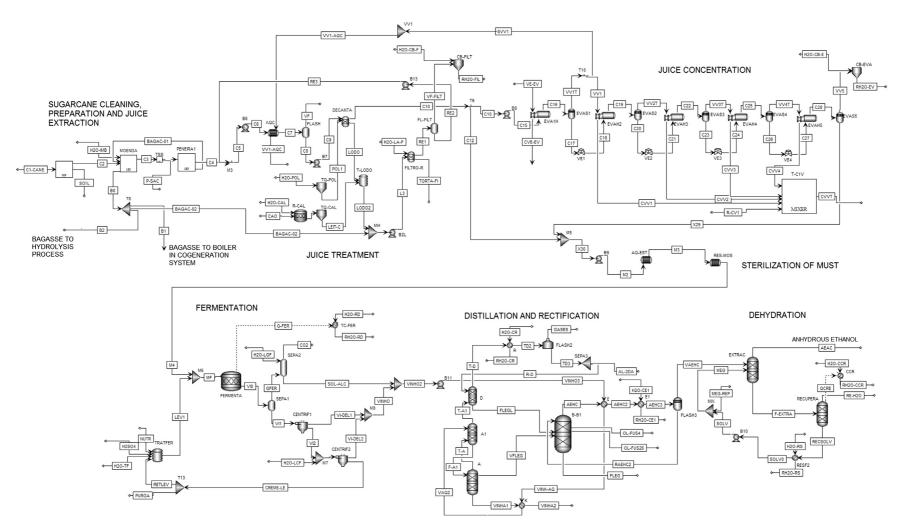


Fig. 2. Flow sheet of the conventional ethanol production process in Aspen Plus®.

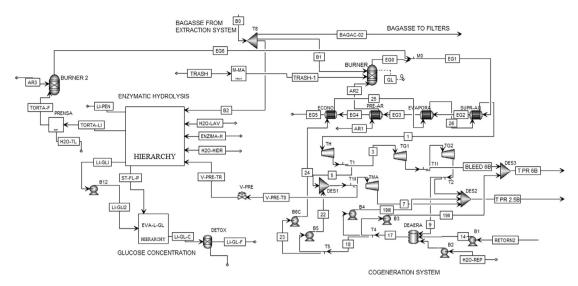


Fig. 3. Flow sheet of the cogeneration system in Aspen Plus®.

analysis of the integrated first- and second-generation ethanol production process was performed by Mosqueira Salazar [20]; the overall plant was divided into 10 subsystems for the conventional process (Base Case), and into 13 subsystems for the integrated plant with bagasse enzymatic hydrolysis (Cases EV and ME). Fig. 5 shows the plant diagram (production structure) for the Base Case, with circles representing flow distributors. Figs. 6 and 7 show the flow sheet for Cases EV and ME respectively. Table 7 shows the flow description for Figs. 5–7.

#### 3.1. Exergy calculation

Exergy of streams was calculated as the sum of both physical and chemical exergy:

$$e = e^{PH} + e^{CH} \tag{1}$$

If the potential and kinetic components of exergy are neglected, the physical exergy can be calculated by the following expression:

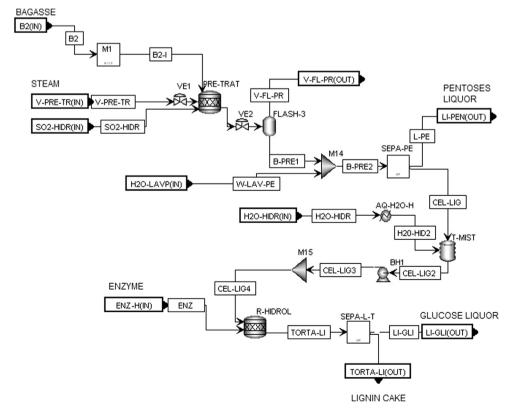


Fig. 4. Flow sheet of the operations in the enzymatic hydrolysis process.

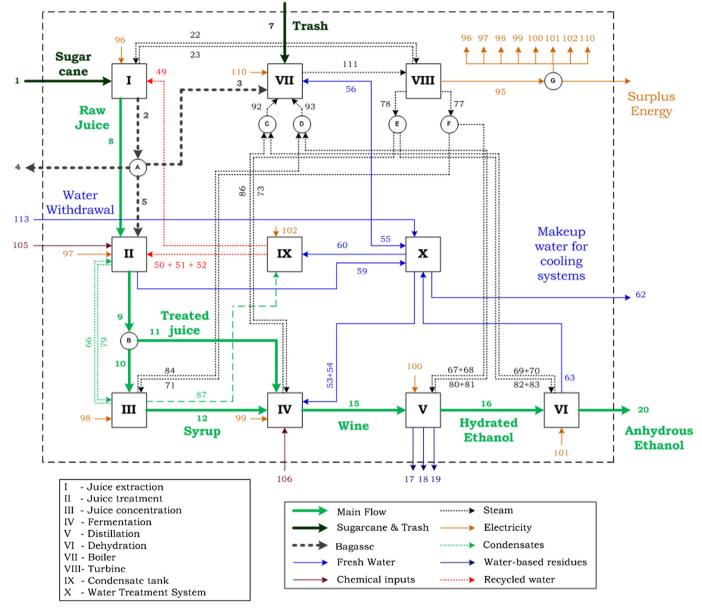


Fig. 5. Flow sheet of ethanol production process — Base Case.

$$e^{PH} = (h - h_0) - T_0(s - s_0) (2)$$

The values of 25  $^{\circ}$ C and 1 bar were taken as reference temperature and pressure. The Szargut et al. reference environment [21] is adopted for chemical exergy calculation. For solutions, chemical exergy is calculated by the following expression:

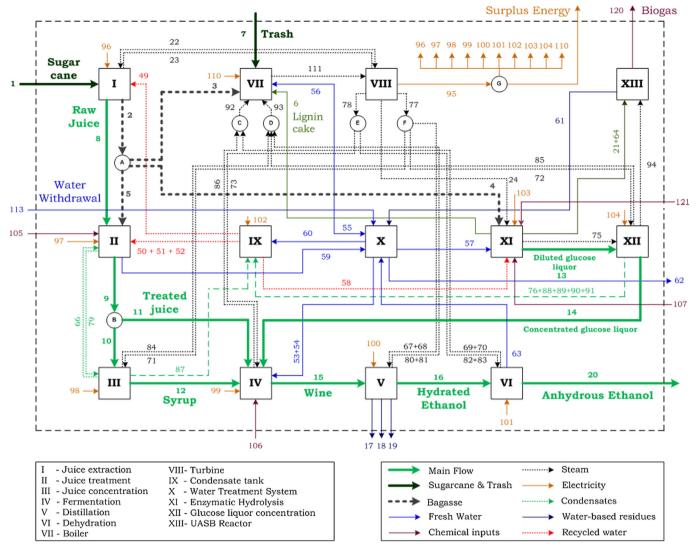
$$e^{CH} = \left(1/\overline{M}_{sol}\right) \left[\sum_{i=1}^{n} y_i \cdot \tilde{\varepsilon}_i^0 + \overline{R} \cdot T_0 \sum_{i=1}^{n} y_i \cdot \ln a_i\right]$$
(3)

In Eq. (3), the first term represents the standard chemical exergy of the pure components [21], and the second one, the exergy destruction from the dissolution process. Exergies of sucrose and glucose solutions were calculated according to Refs. [22,23]. The exergies of ethanol—water solutions, such as hydrated ethanol (stream 16) and anhydrous ethanol (stream 20), were calculated following the procedure reported in Refs. [22,24]. For the purpose of calculating their chemical exergies, wine (stream 15) produced in

fermentation, vinasse (stream 18) and phlegmasse (stream 19) from distillation columns, and pentose liquor (stream 21) obtained by hydrolysis were regarded as ideal solutions, and molar concentration was used instead of activity (Eq. (4)).

$$e^{CH} = \left(1/\overline{M}_{sol}\right) \left[\sum_{i=1}^{n} y_i \cdot \tilde{\varepsilon}_i^0 + \overline{R} \cdot T_0 \sum_{i=1}^{n} y_i \cdot \ln y_i\right]$$
 (4)

This was done because these are very diluted solutions, and activity data for some components are not available in the literature. Moreover, the dissolution exergy fraction is very small in comparison to the standard chemical exergy of the pure components fraction. The standard chemical exergy of pure components was obtained from Szargut et al. [21]. However, data were not available for some components such as aconitic acid ( $C_6H_6O_6$ ), glycerol ( $C_3H_8O_3$ ), furfural ( $C_5H_4O_2$ ), xylose ( $C_5H_{10}O_5$ ), sulfurous acid ( $H_2SO_3$ ), and enzymes.



**Fig. 6.** Flow sheet of ethanol production process – Case EV.

Aconitic acid is found in sugarcane, and glycerol is a by-product of fermentation. Furfural and xylose appear in the pre-treatment of sugarcane bagasse from the hydrolysis of hemicelluloses. It is assumed that sulfurous acid is formed in the pre-treatment reactor from the catalyst SO<sub>2</sub>. Enzymes are biological catalysts of hydrolysis.

For sulfurous acid, standard chemical exergy was calculated using the standard Gibbs free energy of formation [25]. Both its formation from  $SO_2$  and  $H_2O$  and its ionic dissociation were taken into account, according to literature data:

$$SO_{2(aq)} + H_2O \rightarrow HSO_3^- + H^+...k^* = 1.2 \times 10^{-2}$$
 (5)

$$HSO_3^- \to H^+ + SO_3^{-2}...k^* = 6.6 \times 10^{-8}$$
 (6)

In this case, the free energy of reaction can be obtained from equilibrium constants  $k^*$ . For aconitic acid, furfural, glycerol, xylose, and enzymes (since they are a biomass), the standard chemical exergy was calculated according to the technical fuels procedure [21], based on net calorific values and atomic ratios. For the enzymes, the composition (CH<sub>1.57</sub>N<sub>0.29</sub>O<sub>0.31</sub>S<sub>0.007</sub>) was assumed, as per Ref. [18]. Sugarcane bagasse and trash exergies were calculated according to the procedure reported in Refs. [22,26].

#### 3.2. Exergy destruction, exergy losses, and exergetic efficiency

The exergy balance in this section is laid out with the subsequent exergetic cost assessment in mind. In the exergetic analysis carried out in this study, exergetic products (P) and fuels (F), as well exergy destruction (D) and losses (L), are identified in each control volume. The exergy destruction occurs within the system because of irreversible processes, while exergy losses are associated with mass losses; nevertheless, for the process, both are irreversibilities.

Exergy destruction and losses and the exergetic efficiency for each subsystem i were calculated by Eqs. (7) and (8) respectively. Exergetic fuel and product rates of each subsystem are listed in Tables 8–10 for Base Case, Case EV and Case ME respectively.

$$D_i + L_i = F_i - P_i \tag{7}$$

$$\varepsilon = \frac{P_i}{F_i} = 1 - \frac{D_i + L_i}{F_i} \tag{8}$$

For each subsystem, exergy destruction and losses are shown in Table 11, and exergetic efficiencies in Table 12.

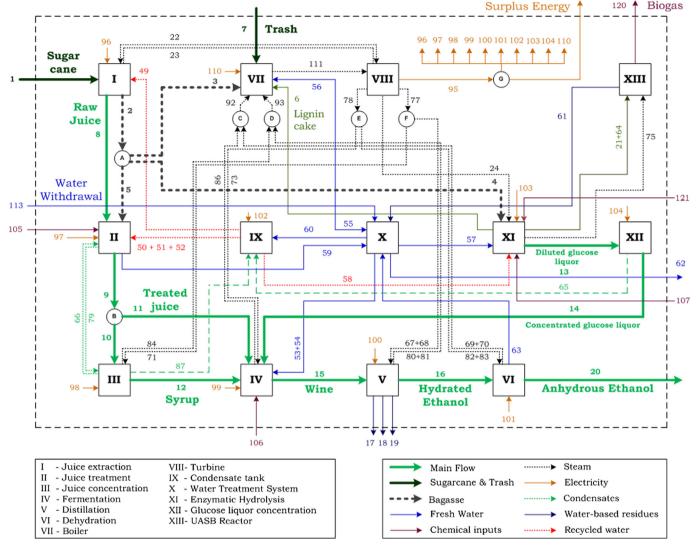


Fig. 7. Flow sheet of ethanol production process — Case ME.

#### 4. Exergetic cost assessment

The methodology used to perform the exergetic cost analysis is the Theory of Exergetic Cost proposed by Lozano and Valero [29]. It was selected because the energy carrier, steam, is produced at the very beginning, and its energy/exergy is used in the subsequent stages of the process. The basis of the theory is the exergetic cost balance equation, applied to each control volume:

$$\sum E_{\rm in}^c = \sum E_{\rm out}^c \tag{9}$$

The exergetic cost of a stream i is defined as:

$$E_i^c = k_i E_i \tag{10}$$

where k is the unitary exergy cost, defined as the amount of exergy resources necessary to produce a unit of the stream exergy,  $E_i$ .

For instance, Eqs. (9) and (10) can be applied to the control volume I (juice extraction in Figs. 5–7).

$$\begin{array}{l} E_1^c + E_{49}^c + E_{96}^c + \left(E_{22}^c + E_{23}^c\right) - E_2^c &= E_8^c \\ k_1 E_1 + k_{49} E_{49} + k_{96} E_{96} + \left(k_{22} E_{22} + k_{23} E_{23}\right) - k_2 E_2 &= k_8 E_8 \end{array}$$

The exergy of streams  $(E_i)$  can be calculated from Table 7 taking into account the mass flow and the specific exergy (ex).

The application of Eq. (9) to all control volumes produces a set of linear equations with more unknowns than equations. In order to obtain a set with a unique solution, additional equations were included as proposed by Lozano and Valero [29]. These equations are presented in the next section.

#### 4.1. First-generation ethanol — Base Case

For the unitary exergy costs of the inputs (sugarcane, trash, freshwater and chemical inputs), a unitary value is assigned. Sugarcane bagasse, a by-product of the extraction system, is assumed to have the same unitary exergy cost of sugarcane:

$$k_2 = k_1 \tag{11}$$

In the distributors (represented by circles in Figs. 5–7), where neither exergy destruction nor losses take place, input and output streams have the same unitary exergetic costs. Thus, Eqs. (12)–(14) are obtained for bagasse, treated juice and electricity, respectively. Steam currents, regarded as having the

**Table 7** Flow description for Figs. 5–7.

Descripti	on	m (kg/s)	T(°C)	P (bar)	Brix (%)	w (%)	ex (kJ/kg)
1	Sugarcane	138.9	25	1	16	_	5762
2	Bagasse produced in extraction system	38.4	30	1	3	_	9979
3	Bagasse for cogeneration	22.4	30	1	3	_	9979
4	Bagasse for hydrolysis	15.3	30	1	3	_	9979
5	Bagasse for filters (fine particles)	0.7	30	1	3	_	9979
6	Lignin cake	6.5	50	1	_	_	10,802
7	Sugarcane trash	10.8	25	1	_	_	15,880
8	Raw juice	140	30	1	15	_	2697
9	Treated juice	141.1	98	1	15	_	2660
10	Treated juice for concentration	41.2	98	1	15	_	2660
11	Treated juice for must preparation	99.9	98	1	15	_	2660
12	Syrup	9.4	59	0.2	65	_	11,424
13	Diluted glucose liquor	105.7	50	1	_	_	480
14	Concentrated glucose liquor	13.8	56	0.2	_	_	3265
15	Wine	158.7	31	1	_	6	2177
16	Hydrated ethanol	10.1	82	1.2	_	94	27,635
17	Second-grade alcohol	0.3	34	1.3	_	91	26,916
18	Vinhasse	136.3	75	1.4	_	_	443
19	Phlegmasse	11.7	104	1.2	_	_	105
20	Anhydrous ethanol	9.5	78	1.2	_	99	29,435
21	Pentoses liquor	130	76 37	1	_	- -	322
22	Steam bleed for extraction system turbines (direct drive)	34.8	290	22	_	_	1058
	· · · · · · · · · · · · · · · · · · ·			2.5	_	_	
23	Exhaust steam of extraction system turbines	34.8	157		_		686
24	Steam bleed for bagasse pre-treatment	8.4	282	12.5	_	_	989
49	Imbibition water	41.7	50	1	_	_	54
50	Water for polymer dilution	2.1	25	1	_	_	50
51	Water for filter cake washing	4.2	80	1.5	_	_	69
52	Water for Ca(OH) <sub>2</sub> dilution	1.1	25	1	_	_	50
53	Water for fermentation gases washing	4	25	1	_	_	50
54	Water for yeast dilution	21.9	29	1	_	_	50
55	Boiler blowdown	12.5	29	1	_	_	50
56	Make-up water for boiler	12.5	29	1	_	_	50
57	Water for pre-treated bagasse washing	123.4	29	1	_	_	50
58	Water for enzymatic hydrolysis of bagasse	103	50	2.5	_	_	54
59	Condensate of filter cake washing	1	69	0.3	_	_	363
60	Water shortfall in condensate tank	28.3	25	1	_	_	50
61	Effluent of UASB reactor	136.2	25	1	_	_	50
62	Make-up water for general uses	103.5	25	1	_	_	50
63	Water recovery from distillation	0.6	61	0.2	_	_	306
64	Water recovery from lignin cake dewatering	5.3	50	1	_	_	908
65	Water separated by membrane	0	50	1.7	_	_	54
66	Vapour bleed for heating juice	20	116	1.7	_	_	616
67	Steam for distillation column	22.1	127	2.5	_	_	668
68	Steam for rectification column	15.1	127	2.5	_	_	668
69	Steam for dehydration column (extractive column)	3.6	159	6	_	_	796
70	Steam for dehydration column (extractive column)	1.3	159	6	_	_	796
	, , ,				_		
71	Steam for juice concentration	23.3	127	2.5	_	_	668
72	Steam for glucose liquor concentration	25.9	127	2.5	_	_	669
73	Steam for must sterilization	8.5	159	6	_	_	796
75	Vapour recovered from bagasse pre-treatment	3.6	101	1	_	_	822
76	Vapour of 5th effect — Glucose liquor concentration system	20.6	56	0.2	_	_	56
77	Steam for process (2.5 bar)	86.4	127	2.5	_	_	668
78	Steam bleed for process (6 bar)	13.4	159	6	_	_	796
79	Condensate of vapour bleeds (evaporation system)	20	115	1.7	_	_	98
80	Condensate of exhaust steam — Distillation column	22.1	127	2.5	_	_	111
81	Condensate of exhaust steam — Rectification column	15.1	127	2.5	_	_	111
82	Condensate of steam bleed — Dehydration column	3.6	159	6	_	_	149
83	Condensate of steam bleed — Recovery column	1.3	159	6	_	_	149
84	Condensate of exhaust steam — Juice concentration	23.3	127	2.5	_	_	111
85	Condensate of exhaust steam — Glucose liquor concentration	25.9	127	2.5	_	_	111
86	Condensate of exhaust steam — Must sterilization	8.5	159	6	_	_	149
87	Condensate of vapour (evaporation system)	31.8	83	0.5	_	_	71
88	Condensate of vapour (evaporation system)  Condensate of vapour 1° effect (glucose liquor)	16.1	115	1.7	_	_	98
89	Condensate of vapour 1° effect (glucose liquor)  Condensate of vapour 2° effect (glucose liquor)	17.3	107	1.7	_	_	90
90	Condensate of vapour 3° effect (glucose liquor)	18.4	98	0.9	_	_	82
	1 (0 1 )				_		
91	Condensate of vapour 3° effect (glucose liquor)	19.5	83	0.5	_	_	71
92	Condensate (6 bar)	13.4	159	6	_	_	149
93	Condensate (2.5 bar)	86.5	127	2.5	_	_	111
94	Condensate of steam bleed (bagasse pre-treatment)	3.6	100	1	_	_	365
105	Calcium oxide	0.1	25	1	_	_	1965
106	Sulphuric acid	0	29	1	_	_	1666
107	Sulfur dioxide	0.3	25	1	_	_	4892
111	Steam generated at boiler (480 $^{\circ}$ C $-$ 67 bar)	110.3	480	67	_	_	1405
113	Water withdrawal	143.3	25	1	_	_	50
120	Biogas	0.924	55	1	_	_	30,233
		0.6	29	1		_	23,730

**Table 8**Definition of the fuel—product matrix: Base Case.

Sub-system		Fuel	Product
I	Juice extraction	$E_1 + E_{49} + E_{96} + (E_{22} - E_{23}) - E_2$	
II	Juice treatment	$E_5 + E_8 + E_{50} + E_{51} + E_{52} - E_{59} + (E_{66} - E_{79}) + E_{97} + E_{105}$	E <sub>9</sub>
III	Juice concentration	$E_{10} + E_{98} + (E_{71} - E_{84}) - (E_{66} - E_{79}) - E_{87}$	E <sub>12</sub>
IV	Fermentation	$E_{11} + E_{12} + E_{14} + (E_{73} - E_{86}) + E_{53} + E_{54} + E_{99} + E_{106}$	E <sub>15</sub>
V	Distillation	$E_{15} + E_{100} + (E_{67} - E_{80}) + (E_{68} - E_{81}) - (E_{17} + E_{18} + E_{19})$	E <sub>16</sub>
VI	Dehydration	$E_{16} - E_{63} + E_{101} + (E_{69} - E_{82}) + (E_{70} - E_{83})$	E <sub>20</sub>
VII	Boiler	$E_3 + E_7 + (E_{56} - E_{55}) + E_{110}$	$E_{111}-(E_{92}+E_{93})$
VIII	Turbine	$E_{111} - (E_{22} - E_{23}) - (E_{77} + E_{78})$	E <sub>95</sub>
IX	Condensate tank	$E_{60} + E_{87} + E_{102}$	$E_{49} + E_{50} + E_{51} + E_{52}$
X	Water treatment system	$E_{55} + E_{59} + E_{63} + E_{113}$	$E_{53} + E_{54} + E_{56} + E_{60} + E_{62}$

**Table 9**Definition of the fuel—product matrix: Case EV.

Sub-s	ystem	Fuel	Product
I	Juice extraction	$E_1 + E_{49} + E_{96} + (E_{22} - E_{23}) - E_2$	E <sub>8</sub>
II	Juice treatment	$E_5 + E_8 + E_{50} + E_{51} + E_{52} - E_{59} + (E_{66} - E_{79}) + E_{97} + E_{105}$	E <sub>9</sub>
III	Juice concentration	$E_{10} + E_{98} + (E_{71} - E_{84}) - (E_{66} - E_{79}) - E_{87}$	E <sub>12</sub>
IV	Fermentation	$E_{11} + E_{12} + E_{14} + (E_{73} - E_{86}) + E_{53} + E_{54} + E_{99} + E_{106}$	E <sub>15</sub>
V	Distillation	$E_{15} + E_{100} + (E_{67} - E_{80}) + (E_{68} - E_{81}) - (E_{17} + E_{18} + E_{19})$	E <sub>16</sub>
VI	Dehydration	$E_{16} - E_{63} + E_{101} + (E_{69} - E_{82}) + (E_{70} - E_{83})$	$E_{20}$
VII	Boiler	$E_3 + E_6 + E_7 + (E_{56} - E_{55}) + E_{110}$	$E_{111}-(E_{92}+E_{93})$
VIII	Turbine	$E_{111} - (E_{22} - E_{23}) - E_{24} - (E_{77} + E_{78})$	E <sub>95</sub>
IX	Condensate tank	$E_{60} + E_{76} + E_{87} + E_{88} + E_{89} + E_{90} + E_{91} + E_{102}$	$E_{49} + E_{50} + E_{51} + E_{52} + E_{58}$
X	Water treatment system	$E_{55} + E_{59} + E_{61} + E_{63} + E_{113}$	$E_{53} + E_{54} + E_{56} + E_{57} + E_{60} + E_{62}$
XI	Enzymatic hydrolysis	$E_4 + E_{57} + E_{58} + (E_{24} - E_{75}) + E_{103} + E_{107} - E_6 - E_{21} - E_{64}$	E <sub>13</sub>
XII	Glucose liquor concentration	$E_{13} + E_{104} + (E_{75} - E_{94}) + (E_{72} - E_{85}) - (E_{76} + E_{88} + E_{89} + E_{90} + E_{91})$	E <sub>14</sub>
XIII	Upflow anaerobic sludge blanket reactor (UASB)	$E_{21} + E_{64} + E_{94} - E_{61}$	$E_{120}$

**Table 10**Definition of the fuel—product matrix: Case ME.

Sub-sys	stem	Fuel	Product
I	Juice extraction	$E_1 + E_{49} + E_{96} + (E_{22} - E_{23}) - E_2$	E <sub>8</sub>
II	Juice treatment	$E_5 + E_8 + E_{50} + E_{51} + E_{52} - E_{59} + (E_{66} - E_{79}) + E_{97} + E_{105}$	E <sub>9</sub>
III	Juice concentration	$E_{10} + E_{98} + (E_{71} - E_{84}) - (E_{66} - E_{79}) - E_{87}$	E <sub>12</sub>
IV	Fermentation	$E_{11} + E_{12} + E_{14} + (E_{73} - E_{86}) + E_{53} + E_{54} + E_{99} + E_{106}$	E <sub>15</sub>
V	Distillation	$E_{15} + E_{100} + (E_{67} - E_{80}) + (E_{68} - E_{81}) - (E_{17} + E_{18} + E_{19})$	E <sub>16</sub>
VI	Dehydration	$E_{16} - E_{63} + E_{101} + (E_{69} - E_{82}) + (E_{70} - E_{83})$	E <sub>20</sub>
VII	Boiler	$E_3 + E_6 + E_7 + (E_{56} - E_{55}) + E_{110}$	$E_{111}-(E_{92}+E_{93})$
VIII	Turbine	$E_{111} - (E_{22} - E_{23}) - E_{24} - (E_{77} + E_{78})$	E <sub>95</sub>
IX	Condensate tank	$E_{60} + E_{65} + E_{87} + E_{102}$	$E_{49} + E_{50} + E_{51} + E_{52} + E_{58}$
X	Water treatment system	$E_{55} + E_{59} + E_{61} + E_{63} + E_{113}$	$E_{53} + E_{54} + E_{56} + E_{57} + E_{60} + E_{62}$
XI	Enzymatic hydrolysis	$E_4 + E_{57} + E_{58} + (E_{24} - E_{75}) + E_{103} + E_{107} - E_6 - E_{21} - E_{64}$	E <sub>13</sub>
XII	Glucose liquor concentration	$E_{13} + E_{104} - E_{65}$	$E_{14}$
XIII	Upflow anaerobic sludge blanket reactor (UASB)	$E_{21} + E_{64} + E_{75} - E_{61}$	$E_{120}$

**Table 11** Exergy destruction and losses (kWh) per liter of ethanol produced.

Sub-sys	stem	Base Case	EV5	EV8	EV10	ME5	ME8	ME10
I	Juice extraction	1.428	1.292	1.271	1.262	1.209	1.224	1.232
II	Juice treatment	0.531	0.484	0.476	0.472	0.453	0.458	0.461
III	Juice concentration	0.106	0.098	0.097	0.096	0.090	0.091	0.092
IV	Fermentation	1.875	1.844	1.858	1.872	1.880	1.885	1.884
V	Distillation	0.461	0.449	0.442	0.441	0.434	0.439	0.409
VI	Dehydration	0.047	0.046	0.046	0.046	0.052	0.052	0.046
VII	Boiler	5.029	7.606	7.109	6.844	6.131	6.218	6.286
VIII	Turbine	0.159	0.283	0.166	0.120	0.220	0.221	0.220
IX	Condensate tank	0.018	0.066	0.050	0.043	0.013	0.018	0.014
X	Water treatment system	0.011	0.010	0.010	0.010	0.009	0.009	0.009
XI	Enzymatic hydrolysis	_	0.602	0.746	0.840	1.067	1.134	1.179
XII	Glucose liquor concentration	_	0.364	0.274	0.232	0.048	0.044	0.050
XIII	Upflow anaerobic sludge blanket reactor (UASB)	_	0.310	0.409	0.466	0.513	0.541	0.558
	Total	9.665	13.453	12.954	12.744	12.120	12.335	12.440

**Table 12** Exergetic efficiencies (%).

Sub-	-system	Base Case (%)	EV5 (%)	EV8 (%)	EV10 (%)	ME5 (%)	ME8 (%)	ME10 (%)
I	Juice extraction	87	87	87	87	87	87	87
II	Juice treatment	95	95	95	95	95	95	95
III	Juice concentration	96	96	96	96	96	96	96
IV	Fermentation	80	81	81	81	81	81	81
V	Distillation	94	93	94	94	94	94	94
VI	Dehydration	99	99	99	99	99	99	99
VII	Boiler	30	30	30	30	30	30	30
VIII	Turbine	82	80	87	91	79	80	80
IX	Condensate tank	79	74	76	77	95	91	92
X	Water treatment system	92	97	98	98	98	98	98
ΧI	Enzymatic hydrolysis	_	66	64	63	65	61	59
XII	Glucose liquor concentration	_	74	82	85	97	97	97
XIII	Upflow anaerobic sludge blanket reactor (UASB)	_	68	68	67	68	68	68

same unitary exergetic cost, are drawn with a discontinuous black line.

$$k_2 = k_3 = k_4 = k_5 \tag{12}$$

$$k_9 = k_{10} = k_{11} \tag{13}$$

$$k_{95} = k_{96} = k_{97} = k_{98} = k_{99} = k_{100} = k_{101} = k_{102} = k_{110} = k_{Wexc}$$
(14)

All energy carriers in the process — steam, condensates and bleed vapour in the juice concentration stage — are assigned the same value of unitary exergy cost, which corresponds to the value of the steam leaving the boiler.

$$k_{71 (vapour)} = k_{66} = k_{79} = k_{87}$$
 (15)

The condensate tank supplies streams composed of condensates and freshwater having the same thermodynamic quality. The same unitary exergy cost is assigned to all the streams.

$$k_{49} = k_{50} = k_{51} = k_{52}$$
 (16)

Distillation by-products such as second-grade alcohol, phlegmasse and vinasse, are special cases. Because second-grade alcohol and hydrous ethanol have similar compositions and thermodynamic properties, their unitary exergetic costs are considered to be equal (Eq. (17)). The unitary costs of vinasse and phlegmasse are set to the same value as the main flow input, the wine (Eq. (18)).

$$k_{16} = k_{17} (17)$$

$$k_{15} = k_{18} = k_{19} \tag{18}$$

Water for the different processes, whether withdrawn or coming from treated effluents, must be of high quality. Thus, both are assigned the same unitary exergetic costs (Eq. (19)).

$$k_{53} = k_{54} = k_{56} = k_{62}$$
 (19)

The water treatment system receives a number of effluents with different thermodynamic qualities. The unitary exergetic cost of the washing filter condensate (stream 59), a by-product of the juice treatment, is assigned the same cost as the raw juice (Eq. (20)). Boiler purge (stream 56) is treated in the water treatment system, and is regarded as having the same quality as the steam (Eq. (21)). Finally, the unitary exergetic cost of water recovered from the dehydration process is the same as that of the hydrous ethanol (Eq. (22)).

$$k_{59} = k_8$$
 (20)

$$k_{56} = k_{111 \ (vapor)} \tag{21}$$

$$k_{63} = k_{16} (22)$$

#### 4.2. First- and second-generation ethanol — Cases EV and ME

All assumptions made for the Base Case are retained for Cases EV and ME. In the enzymatic hydrolysis stage, the exergies of the byproducts dewatered lignin cake and liquor pentoses (streams 6 and 21 respectively, in Figs. 6 and 7) are counted as part of the exergy of unused bagasse, with the same unitary exergetic cost.

$$k_4 = k_6 = k_{21} (23)$$

The effluent from pressing lignin cake (stream 64) is considered to be a co-product from the dewatering process, and its unitary cost is:

$$k_{64} = k_{21} (24)$$

In the condensate tank, the unitary exergetic cost of the water flow (stream 58) for the hydrolysis process is set to the same value as the other products of the process.

$$k_{49} = k_{50} = k_{51} = k_{52} = k_{58}$$
 (25)

In the UASB reactor, the biogas carries all the exergy destruction of the process, and consequently the unitary cost for the effluent (stream 61) is the same as for the principal affluent, the liquor pentoses.

$$k_{61} = k_{21} (26)$$

Water for washing pre-treated bagasse (stream 57) is a coproduct of the water treatment system, and has the same cost as the other streams of that subsystem.

$$k_{57} = k_{53} = k_{54} = k_{56} = k_{62}$$
 (27)

In liquor glucose concentration by evaporation (Case EV), vapour condensates are produced; their exergies are regarded as part of the exergy supplied by the exhaust steam.

$$k_{72 (vapour)} = k_{76} = k_{88} = k_{89} = k_{90} = k_{91}$$
 (28)

In glucose concentration by separation with membranes (Case ME), a by-product stream (65) is obtained, instead of the condensates found in Cases EV. It is composed mainly of water, and it is directed to the condensate tank to minimize external water withdrawal. Its assigned unitary exergetic cost is the same as that of diluted glucose liquor.

$$k_{65} = k_{13} (29)$$

#### 4.3. Exergetic costs

With the inclusion of the equations above, the number of equations equals the number of variables. The system was solved using the EES® software [30]. Results of unitary exergetic costs for the main flows are shown in Table 14.

#### 4.4. Exergetic cost formation

However, obtaining the magnitudes of the exergetic costs of the products and internal flows is not enough to provide a complete picture of the impact of each subsystem on the final product cost.

**Table 13** Global plant exergy efficiencies (%).

Base Case	EV5	EV8	EV10	ME5	ME8	ME10
28.4%	34.7%	35.9%	36.6%	36.6%	36.5%	36.4%

**Table 14** Unitary exergetic cost of main flows.

Flow description	Base Case	EV5	EV8	EV10	ME5	ME8	ME10
Raw juice (8)	1.259	1.265	1.261	1.258	1.255	1.256	1.257
Treated juice (9)	1.393	1.404	1.398	1.393	1.393	1.395	1.395
Syrup (12)	1.486	1.499	1.489	1.482	1.489	1.490	1.491
Wine (15)	1.799	2.114	2.067	2.050	2.073	2.092	2.106
Hydrated ethanol (16)	2.038	2.358	2.307	2.287	2.313	2.332	2.338
Anhydrous ethanol (20)	2.071	2.390	2.339	2.318	2.348	2.368	2.371
Steam	3.320	3.446	3.426	3.383	3.429	3.428	3.435
Electricity	4.066	4.283	3.920	3.738	4.321	4.310	4.313
Reused water (from condensates)	3.580	4.281	4.022	3.834	2.737	2.935	2.941
Treated water from WTS	1.192	1.185	1.178	1.173	1.177	1.177	1.177
Diluted glucose liquor (13)	_	2.694	2.505	2.474	2.641	2.787	2.900
Concentrated glucose liquor (14)	-	3.830	3.195	3.013	2.735	2.880	3.009
Biogas (120)	-	1.597	1.597	1.597	1.591	1.593	1.595

The possibility of disaggregation, provided by the exergetic cost formation method, allows the clarification of these issues.

The TAESS software (Thermoeconomic Analysis of Energy Systems Software) was used to evaluate the unitary exergetic cost formation of the products. The only required inputs were the exergies obtained in Section 3, and the production structure [31].

To illustrate this, the Base Case, Case EV5 and Case ME5 were evaluated. Fig. 8 shows how the unitary exergetic cost of products for the Base Case in each subsystem is formed due to exergy

destruction and losses occurring in the different devices. If all components were ideal, with no exergy destruction or losses, product costs would be equal to one.

The exergy destruction of sugarcane bagasse combustion in the boiler severely penalizes steam production, which carries this malfunction to other subsystems which demand it. Thus, it has the largest impact on all streams and products, especially in power generation, where more than four exergy units of external resources are needed to produce one exergy unit.

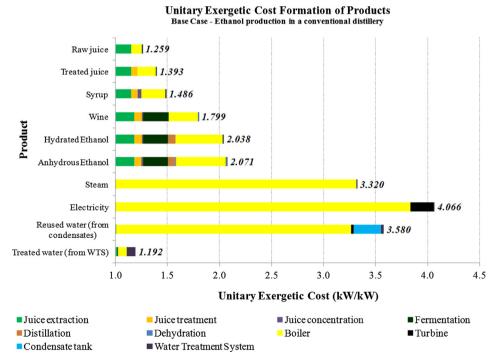
Equating the unitary exergetic costs of sugarcane and bagasse causes the raw juice to carry the malfunction of the juice extraction process to the other products, as indicated by the green segment in the formation costs.

The high cost of producing reused water from condensates is mainly a consequence of regarding vapour condensates as having the same cost as steam generated in the boiler: the former carries the exergy destruction of the steam into the other cost flows.

Fig. 9 shows the unitary exergetic cost formation of products for Case EV5. This case exhibits a general cost increase in comparison with the Base Case, and the main cause is the rise in the amount of steam required for glucose liquor production.

The impact of enzymatic hydrolysis on the unitary exergetic cost of the glucose liquor is evident from this figure. Therefore, a search for better production strategies is recommended, either by alternative pre-treatments or by increasing sugar conversion efficiencies in the hydrolysis stage. Moreover, the process of glucose liquor concentration also affects the cost of the concentrated glucose liquor due to losses occurring during evaporation.

Since pentose liquor is the main inflow of the UASB reactor for biogas production, and since its unitary exergetic cost — similarly to that of bagasse — is equal to one, the cost of biogas is determined primarily by the efficiency of the methanation process of organic matter in the reactor. Additionally, since its liquid effluent is regarded as a by-product with a unitary exergetic cost equal to that of liquor pentoses, it carries no malfunction which might affect the costs of other processes.



**Fig. 8.** Unitary exergetic cost formation of products – Base Case.

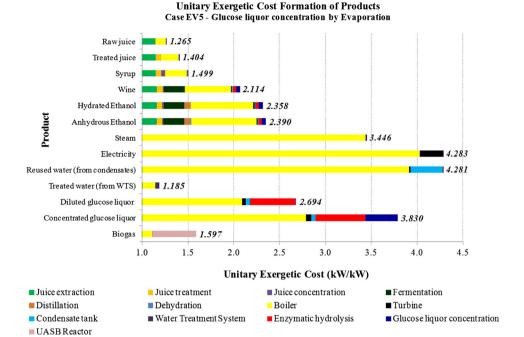


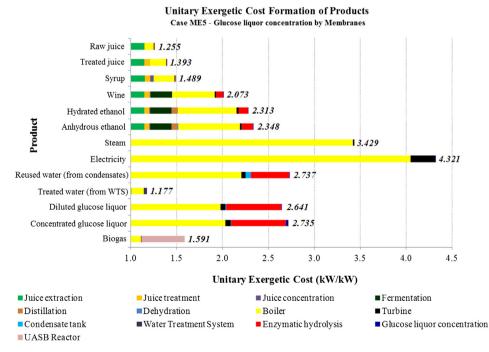
Fig. 9. Unitary exergetic cost formation of products - Case EV5.

Finally, the use of membranes results in important differences in the cost formation of products (Fig. 10). Except for the cost of electricity, all product unitary exergetic costs of the thirteen subsystems for Case ME5 are smaller than those of Case EV5. The main reason for this is the decreased steam production, and the smaller amounts of bagasse used in the boiler, resulting in lower exergy destruction, and therefore a lower steam cost, an effect that propagates to the cost formation of end products of all subsystems.

In the production of concentrated glucose liquor, no steam is needed (in contrast with Case EV5, which is penalized by its steam requirement). The influence of steam is minimal in the unitary exergetic cost formation, as seen in Fig. 10, where it is specifically represented by the size of the blue segment.

#### 5. Results and discussion

From Tables 11 and 12, the boiler was found to be the main location of exergy destruction and losses. The cogeneration system, comprising boiler and turbine, is responsible for more than half of the exergy destruction and losses in all cases; of these,



**Fig. 10.** Unitary exergetic cost formation of products — Case ME5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approximately 96% occur in the boiler, making the malfunction of the combustion process the main source of exergy destruction. Higher exergy destruction in the boiler occurs for Case EV, due to greater volumes of steam required for the glucose liquor concentration stage. The subsystem with the second highest exergy loss is the fermentation process; its inefficiency is caused mainly by the biochemical reactions in the vats, and by heat dissipation due to the exothermic nature of the reactions. Measures to increase fermentation efficiency include better vat temperature control and the adoption of extractive fermentation [27,28]. Despite having a slightly better exergetic performance than the fermentation, juice extraction also destroys large amounts of exergy. This is mainly related to the loss of sucrose, and the high power consumption in cane preparation and milling equipment driven by low efficiency steam turbines. Possible paths to reduce those losses could be the use of diffusers to increase sugar recovery, and the replacement of steam turbines by electric motors. The exergy destruction and losses caused by the introduction of the enzymatic hydrolysis of bagasse represent a significant fraction of the total when the enzymes exergy is included in the calculation. Combined, enzymatic hydrolysis and glucose liquor concentration represent approximately 7–10% of the total. The higher exergy destruction and losses in enzymatic hydrolysis found in cases ME are due to the high enzyme consumption and the increased amount of bagasse to be hydrolyzed, which, if not burned in the boiler to produce excess steam, is directed to hydrolysis to increase ethanol production. Moreover, the low efficiency of the hydrolysis process is associated to the pre-treatment of bagasse and the reactions occurring in the reactors, where sugar recovery by enzymatic attack is not complete. As seen in Table 12, the exergetic efficiency of enzymatic hydrolysis is one of the lowest, varying from 59% to 66%. Possible improvements should be contemplated, such as the use of other bagasse pre-treatment routes, as well as measures to increase the efficiency of the hydrolysis process. Superior performances in resource management for the overall plant were achieved in the integrated process, as shown in Table 13, because it offers a third major product – biogas – in addition to ethanol and surplus electricity produced by the conventional process.

These results can be compared with others in the literature. Ojeda et al. [8] studied ethanol production by enzymatic hydrolysis of sugarcane bagasse (without integration with the conventional process). These authors adopted an acid-catalyzed steam explosion pre-treatment, pentose fermentation, SSF (simultaneous saccharification and fermentation) for cellulose, distillation and rectification, and molecular sieves for anhydrous ethanol production. The reported exergetic efficiencies were 87.5% for pre-treatment, 65% for pentose fermentation, 48% for SSF and 68.2% for purification (distillation and dehydration). Velazquez Arredondo et al. [11] also performed an exergetic evaluation of liquid biofuels using different raw materials. For flower stalks of banana brunch, these authors reported exergetic efficiencies of 20.3% and 75.3% for the stages of enzymatic hydrolysis and fermentation respectively.

Regarding exergetic costs, the main indication provided by Table 14 is that integrating bagasse enzymatic hydrolysis into a conventional plant leads to increases from 12% to 15% in the unitary exergetic cost of anhydrous ethanol when compared with the Base Case. The highest increase was observed in Case EV5 (15.5%); it is associated to the larger amounts of steam necessary for glucose liquor concentration. The second highest increase was observed in Case ME10 (14.5%); it is linked to the larger amounts of bagasse for hydrolysis and enzymes used in this case. The lowest increase was that of Case EV10 (12%).

These results are primarily a consequence of exergy destruction and losses associated with enzymatic hydrolysis and the glucose liquor concentration process, which are carried into the next process via the glucose liquor. Furthermore, the increase in the unitary exergetic costs of steam and electricity is related to the rise of mass flows of steam generated in the boiler to meet the thermal needs of the plant. The increased thermal needs result from the concentration of the diluted glucose liquor, and from the distillation and dehydration columns, since there is an increase in the amount of anhydrous ethanol produced.

#### 6. Conclusions

This study conducted an assessment of the exergy and exergetic cost associated with the ethanol production process from sugarcane biomass, including the route of bagasse enzymatic hydrolysis.

Exergy destruction and losses caused by the introduction of bagasse enzymatic hydrolysis represent a significant portion — between 7 and 10% — of the total exergy destruction and losses of the process as a whole.

Regarding the calculation of exergetic efficiencies, whereas in the conventional process anhydrous ethanol and electricity surplus are adopted as the major products, in the process including hydrolysis, biogas is regarded as an additional product. Results show that in spite of the increase in the exergetic cost of the main products, the global exergetic efficiency (i.e., for the system as a whole) is higher for the integrated plant in comparison with the conventional plant, reaching 36.6% in the Best Case, compared to 28.4% for the Base Case.

Unitary exergetic costs of the final products are higher for cases integrating first- and second-generation ethanol production. For instance, anhydrous ethanol had increases of 12% and 14.5% for the cases of glucose concentration by a multiple-effect evaporation system (Case EV10) and a membrane separation system (Case ME10), respectively, in comparison with the conventional process (Base Case). These higher values of exergetic cost are not surprising in view of the increased complexity of the production process.

Considering the process as a whole, it was found that the introduction of the second-generation production process brought about an increase of production and a higher global exergetic efficiency.

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