

COMPARED EXERGY ANALYSIS OF SEQUENTIAL ENZYMATIC HYDROLYSIS - FERMENTATION AND SIMULTANEOUS SACCHARIFICATION – FERMENTATION OF SUGARCANE BAGASSE

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ABSTRACT

This paper presents the compared exergy analysis of the enzymatic hydrolysis of sugarcane bagasse through Sequential Hydrolysis and Fermentation (SHF) and Simultaneous Saccharification and Fermentation (SSF) configurations in order to get lignocellulosic ethanol. Hydrolysis is a process step in a biochemical route of ethanol production by biomass-sugar conversion.

The exergy analysis of several pretreatment processes was considered. The selected pretreatment technologies were: Steam Explosion SE (Cases 1 and 2), Organosolv (Cases 3 and 4), Liquid Hot Water LHW (Cases 5 and 6), and a combined SE and LHW method (Cases 7 and 8). The pretreatments analyzed simultaneously with the SHF (Cases 1, 3, 5 and 7) and SSF (Cases 2, 4, 6 and 8) configurations were carried out for the overall system. Processes simulations were performed by using Aspen Plus[®] software to a plant with 500 t/h milling capacity.

The results for SHF configurations in terms of exergy efficiency rate were 60.0% for case 1, 56.5% for case 3, 58.3% for case 5 and 59.7% for case 7. However, using the SSF configurations, the exergy efficiency obtained in case 2, case 4, case 6 and case 8 were 62.4%, 58.3%, 60.7% and 61.8%, respectively. These results show the variation of pretreated bagasse constituents and the ranges of exergy efficiency for each hydrolysis configuration highlighting the relevance of such processes in the overall performance of second-generation bioethanol production routes.

INTRODUCTION

Bioethanol converted from lignocellulosic feedstock, such as sugarcane, is considered one of the technological routes to be developed in the biofuels industry. The use of bioethanol as an alternative fuel has become more popular recently due to the high prices and environmental problems associated with fossil fuels (Wirawan et al., 2012). Therefore, second-generation biofuels produced from lignocellulosic feedstock should be promoted. For instance, the agreement implemented by the Policy Energy Act (PEA) followed by the Energy Independence and Security Act (EISA) aims to reach 36 billion gallons (136.27 billion liters) of bioethanol by the year 2022 (Limayem and Ricke, 2012).

The main stages of the bioethanol (cellulosic) production process are pretreatment, hydrolysis, fermentation, distillation, and further fuel upgrading. Lignocellulose must thus be pretreated before it can be converted to bioethanol. In this stage, the lignocellulose can either be pretreated by acid or base, depending on the desired type of sugar.

After the pretreatment stage, the lignocellulose can be hydrolyzed to produce sugars. There are at least three methods of enzymatic hydrolysis, including dilute acid hydrolysis, concentrated acid hydrolysis, and enzymatic hydrolysis. Nowadays, the prevalent technique for bioethanol production is an enzyme-based process because it gives higher hydrolysis yield than acid hydrolysis (Zheng et al., 2009). It is worth noting that the pretreatment and hydrolysis steps have been highlighted as the most costly stages in the bioprocessing of lignocellulosic materials (Modenbach and Nokes, 2013). For example, pretreatment as a first step is the most costly operation and accounts for approximately 33% of the total cost with respect to the economic feasibility of each step (Limayem and Ricke, 2012).

In this paper, a performance comparison in terms of exergy efficiency and destroyed exergy rate of the cases studied is summarized in Fig.1. Based on the outcomes, the impact of SHF and SSF configurations on the average exergy efficiency of the ethanol production is discussed.

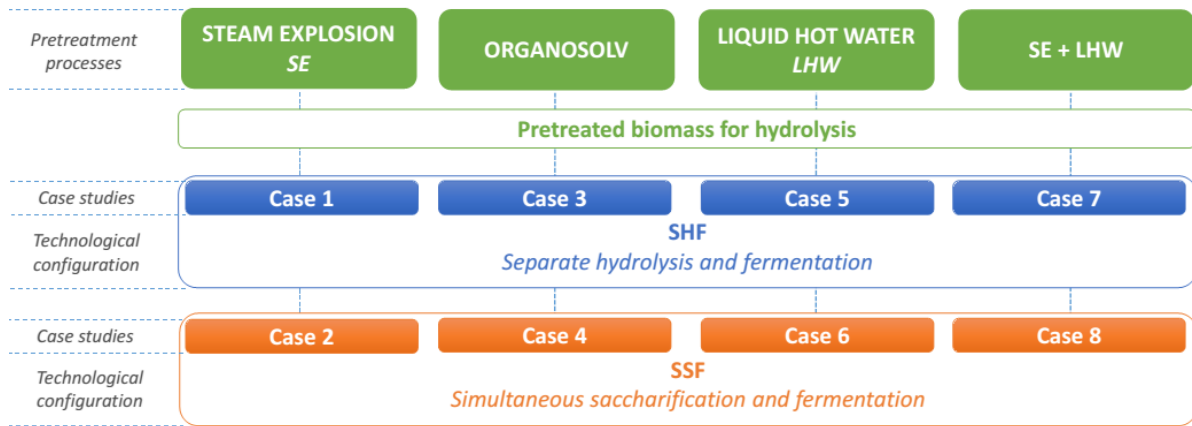


Fig.1. Description of the evaluated case studies

SECOND-GENERATION BIOETHANOL PRODUCTION

Lignocellulosic Biomass

Lignocellulosic biomass is considered an attractive feedstock of ethanol production because of its availability in large quantities, at low cost, and its reduced competition with food but not necessarily with feed (Cheng et al., 2008), and taking into account that the raw material constitutes about 40-70% of the production cost (Quintero et al., 2008).

In general, prospective lignocellulosic materials for bioethanol production can be divided into six main groups: *crop residues* (sugarcane bagasse, corn stover, wheat straw, rice straw, rice hulls, barley straw, sweet sorghum bagasse, olive stones, and pulp), *hardwood* (aspen, poplar), *softwood* (pine, spruce), *cellulose wastes* (newsprint, waste office paper, recycled paper sludge), *herbaceous biomass* (alfalfa hay, switchgrass, reed canary grass, timothy grass, miscanthus grass), and *municipal solid wastes* (Pandey et al., 2011).

Process Configurations - Saccharification and fermentation route

The conventional technologies employed for fermenting biomass hydrolysates involves a sequential process in which the hydrolysis of cellulose and the fermentation are carried out in different units. This configuration is known as separate hydrolysis and fermentation (SHF). Alternatively, the enzymatic treatment can be accomplished simultaneously with the engineered fermentation process; it is recognized as simultaneous saccharification and fermentation (SSF), in which hydrolysis and fermentation are performed in a single unit. The most employed microorganism in corn-based and sugar-based biofuel industries for fermenting lignocellulosic hydrolysates is *Saccharomyces cerevisiae* (*S. cerevisiae*). This yeast ferments the hexoses contained in the hydrolysate but not the pentoses. *S. cerevisiae* can generate a high yield of ethanol (12.0-17.0% w/v; 90% of the theoretical value) from hexose sugars (Limayem and Ricke, 2012). Another technological alternative is the integration of the pentose fermentation in the process. This route is known as simultaneous saccharification and co-fermentation (SSCF). A scheme of bioethanol production processes from lignocellulosic biomass is given in Fig. 2.

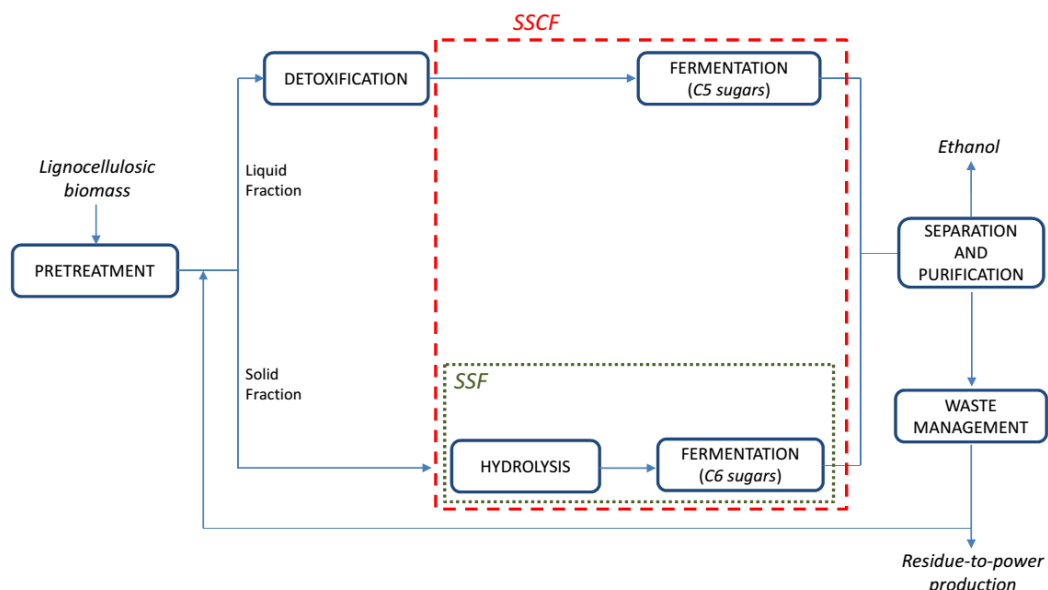


Fig.2. Configurations of processes of bioethanol production from sugarcane bagasse

Separate (or sequential) hydrolysis and fermentation (SHF)

When the SHF process is used, the solid fraction of pretreated lignocellulosic material undergoes hydrolysis (saccharification). This fraction contains the cellulose in an accessible form to acids or enzymes. Once hydrolysis is completed, the resulting cellulose hydrolysate is fermented and converted into ethanol. One of the main features of the SHF process is that each step can be performed at its optimal operating conditions. The most important factors to consider for the saccharification step are reaction time, temperature, pH, enzyme dosage, and substrate load.

Testing of lignocellulosic biomass from sugarcane leaves have found the best values of all these parameters and 65–70% cellulose conversion was achieved at 50°C and a pH of 4.5. Although enzyme doses of 100 FPU/g cellulose resulted in close to 100% hydrolysis, this amount of cellulases is not economically justifiable. Hence, 40 FPU/g cellulose dosage was proposed obtaining only 13% reduction in conversion. Regarding the substrate concentration, solids loads of 10% were defined as the most adequate considering arising mixing difficulties and accumulation of inhibitors in the reactive medium (Sánchez and Cardona, 2008).

Simultaneous saccharification and fermentation (SSF)

The SSF process reducing sugars produced in cellulose hydrolysis are simultaneously fermented to ethanol which greatly reduces the product inhibition to the hydrolysis. This process shows more attractive indexes than SHF, such as higher ethanol yields and less energy consumption. In this case, the cellulase enzymes and microorganisms are added to the same process unit allowing the glucose formed during the enzymatic hydrolysis of cellulose to be immediately consumed by the microbial cells converting it into ethanol.

However, the need of employing more dilute media to reach suitable rheological properties makes the final product concentration be low. In addition, this process operates at non-optimal conditions for hydrolysis and requires higher enzyme dosage, which influences substrate conversion positively but process costs negatively. Considering that enzymes account for an important share of production costs, it is necessary to find methods to reduce the cellulases doses to be utilized (Sánchez and Cardona, 2008).

Simultaneous saccharification and co-fermentation (SSCF)

Another technological alternative is the integration of the pentose fermentation (C5 sugars) in the SSF. This process is called simultaneous saccharification and co-fermentation (SSCF). This configuration is accomplished by combining the enzymatic hydrolysis of cellulose to the glucose process and the co-fermentation of pentose and hexose sugars process in one reaction vessel. Both fermenting microorganisms have to be compatible in terms of operating pH and temperature. This reduces the number of reactors involved by eliminating the separate hydrolysis reactor and avoids the problem of product inhibition associated with enzymes (Hamelinck et al., 2005).

Some drawbacks of this configuration are the high byproduct formation in the form of CO₂ and xylitol, poor enzyme stability, incompatible pH and temperature (pH of 7.0 and 70°C for the isomerization process), and the reversibility of the enzyme transformation (Sánchez and Cardona, 2008).

A process challenge in the biotechnological conversion of lignocellulosic material in these technological pathways is the efficient conversion of all sugars (C5 and C6) to bioethanol, especially for hardwoods feedstock which have greater amounts of pentoses (Pandey et al., 2011).

DESCRIPTION OF PROCESSES

In this work, four pretreatment processes for sugarcane bagasse and two bioethanol production configurations (SHF and SSF) were simulated, using Aspen Plus® to a plant with 500 t/h milling capacity considering steady-state conditions for all cases. Process simulations to evaluate mass, energy and exergy balances were performed. Regarding convergence in simulation, the Wegstein method was used by the simulator (default method in Aspen Plus®) to carry out mass and energy balances in each operation.

Eight case studies combined SHF and SSF configurations with the following pretreatment technologies are studied: Steam Explosion SE, Organosolv, Liquid Hot Water LHW and SE+LHW. These processes are the most used as pretreatment methods when sugarcane bagasse is the feedstock (Hamelinck et al., 2005), (Carrasco et al., 2010), (Dias et al., 2012).

It must be pointed out that enzymatic hydrolysis is usually catalyzed by cellulase enzymes and the fermentation is carried out by yeast or bacteria. Cellobiose and glucose are known to inhibit the activities of cellulase enzymes even at low concentrations. When SHF is performed, enzymatic hydrolysis and fermentation are run in two different vessels. In this process, each step can be conducted at optimal conditions of pH and temperature. However, glucose and cellobiose accumulation in the hydrolysis step inhibits the activity of the cellulose enzymes.

In a SSF process, the enzymatic hydrolysis and fermentation are run in the same vessel. Thus glucose released by the action of cellulose enzymes is converted directly to ethanol by the fermenting microorganism and this continuous removal of glucose from the medium minimizes the end-product inhibition on enzyme activity (Ojeda et al., 2011b).

Raw material

For all cases, the sugarcane bagasse is the feedstock considered in the simulations performed. This lignocellulosic material is assumed to have the following typical chemical normalized composition (w/w): cellulose 43.38%, hemicellulose 25.63%, lignin 23.24%, ash 2.94%, and extractives 4.81%. The extractives were represented as organic acids. These components were inserted in the simulator with molecular formula $C_6H_6O_6$. The moisture content of the bagasse produced in the mills was set as 50%.

This average composition is reported in (Rocha et al., 2010), in which 50 samples of bagasse from mills located in different parts of Brazil and at different times were measured. The properties of the components of the lignocellulosic material were obtained from the databank for biofuel components developed by NREL (Wooley and Putsche, 1996).

Reactor models

Stoichiometric reactors (RStoic model) were used in the simulator to represent the reactions involved in the hydrolysis–saccharification (R-HYDRO) and fermentation processes (R-FERM). Table 1 shows the reactions and conversion yields considering 10% of solids content in the hydrolysis reactor, according to NREL (Humbird et al., 2011). Furthermore, this table indicates the formation of the main components in the reactors.

Table 1. Saccharification-fermentation reactions and conversion rates.

Reactions	Yield Conversion (%)
Saccharification	
CELLULOSE ($C_6H_{10}O_5$) + WATER (H_2O) → GLUCOSE ($C_6H_{12}O_6$)	55.8
HEMICELLULOSE ($C_5H_8O_4$) + WATER (H_2O) → XYLOSE ($C_5H_{10}O_5$)	40.6
Fermentation	
GLUCOSE ($C_6H_{12}O_6$) → 2 ETHANOL (C_2H_6O) + 2 CO_2	90
GLUCOSE ($C_6H_{12}O_6$) + 2 WATER (H_2O) → 2 GLYCEROL ($C_3H_8O_3$) + O_2	0.4
GLUCOSE ($C_6H_{12}O_6$) + 2 CO_2 → 2 SUCCINIC ACID ($C_4H_6O_4$) + O_2	0.6
3 XYLOSE ($C_5H_{10}O_5$) → 5 ETHANOL (C_2H_6O) + 5 CO_2	80
3 XYLOSE + 5 CO_2 → 5 ACETIC ACID ($C_2H_4O_2$) + 2.5 O_2	0.9

Table 2 provides the operating conditions defined for the SHF and SSF processes. For each configuration, water was added in order to remove xylose and inhibitors components, as well as to adjust the concentration of water-insoluble solids in the hydrolysis reactor. The water evaluated for the washing step (H2O-WASH) was 123.4 kg/s, at a temperature of 25°C and a pressure of 1.01325 bar; these were adopted as input parameters in the simulations. Meanwhile, the operating conditions defined for water of the enzymatic hydrolysis of bagasse (H2O-HYD) was 103 kg/s, at a temperature of 25°C and a pressure of 2.5 bar, according to the operational parameters of the integrated 1G and 2G ethanol production from sugarcane reported by (Palacios-Bereche et al., 2013).

Additionally, cellulase enzyme in the reactors as bioagent was adopted, according to the processes analyzed, as per (Ojeda et al., 2011b). For the simulations, an average value of 0.114 g enzyme/g dry pre-treated pulp was considered (Carrasco et al., 2010).

Table 2. Saccharification-fermentation operational conditions.

Parameter	SHF	SSF
Cellulase Enzyme	15 FPU/g	15 FPU/g
Pressure	101.325 kPa	101.325 kPa
Temperature	321 K	308 K
Bioagent	S. cerevisiae	S. cerevisiae

In each case analyzed, the pretreated biomass was sent to SHF (Fig. 3) and SSF (Fig. 4) configuration, respectively. Initially, the mixture composed of the pretreated bagasse and the washing water, B-PRET stream, goes through a separated unit (SEPA-PE) to split the liquid fraction (PEN-LIQ) xylose liquor (pentose) from the solid fraction of cellulose and lignin (CEL-LIG). In this study, the use of xylose liquor was not considered.

For the next stage, water is added to the process (stream H2O-HYD) in tank T-MIST, to achieve an appropriate concentration of water insoluble solids in the hydrolysis reactor. In the next step, stream CEL-LIG2 goes to the hydrolysis reactor (R-HYDRO), where enzymes are added to catalyze the simultaneous reactions involved in this process. After the hydrolysis stage in both models, the hydrolysate goes through a filter in order to separate the lignin cake (solid fraction) from the glucose liquor (GLU-LIQ).

Before the glucose liquor can proceed to fermentation, it needs to be concentrated. This process takes place in a multiple-effect evaporation system. The hierarchy model (CONC) was performed in Aspen Plus® to represent this process. At first, the hydrolysate (GLU-LIQ) is preheated before entering the evaporation system, which operates with exhaust steam at 2.5 bar. A five-stage evaporation system was assumed to reduce the steam consumption. Each stage of the evaporation system was considered to have two unit operations, a heat exchanger and a flash separator. The evaluated steam flow (STEAM-EV) was 25.9 kg/s, a temperature of 127°C and a pressure of 2.5 bar based on (Palacios-Bereche et al., 2013). The products obtained from the CONC model were juice vapor (JUICEVAP) condensates of exhaust steam (CONDESA) and glucose hydrolysate (HYD-GLU).

It must be pointed out that due to the possible presence of soluble lignin in glucose hydrolysate, as well as phenolic groups, the HYD-GLU steam is prepared via detoxification before performing the fermentation process (R-FERM). In this study, fermentation was based on the Melle-Boinot process (cell-recycle batch) to ferment the xylose.

In a conventional autonomous distillery, vapor bleedings and condensates with different pressures and temperatures resulting from the concentration of the glucose process are used in the evaporation system and as input of other processes. Table 3 provides an overview of the parameters evaluated in the multiple-effect evaporation system.

Table 3. Specifications of the Concentration - Evaporation system.

Parameter	Value
Pressure 1st effect, bar	1.69
Pressure 2nd effect, bar	1.31
Pressure 3rd effect, bar	0.93
Pressure 4th effect, bar	0.54
Pressure 5th effect, bar	0.16
Solid content in concentrate hydrolysate, %	19

Fig. 3 shows the schematic representation of the SHF process. This configuration is divided into two reactors. The first one represents the hydrolysis reactor (R-HYDRO) and the second one the sugars fermentation.

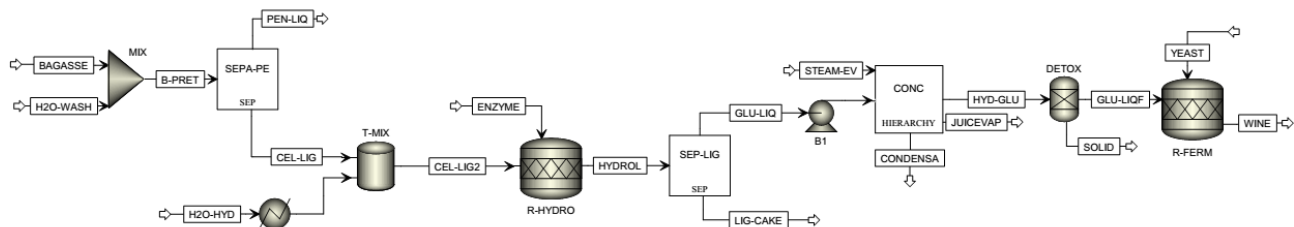


Fig.3. Flow sheet of the SHF process configuration

A scheme of SSF configuration on Aspen Plus® software is given in Fig. 4, where saccharification (hydrolysis) and fermentation processes occur simultaneously in the reactor (R-HYDFER).

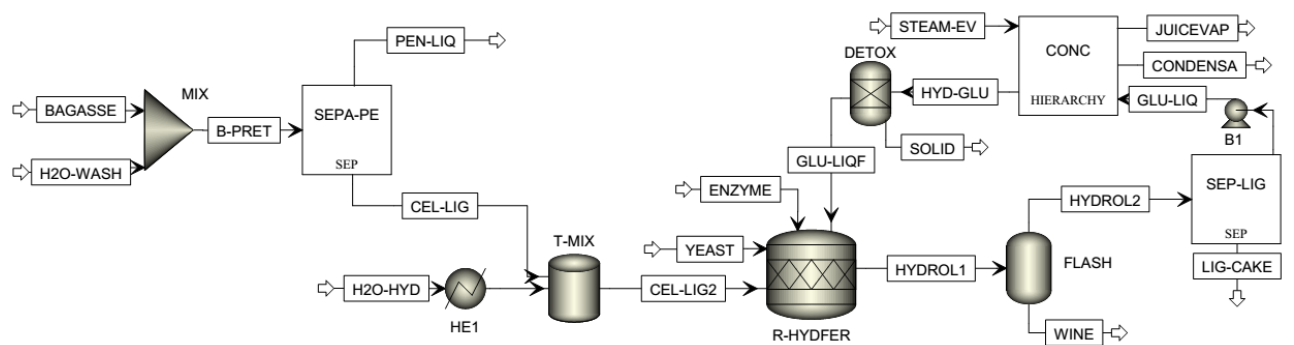


Fig.4. Flow sheet of the SSF process configuration

EXERGY ANALYSIS

The exergy analysis method consists in using the First and Second laws of Thermodynamics together for furthering the goal of more effective energy resource use, for it allows the location, cause, and true magnitude of waste and loss to be determined. Such information can be used in the design of new energy efficient systems and for increasing the efficiency of existing systems (Bejan, 1996).

The exergy analysis was carried on to develop the procedure based on the methodology proposed in (Silva-Ortiz and Oliveira Jr, 2013). In this sense, a Microsoft Excel[®] tool has been developed to perform the exergy analysis for the proposed routes. This application is needed because Aspen Plus[®] does not have an integrated function to calculate the exergy of each stream presented in the processes, or to evaluate thermoeconomic costs, although it gives enough thermodynamic data and can also estimate capital costs. In order to calculate the exergy of matter streams, some authors have approached it in several ways, including Fortran subroutines (Mosqueira-Salazar et al., 2013, Palacios-Bereche et al., 2013), compiled applications within the Aspen Plus[®] interface (Ojeda et al., 2011a, Ojeda et al., 2011b), a Microsoft Excel[®] VBA supplement (Querol et al., 2011) or hand-made calculations.

The systematic procedure involved in the assessment of SHF and SSF processes via exergy analysis is shown in Fig. 5.

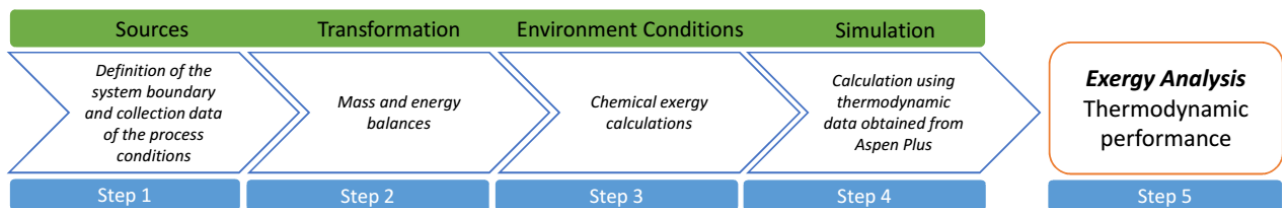


Fig.5. Procedure for exergy analysis of SHF and SSF configurations

Different process configurations have been investigated to apply and to develop an efficient conversion process for second-generation ethanol production (Dias et al., 2013; Dias et al., 2012; Quintero and Cardona, 2011; Sánchez and Cardona, 2012).

For the routes proposed, thermodynamic data of the streams and substances present in the processes are necessary. The exergy analysis throughout this work was conducted in Aspen Plus[®], using the data from the different matter streams: mass flow rate, temperature, pressure and composition. The enthalpy and entropy of the streams with the same composition are also obtained, considering that they are at ambient temperature and pressure. Thus, a conventional reference environment is established, at $T_0=298.15$ K (25°C) and $p_0=1$ atm (1.013 bar), since most of the thermodynamic properties are tabulated at T_0 , p_0 .

The chemical exergies of pure components were obtained from (Szargut et al., 1988) and (Ojeda et al., 2011b). 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), yeast ($CH_{1.8}O_{0.9}N_{0.1}$) and enzymes ($CH_{1.57}N_{0.29}O_{0.31}S_{0.007}$). Aconitic acid is found in sugarcane, and glycerol is a by-product of fermentation. Furfural and xylose appear in the pretreatment of sugarcane bagasse from the hydrolysis of hemicelluloses.

For sulfurous acid, standard chemical exergy was evaluated based on (Palacios-Bereche et al., 2013). For aconitic acid, furfural, glycerol, xylose, yeast and enzymes, the standard chemical exergy was calculated according to the technical fuels procedure (Szargut et al., 1988), based on net calorific values and atomic ratios. For the cellulase enzyme, the composition was assumed, as per (Wooley and Putsche, 1996). The chemical exergies of the substances involved in the processes are listed in Table 4.

Table 4. Specific chemical exergy of the substances studied in the processes.

Formula	Substance	Component ID Aspen Plus®	b _{CH} specific kJ/kg
C ₆ H ₁₀ O ₅	CELLULOSE	CELU	18,875
C ₅ H ₈ O ₄	HEMICELLULOSE	HEMI	19,177
C _{7.3} H _{13.9} O _{1.3}	LIGNIN	LIGN	37,133
C ₁₂ H ₂₂ O ₁₁	SUCROSE	C12H22O11	18,185
C ₆ H ₁₂ O ₆	GLUCOSE	C6H12-01	17,583
K ₂ O	POTASSIUM OXIDE	K2O	4395
KCL	POTASSIUM CHLORIDE	KCL	261
H ₂ O	WATER (L)	H2O	50
SiO ₂	SILICON DIOXIDE	SiO2	59*
C ₅ H ₁₀ O ₅	XYLOSE	C5H10-01	17,583
C ₅ H ₄ O ₂	FURFURAL	C5H4O-01	24,437
H ₂ SO ₃	SULFUROUS ACID	H2SO3	3,962
CH _{1.57} N _{0.29} O _{0.31} S _{0.007}	ENZYME	ENZYME	24,967
CH _{1.8} O _{0.9} N _{0.1}	YEAST	YEAST	17,350
C ₂ H ₆ O	ETHANOL	C2H6O-2	29,471
CO ₂	CARBON DIOXIDE	CO2	451
C ₄ H ₆ O ₄	SUCCINIC ACID	C4H6O-01	15,949
C ₂ H ₄ O ₂	ACETIC ACID	C2H4O-01	17,583
C ₅ H ₁₂ O	AMYL ALCOHOL	C5H12O-03	38,389
C ₃ H ₈ O ₃	GLYCEROL	C3H8O-01	19,667
NH ₃	AMMONIA	NH3	19,876
C ₆ H ₆ O ₆	ORGANIC ACIDS	C6H6O-01	14,275

*To determine the specific chemical exergy of SiO₂ a content of amorphous material of 25% was considered. Besides that, the proportions of cristobalite and quartz were assumed to have 16% and 59% (in mass), according to the parameters for sugarcane bagasse ash reported in Cordeiro et al., 2008.

RESULTS AND DISCUSSION

Exergy analysis is fundamental for accounting both for materials use and waste residuals. Irreversibility rate represents the loss of quality of the energy conversion process. In the exergy analysis performed in this paper, the entropy generation (destroyed exergy rate) and the exergy efficiency were calculated for each case establishing a relationship between them seeking to improve the configurations efficiency and sustainability.

Tables 5 to 8 show the values of some parameters used in the evaluation of the SHF and SSF technologies. Results show that all cases of separate saccharification and fermentation SHF configuration have the lowest exergy efficiencies. One of the main reasons for these irreversibilities is the inhibition effect of glucose and cellobiose accumulation in the SHF reactor. Hence, the inhibitor substantially reduces the enzyme velocity at low substrate concentrations reducing the exergy efficiency of the processes.

These results also suggest some improvements in wine production processes via enzymatic technology, SHF and SSF configurations, using pretreated bagasse. It is evident that wine production for cases studied are a function of the mass flow inlet of pretreated sugarcane bagasse as illustrated in Tab. 6 for cases 3 and 4.

A sensitivity analysis for the cases studied was performed, varying the mass flow rate of the enzyme in order to evaluate their impact on wine production. The results show that it does not represent a significant fraction (less than 2%) for increasing the total wine production for all cases. For this reason, mass flow rate of the enzyme was fixed in the configurations. In fact, the cost of enzymes is one of the most important challenges in cellulosic ethanol production. Thus, technological pathways proposed in this matter have addressed concerns to achieve the rational use of resources, especially with regard to the identification of optimal dosages for the enzymes.

Furthermore, cases 1 and 2 represent the best option regarding the production of xylose liquor (pentose). This product can be used as a main input for an upflow anaerobic sludge blanket reactor to produce biogas from the organic matter present in it.

Table 5. Inlet and outlet parameters of mass flow rates of cases 1 and 2

Parameter	Streams	Configuration	Mass Flow (kg/s)	T(K)	P(kPa)	b(kJ/kg)	b _{tot} (kW)
<i>Inlets</i>	PRETREATED BAGASSE	SHF, SSF	16.94	298.15	101,325	10,570	179,056
	ENZYME	SHF, SSF	0.60	302.15	101,325	23,730	14,238
	H2O-HYD	SHF, SSF	135.15	323.15	250	54.3	7,339
	H2O-WASH	SHF, SSF	161.92	298.15	101,325	50	8,096
	STEAM-EV	SHF, SSF	33.98	400.15	250	110.3	3,748
	YEAST	SHF, SSF	3.54	304.15	101,325	1,177	4,167
<i>Outlets</i>	LIG-CAKE	SHF	11.14	323.15	101,325	1,226	13,658
		SSF	15.14			1,072	16,230
	PEN-LIQ	SHF	120.58	310.15	101,325	138	16,640
		SSF	121.46			140	17,004
	SOLID	SHF	3.91	323.15	101,325	1,298	5,075
		SSF	5.71			1,135	6,481
	WINE	SHF	124.39	304.15	101,325	706	87,819
		SSF	126.15			708	89,314
	CONDENSA	SHF	30.90	400.15	250	110.3	3,408
		SSF	29.90			110.3	3,298
	JUICEVAP	SHF	61.22	329.15	50	56.3	3,447
		SSF	53.78			56.3	3,028

Table 6. Inlet and outlet parameters of mass flow rates of cases 3 and 4

Parameter	Streams	Configuration	Mass Flow (kg/s)	T(K)	P(kPa)	b(kJ/kg)	b _{tot} (kW)
<i>Inlets</i>	PRETREATED BAGASSE	SHF, SSF	21.97	298.15	101.325	10,570	232,223
	ENZYME	SHF, SSF	0.60	302.15	101.325	23,730	14,238
	H2O-HYD	SHF, SSF	175.28	323.15	250	54.3	9,518
	H2O-WASH	SHF, SSF	210	298.15	101.325	50	10,500
	STEAM-EV	SHF, SSF	44.08	400.15	250	110.3	4,862
	YEAST	SHF, SSF	3.54	304.15	101.325	1,177	4,167
<i>Outlets</i>	LIG-CAKE	SHF	14.39	323.15	101.325	1,015	14,606
		SSF	13.39			1,115	14,930
	PEN-LIQ	SHF	115.41	310.15	101.325	218	25,159
		SSF	117.66			238	28,003
	SOLID	SHF	5.80	323.15	101.325	1,030	5,974
		SSF	4.80			1,130	5,424
	WINE	SHF	127.39	304.15	101.325	741	94,396
		SSF	129.21			749	96,778
	CONDENSA	SHF	89.23	400.15	250	110.3	9,842
		SSF	89.23			110.3	9,842
	JUICEVAP	SHF	103.26	329.15	50	56.3	5,814
		SSF	101.19			56.3	5,697

Table 7. Inlet and outlet parameters of mass flow rates of cases 5 and 6

Parameter	Streams	Configuration	Mass Flow (kg/s)	T(K)	P(kPa)	b(kJ/kg)	b _{tot} (kW)
<i>Inlets</i>	PRETREATED BAGASSE	SHF, SSF	12.91	298.15	101.325	10,570	136,459
	ENZYME	SHF, SSF	0.60	302.15	101.325	23,730	14,238
	H2O-HYD	SHF, SSF	103	323.15	250	54.3	5,593
	H2O-WASH	SHF, SSF	123.40	298.15	101.325	50	6,170
	STEAM-EV	SHF, SSF	25.90	400.15	250	110	2,849
	YEAST	SHF, SSF	3.54	304.15	101.325	1,177	4,167
<i>Outlets</i>	LIG-CAKE	SHF	8.77	323.15	101.325	1,145	10,042
		SSF	9.39			1,006	9,446
	PEN-LIQ	SHF	102.75	310.15	101.325	101	10,378
		SSF	105.34			102	10,745
	SOLID	SHF	1.28	323.15	101.325	1,178	1,508
		SSF	3.07			1,024	3,144
	WINE	SHF	113.46	304.15	101.325	645	73,182
		SSF	115.19			661	76,141
	CONDENSA	SHF	24.90	400.15	250	110.3	2,746
		SSF	25.90			110.3	2,857
	JUICEVAP	SHF	18.20	329.15	50	56.3	1,025
		SSF	10.48			56.3	5,90

Table 8. Inlet and outlet parameters of mass flow rates of cases 7 and 8

Parameter	Streams	Configuration	Mass Flow (kg/s)	T(K)	P(kPa)	b(kJ/kg)	b _{tot} (kW)
<i>Inlets</i>	PRETREATED BAGASSE	SHF, SSF	12.96	298.15	101.325	10,570	136,987
	ENZYME	SHF, SSF	0.60	302.15	101.325	23,730	14,238
	H2O-HYD	SHF, SSF	103.40	323.15	250	54.3	5,615
	H2O-WASH	SHF, SSF	123.88	298.15	101.325	50	6,194
	STEAM-EV	SHF, SSF	26	400.15	250	110	2,860
	YEAST	SHF, SSF	3.54	304.15	101.325	1,177	4,167
<i>Outlets</i>	LIG-CAKE	SHF	8.42	323.15	101.325	1,008	8,487
		SSF	8.42			1,054	8,875
	PEN-LIQ	SHF	110.70	310.15	101.325	116	12,841
		SSF	113.70			128	14,554
	SOLID	SHF	1.91	323.15	101.325	1,022	1,952
		SSF	1.91			1,062	2,028
	WINE	SHF	116.73	304.15	101.325	645	75,291
		SSF	118.73			649	77,056
	CONDENSA	SHF	22.12	400.15	250	110.3	2,440
		SSF	19.12			110.3	2,109
	JUICEVAP	SHF	10.50	329.15	50	56.3	5,91
		SSF	8.50			56.3	4,79

A performance comparison of the SHF and SSF configurations in terms of exergy efficiency and irreversibility rate are summarized in Fig. 6 and Fig. 7, respectively.

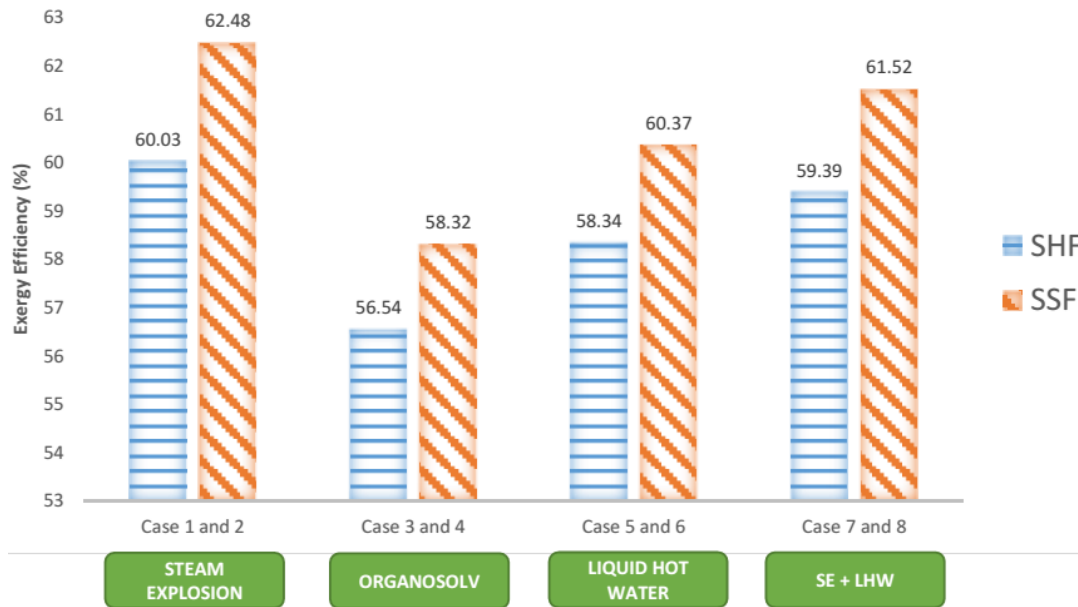


Fig.6. Exergy efficiency of the SHF and SSF configurations

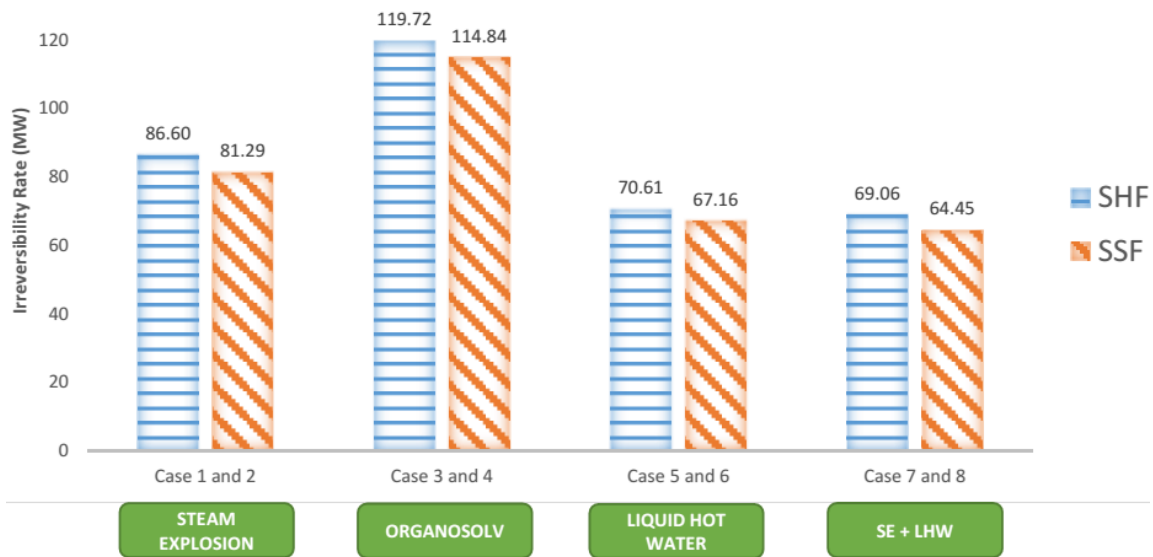


Fig.7. Irreversibility rate of the SHF and SSF configurations

The higher exergy destruction and losses in enzymatic hydrolysis found in cases 3 and 4 are due to the high enzyme consumption and the amount of bagasse to be hydrolyzed. Moreover, the efficiency of the hydrolysis configurations is associated to the pretreatment processes of bagasse and the reactions occurring in the reactors, where sugar recovery by enzymatic attack is not complete.

These results can be compared with others in the literature. Ojeda et al. performed an application of computer-aided process engineering and exergy analysis to evaluate different routes of bioethanol production from lignocellulosic biomass applying the SSF configuration. The reported exergy efficiency for the case study using steam explosion pretreatment (case 2) was 62.85 % and for Organosolv method (case 4) was 58.09 % (Ojeda et al., 2011c).

Ojeda et al. studied ethanol production by enzymatic hydrolysis of sugarcane bagasse. These authors adopted an acid-catalyzed steam explosion pretreatment, pentose fermentation, SSF for cellulose, distillation and rectification, and molecular sieves for anhydrous ethanol production. The reported exergy efficiencies were 87.5% for pretreatment, 65% for pentose fermentation, 48% for SSF and 68.2% for purification (distillation and dehydration). Moreover, these authors performed a comparison via exergy analysis of SHF, SSF, and SSCF pathways (Ojeda et al., 2011b).

Palacios-Bereche et al. carried out an exergy analysis and an exergy cost analysis of the bioethanol production by enzymatic hydrolysis of sugarcane bagasse integrating with and without the conventional process. These authors, adopted steam explosion as the pretreatment technology, and found an exergy efficiency of 63% for the enzymatic hydrolysis process using an evaporation system, and considering 10% of solids content in the hydrolysis reactor (Palacios-Bereche et al., 2013). Thus, the exergy efficiency obtained herein for case 1 is validated with the one reported by these authors.

CONCLUSIONS

In this study, two different configurations for second-generation ethanol production from sugarcane bagasse were simulated and analyzed combined with pretreated bagasse obtained from four pretreatment biomass techniques. The exergy analysis presented herein confirmed its use for the identification of irreversibilities in the route of bagasse enzymatic hydrolysis of second-generation ethanol processes. Based on the exergy efficiency performed, the SSF configurations show the highest values due to the increased rate of saccharification compared with those obtained in SHF processes.

In terms of total wine productivity, it is evident that wine production for the cases studied is a function of the inlet mass flow rate of pretreated sugarcane bagasse. The best alternative to improve the wine production processes via enzymatic technology, SHF and SSF configurations, were obtained through cases 3 and 4, increasing the wine production when compared with the other technologies by 10.94 % and 10.86 %, respectively. Furthermore, when considering the use of xylose liquor (pentose) regarding the production of biogas, cases 1 and 2 represent the best technological options.

Moreover, a sensitivity analysis varying the dosage of the enzymes showed that it does not represent a significant fraction (less than 2%) in increasing the total wine production for all cases. However, a detailed application of techno-economic analysis in this matter is necessary to estimate their impact on second-generation bioethanol production.

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NOMENCLATURE

b	specific exergy, kJ/kg
b_{tot}	exergy rate, kW
FPU	filter paper unit
H2O-WASH	water for pretreated bagasse washing
H2O-HYD	water for enzymatic hydrolysis of bagasse
JUICEVAP	vapor of 5 th effect-glucose liquor concentration system
PEN-LIQ	pentose liquor
STEAM-EV	steam evaporation system
t/h	tons per hour
w/v	weight per volume

REFERENCES

- Bejan, A. Tsatsaronics, G. Moran, M. 1996. *Thermal design and optimization*. John Wiley and Sons, Inc.; 113-114.
- Carrasco, C. Baudel, H. Sendelius, J. Modig, T. Roslander, C. Galbe, M. Hahn-Hägerdal, B. Zacchi, G. Lidén, G. 2010. SO₂-catalyzed steam pretreatment and fermentation of enzymatically hydrolyzed sugarcane bagasse. *Enzyme and Microbial Technology* 46:64–73.
- Cordeiro GC, Toledo Filho RD, Tavares LM, Fairbairn EMR. 2008. Pozzolan activity and filler effect of sugar cane bagasse ash in Portland cement and lime mortars. *Cement and Concrete Composites* 30:410–418.
- Cheng, K. Bai-Yan, C. Jian-An, Z. Hong-Zhi, L. Yu-Jie, Z. Jing-Ping, G. Jing-Ming, X. 2008. Sugarcane bagasse hemicellulose hydrolysate for ethanol production by acid recovery process. *Biochemical Engineering Journal* 38:105–109.
- Dias, M. Junqueira, T. Cavalett, O. Cunha, M. Jesus, C. Rossell, C. Maciel Filho, R. Bonomi, A. 2012. Integrated versus stand-alone second-generation ethanol production from sugarcane bagasse and trash. *Bioresource Technology* 103:152-161.

- Dias, M. Junqueira, T. Rossell, C. Maciel Filho, R. Bonomi, A. 2013. Evaluation of process configurations for second generation integrated with first generation bioethanol production from sugarcane. *Fuel Processing Technology* 109:84-89.
- Hamelinck, C. Van Hooijdonk, G. Faaij, AP. 2005. Ethanol from lignocellulosic biomass: techno-economic performance in short, middle and long-term. *Biomass and Bioenergy* 28:384-410.
- Humbird, D. Davis, R. Tao, L. Kinchin, C. Hsu, D. Aden, A. 2011. National Renewable Energy Laboratory (NREL). Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. Dilute-acid pretreatment and enzymatic hydrolysis of corn stover.
- Limayem, A. Ricke, S. 2012. Lignocellulosic biomass for bioethanol production-Current perspectives, potential issues and future prospects. *Progress in Energy and Combustion Science* 38:449-467.
- Modenbach, A. Nokes, S. 2013. Enzymatic hydrolysis of biomass at high-solids loadings - A review. *Biomass and Bioenergy* 56:526-544.
- Mosqueira-Salazar, K. Palacios-Bereche, R. Chávez-Rodríguez, M. Seabra, J. Nebra, S. 2013. Reduction of water consumption in an integrated first- and second-generation ethanol plant. *Energy for Sustainable Development* 17:531-535.
- Ojeda, K. Sánchez, E. Kafarov, V. 2011a. Sustainable ethanol production from lignocellulosic biomass: Application of exergy analysis. *Energy* 36:2119-2128.
- Ojeda, K. Sánchez, E. El-Halwagi, M. Kafarov, V., 2011b. Exergy analysis and process integration of bioethanol production from acid pre-treated biomass: Comparison of SHF, SSF, and SSCF pathways. *Chemical Engineering Journal* 176:195-201.
- Ojeda, K. Sánchez, E. Suarez, J. Avila, O. Quintero, V. El-Halwagi, M. Kafarov, V. 2011c. Application of computer-aided process engineering and exergy analysis to evaluate different routes of biofuels production from lignocellulosic biomass. *Industrial and Engineering Chemistry Research* 50:2768-2772.
- Palacios-Bereche, R., Mosqueira-Salazar, K., Modesto, M., Ensinas, A. V., Nebra, S. A., Serra, L. M., Lozano, M. 2013. Exergetic analysis of the integrated first- and second-generation ethanol production from sugarcane. *Energy* 62: 46-61.
- Pandey, A. Larroche, C. Ricke, S. Dussap, C. Gnansounou, E. 2011. Biofuels: Alternative feedstocks and conversion processes. ISBN: 978-0-12-385099-7, Elsevier-Academic Press.
- Querol, E., Gonzalez-Reguer, B., Perez-Benedito, J., L. 2011. Novel application for exergy and thermoeconomic analysis of processes simulated with Aspen Plus®. *Energy* 36:964-974.
- Quintero, J.A. Montoya, M.I. Sánchez, O.J. Giraldo, O.H. Cardona, C.A. 2008. Fuel ethanol production from sugarcane and corn: comparative analysis for a Colombian case. *Energy* 33:385-399.
- Quintero, J.A., Cardona, C.A. 2011. Process Simulation of Fuel Ethanol Production from Lignocellulosics using Aspen Plus. *Industrial and Engineering Chemistry Research* 50:6205-6212.
- Rocha GJM, Gonçalves AR, Oliveira BR, Gómez EO, Rossell CEV. 2010. Compositional variability of raw, steam-exploded and delignified sugarcane bagasse. In Proceedings: 8th International Congress on Distributed Generation and Energy in Rural Areas-AGRENER GD 2010.
- Sánchez, O.J., Cardona, C.A. 2008. Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresource Technology* 99:5270-5295.
- Sánchez, O.J., Cardona, C.A. 2012. Conceptual design of cost-effective and environmentally-friendly configurations for fuel ethanol production from sugarcane by knowledge-based process synthesis. *Bioresource Technology* 104: 305-314.
- Silva-Ortiz, P., Oliveira Jr, S. 2013. Exergy analysis of pretreatment processes of ethanol production based on lignocellulosic biomass. In Proceedings: 8th Conference on Sustainable Development of Energy, Water and Environment Systems-SDEWES Conference 2013, Dubrovnik-Croatia.

Szargut J, Morris DR, Steward FR. 1988. Exergy analysis of thermal, chemical, and metallurgical processes. New York: Hemisphere Publishing Corporation.

Wirawan, F. Cheng, C. Kao, W. Lee, D. Chang, J. 2012. Cellulosic ethanol production performance with SSF and SHF processes using immobilized *Zymomonas mobilis*. *Applied Energy* 100:19–26.

Wooley, R.J., Putsche, V. 1996. National Renewable Energy Laboratory (NREL). Development of an ASPEN PLUS Physical Property Database for Biofuels Components. Report No. NREL/MP-425-20685, Colorado-USA. Available from Internet: <http://www.nrel.gov/docs/legosti/old/20685.pdf>. Accessed on June 26, 2012.

Zheng, Y. Pan, Z. Zhang, R. Wang, D. 2009. Enzymatic saccharification of dilute acid pretreated saline crops for fermentable sugar production. *Applied Energy* 86:2459–2465.