



Exergy analysis of pretreatment processes of bioethanol production based on sugarcane bagasse



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ABSTRACT

Bioethanol produced from LB (lignocellulosic biomass) is a renewable option to decrease fossil fuel demand. LB is considered the future feedstock for bioethanol production because of its low cost and availability. The production of bioethanol from LB involves different steps: pretreatment, hydrolysis, fermentation, and bioethanol recovery. Some pretreatments such as SE (steam explosion), LHW (liquid hot water), ammonia fiber explosion and acid hydrolysis treatment have been used frequently to remove lignin and to improve the saccharification of cell wall carbohydrates. In this work via exergy analysis biomass pretreatment methods to prepare LB for bioethanol production using two typical chemical compositions of sugarcane bagasse are evaluated. Four case studies for the following pretreatment technologies (A) SE, (B) Organosolv, (C) LHW and (D) SE + LHW are studied. Although high exergy values are obtained in all cases of this study (A) 93.2%, (B) 85.4%, (C) 94.1%, and (D) 95.1%, the values of destroyed exergy rate found for the cases analyzed using the raw material 2 are high compared to the input bagasse exergy rate, (A) 7.2%, (B) 24.8%, (C) 6.0%, and (D) 5.5%, highlighting the relevance of such processes in the overall exergy efficiency of second-generation bioethanol production routes.

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1. Introduction

Among the potential bioenergy resources, lignocellulosic biomass has been identified as a cheap and effective feedstock for producing biofuels including bioethanol, biobutanol, and biogas. In general, biomass can be divided into first-generation crops as sugars from sugarcane or sugar beets, and starch from corn, rice, wheat, and on second-generation energy sources including various lignocelluloses. Hence, lignocellulosic biomass for the production of biofuels includes forest residues like wood; agricultural residues of sugarcane bagasse, corn cob, corn stover, wheat, and rice straws; industrial residue such as pulp and paper processing waste; municipal solid wastes; and energy crops like switch grass [1].

In the present work, sugarcane bagasse feedstock is analyzed. The annual world production in 2011 for this resource was 1.6 billion tons and it generated 279 million tons of biomass residues of bagasse and leaves. Theoretically, one ton of bagasse could

yield up to 300 L of bioethanol [2]. For the past three decades, bagasse and leaves have been explored for use in lignocellulosic bioconversion.

Second-generation ethanol production has not yet reached commercial maturity. Nowadays, different process configurations have been investigated in order to apply and to develop efficient conversion processes using this technology [3–5]. Dias et al. [3] evaluated different configurations of the second-generation ethanol production process (e.g. pretreatment with steam explosion coupled or not with delignification, pentose biodigestion or fermentation to ethanol, solids loading on hydrolysis), integrated with first-generation bioethanol production from sugarcane, while Dias et al. [4] assessed second-generation ethanol production processes improvements in the first-generation autonomous distillery processing sugarcane. Moreover, Dias et al. [5] have compared a stand-alone second-generation ethanol production from surplus sugarcane bagasse and trash with conventional first-generation ethanol production from sugarcane and with integrated first- and second-generation.

In this context, pretreatment is one of the most expensive and least technologically mature steps in the process of converting the biomass into fermentable sugars. Hence, it offers a great potential for improvement in efficiency and the reduction of costs through

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Nomenclature

b	specific exergy (kJ/kg)
B_{tot}	exergy rate or flow rate (kW)
h	specific enthalpy (kJ/kg)
LHW	liquid hot water
LIG2-TP	lignin fraction at reference conditions
LFRAC-TP	lignocellulose fraction at reference conditions
T	temperature ($^{\circ}\text{C}$, K)
P	pressure (MPa, kPa)
R_t	Reaction time (min)
SE	steam explosion
SFRAC-TP	solid fraction at reference conditions
SI	solids loading (%)
w/w	weight/weight (%)

research and development. Indeed, 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 [6].

Recently, using an exergy analysis several articles have been published on this topic on studies of pretreatments and biochemical routes [7–9] and for bioethanol production from lignocellulosic materials.

Ofori-Boateng and Lee [7] performed a comparative thermodynamic sustainability assessment of steam explosion, Organosolv and microbial pretreatment methods for bioethanol production via exergy analysis. Ojeda et al. [8] compared via exergy analysis sustainable ethanol production topologies from lignocellulosic biomass using steam explosion, diluted acid and Organosolv process for pretreatment stage of sugarcane bagasse. Moreover, Ojeda et al. [9] analyzed, also via exergy analysis, the bioethanol production from acid-pretreated bagasse using different process configurations that include SHF (sequential hydrolysis and fermentation), SSF (simultaneous saccharification and fermentation), and SSCF (simultaneous saccharification and co-fermentation).

Another interesting application was the production of bioethanol from bananas and their residues using energy, exergy and renewability analyses [10–12].

Velásquez et al. [10] evaluated the effect of chemical and biochemical stages involved in liquid biofuels production processes, while Velásquez et al. [11] applied the exergy analysis method to evaluate the renewability of anhydrous ethanol production from surplus banana fruit production and its lignocellulosic residues. These authors also apply an energy analysis to the production process of anhydrous ethanol obtained from the hydrolysis of starch and cellulosic and hemicellulosic material present in the banana fruit and its residual biomass [12].

In this paper, based on exergy analysis, the following biomass pretreatment methods for second-generation bioethanol production are evaluated: (A) Steam explosion, (B) Organosolv, (C) LHW and (D) SE + LHW, looking for implementation in the production process and to determine the effect of irreversibilities on the overall efficiency of lignocellulosic bioethanol production. Two typical chemical compositions of sugarcane bagasse were considered in the simulations performed to determine the variation of bagasse constituents and the ranges of efficiency for each pretreatment process.

Exergy efficiencies are calculated for the individual process steps. Furthermore, a performance comparison in terms of exergy efficiency and destroyed exergy rate of the cases studied were

determined. Based on the outcomes, the impact of pretreatment methods on the average exergy efficiency of the ethanol production is discussed.

1.1. Biomass pretreatment methods for second-generation biofuels

An important step towards the production of biofuels from lignocellulosic biomass is the pretreatment method. Pretreatment affords the separation of the major biomass components; these being cellulose, hemicellulose and lignin which render the digestibility of lignocellulosic materials. Pretreatments for lignocellulosic biomass are classified in Fig. 1, including: biological, physical (mechanical), chemical methods and various combinations of these (physicochemical).

During the last decades, pretreatment research has been focused on identifying, evaluating, developing, and demonstrating approaches that support the enzymatic hydrolysis of the pretreated biomass with lower enzyme dosages and shorter conversion times. Several pretreatment methods have been investigated with a wide variety of feedstock, and there are recent review articles which provide a general overview of the field [13–15].

Cardona et al. [13] reported the status and perspectives in the production of bioethanol from sugarcane bagasse based on the potential transformation to sugars and ethanol, considering pretreatment technologies, detoxification methods and biological transformation. Menon and Rao [14] described the trends in bioconversion of lignocellulose describing the advancement in recent pretreatment techniques, current global scenario of bioethanol pilot plants and biorefinery concept for the production of biofuels and bioproducts. Cardona and Sánchez [15] used Aspen Plus® to simulate several process configurations for bioethanol production from lignocellulosic biomass focusing on the energy consumption analysis of integrated flowsheets production processes.

Furthermore, a large number of articles have been published on biomass pretreatment methods with analyses of their advantages, limitations, disadvantages and economic assessment [16–18] so as to illustrate the status and perspectives on production of bioethanol from sugarcane bagasse as well as the trends in bioconversion of lignocellulose. Kumar et al. [16] reviewed various pretreatment methods of lignocellulosic biomasses for efficient hydrolysis and biofuel production while Hamelinck et al. [17] performed a techno-economic analysis of ethanol production from lignocellulosic biomass for short, middle and long-term. Moreover, these authors reported a comparison of various pretreatment methods in terms of lignin removal and hemicellulose hydrolysis. Besides, Zheng et al. [18] emphasize the biomass pretreatment in preparation for enzymatic hydrolysis and microbial fermentation for cellulosic ethanol production.

In addition, different studies analyzed the increase in second-generation ethanol production from sugarcane bagasse and trash taking into consideration standalone and integrated plants [3–5]. Moreover, different hydrolysis technologies, including improvements in hydrolysis yields, pentose biodegradation and fermentation for bioethanol production were studied. One of the most important evidences of implementing pretreatment methods successfully for bioethanol production process is the removal of lignin and hemicellulose through a cost-effective process.

1.1.1. Biological pretreatment

Biological delignification is an attractive approach for pretreatment of lignocellulosic biomass. This route is very cost-effective, requires low energy consumption, and produces low formation of toxic materials including furfural, hydroxymethylfurfural, and the like. Using direct microorganisms as well as enzymes extracted

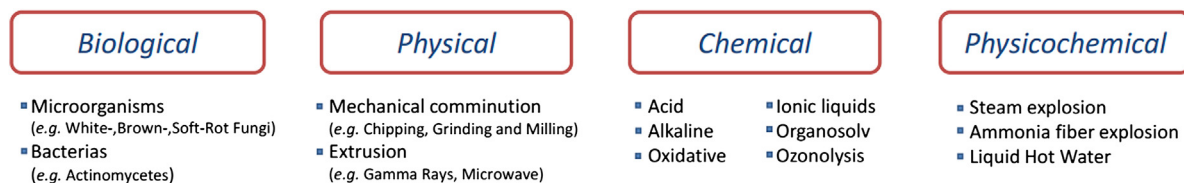


Fig. 1. Biomass pretreatment methods.

from microbes have demonstrated the biological approach. The microbial treatment includes fungi such as white-rot fungi, brown-rot fungi and soft-rot fungi, and bacteria. Both brown-rot and soft-rot fungi principally degrade the plant polysaccharides with minimal lignin degradation, while white-rot fungi are capable of complete mineralization of both the lignin and the polysaccharide components [1].

However, biological pretreatment is a very slow process and some important components such as hemicelluloses and cellulose of biomass are also consumed either by the same microorganism or by some foreign invaders. Furthermore, fermentable sugar loss, low-saccharification rate of 35–40%, and relatively long time of the pretreatment are found when compared with chemical and physical techniques [1].

1.1.2. Physical pretreatment

Most of the lignocellulosic biomass requires some of the mechanical processing for size reduction. Several pretreatment methods such as milling and irradiation are commonly used to improve the enzymatic hydrolysis or biodegradability of lignocellulosic materials. The energy requirements for physical pretreatments are dependent on the final particle size and reduction in crystallinity of the lignocellulosic material [14].

Milling is a mechanical process of pretreatment that breaks down the structure of lignocellulosic materials and reduces the crystallinity of the cellulose. During this process, biomass is grounded with the contact of the balls inside a cycle machine to get the uniform particle size [19]. Buaban et al. [20] reported that the increase in the milling time increased the amounts of sugars such as glucose, $89.2 \pm 0.7\%$ and xylose, $77.2 \pm 0.9\%$ after four hours of milling.

Irradiation pretreatment uses gamma rays in order to allow the breakdown of β -1, 4-glycosidic linkages, thus enhancing the surface area and crystallinity of the cellulose. It is a physical pretreatment which increases the surface area, consequently reducing crystallinity. This method is expensive for large-scale operations with considerable environmental and safety concerns [21].

1.1.3. Chemical pretreatment

Chemical pretreatments have the primary goal of improving the biodegradability of cellulose by removing lignin or hemicellulose, and to a lesser degree, DP (decreasing the polymerization) and crystallinity of the cellulose component. The most commonly used chemical pretreatment techniques for sugarcane bagasse and leaves are Organosolv, alkaline and acid pretreatments.

The Organosolv method is a promising pretreatment strategy, since it has demonstrated its potential for lignocellulosic materials [22]. It uses numerous organic or aqueous solvent mixtures such as methanol, ethanol, acetone, ethylene glycol, triethylene glycol, tetrahydrofurfuryl alcohol, glycerol, aqueous phenol, and aqueous n-butanol [18]. Typical values of ethanol concentration are 35–70% (w/w), liquor pH ranges from 2.0 to 3.8 and liquor to solids ratio may reach 4:1 to 10:1 (w/w) [16]. The main fractions obtained after pretreating biomass are cellulosic fibers, solid lignin obtained after the volatile solvent removal, and liquid solution of hemicellulosic sugars mainly xylose.

During Organosolv pretreatment, removal of solvents from the system is necessary by using appropriate extraction and separation techniques as evaporation and condensation processes. Solvents need to be separated in order to delete inhibitory factors for enzymatic hydrolysis and fermentative microorganisms. Organosolv pretreatment produces a highly digestible cellulose substrate from almost every kind of feedstock, and lignin with the potential of high-value utilization can be recovered after pretreatment [23].

Alkaline pretreatment is one of major chemical pretreatment technologies, counting on numerous studies. It employs various bases, including sodium hydroxide, NaOH, calcium hydroxide, $\text{Ca}(\text{OH})_2$, potassium hydroxide, KOH, aqueous ammonia, ammonium hydroxide, NH_4OH , and sodium hydroxide in combination with hydrogen peroxide, H_2O_2 , and others. Among these alkaline pretreatments, lime has received much more attention since it is inexpensive, about 6% the cost of sodium hydroxide, has improved handling, and can be recovered easily by using carbonated wash water [24].

In comparison with other pretreatment technologies, alkali pretreatment usually requires lower temperatures and pressures or even ambient conditions. Pretreatment time, however, is recorded in terms of hours or days which are much longer than other pretreatment processes as indicated in Table 1.

Acid pretreatment involves the use of concentrated and diluted acids to break the rigid structure of the lignocellulosic material. The most commonly used acid is dilute sulfuric, H_2SO_4 , and hydrochloric acid, HCl; this has been a major technology for hydrolyzing lignocellulosic biomass for fermentable sugar production [14]. In this context, H_2SO_4 at concentrations usually below 4% (w/w) has been of most interest in such studies as it is inexpensive and effective. Two types of dilute-acid pretreatment processes are typically used [16]: High-temperature, $T > 160^\circ\text{C}$ continuous-flow process for low solids loadings where the weight of substrate to the weight of reaction mixture ratio is 5–10%, and low-temperature, $T < 160^\circ\text{C}$, batch process for high solids loadings (10–40%).

Table 1
Comparison of biomass pretreatment processes.

	Pretreatment methods	Operating conditions	References
Chemical	Organosolv (Organic solvents)	T: 150–200 °C P: 2 MPa Rt: 30–90 min	[18] [8] [16]
	Alkaline	Diluted NaOH T: 60 °C Rt: 24 h	$\text{Ca}(\text{OH})_2$ T: 120 °C Rt: 4 h [25]
	Acid (Acid hydrolysis)	T > 160 °C Rt: 2–10 min	[25]
Physicochemical	Liquid hot water (LHW)	T: 190–230 °C P > 5 MPa Rt: 1–46 min SI < 20%	[17] [25] [25] [25]
	Steam explosion	T: 160–260 °C P: 0.6–4.8 MPa	[26]
	Ammonia fiber explosion (AFEX)	T: 40–140 °C P: 1.7–2.1 MPa Rt: ≤30 min	[16]

Table 2
Advantages and disadvantages of pretreatment methods.

Pretreatment methods	Advantages	Disadvantages
<i>Physical</i>		
Milling	This method can be considered environment-friendly due to the absence of added chemicals that produce toxic substances [19].	A disadvantage of milling is the high power required by the machines and consequent high energy costs [19].
Irradiation	Reduces cellulose crystallinity [14].	High Power consumption than inherent biomass energy [14].
<i>Chemical</i>		
Organosolv	Hydrolyzes lignin and hemicelluloses [24]. Relatively pure, low molecular weight lignin is recovered as a by-product [18].	Solvents need to be drained from the reactor, evaporated, condensed, and recycled- reused; high cost [18,24].
Alkaline	Removal of lignin and hemicellulose increases the accessible surface area, thus improving the reactivity of the remaining polysaccharides [24].	The conversion of alkali into irrecoverable salts and the incorporation of salts into the biomass during the pretreatment reactions; Long residence time required [24].
Acid	Significantly higher xylose yield. Using batch dilute sulfuric acid pretreatment process, xylose yield showed to approach 80%–90% of the theoretical value [18].	Corrosion requires expensive construction materials; Gypsum has problematic reverse solubility; Formation of degradation products and release of natural biomass fermentation inhibitors; Biomass particle size reduction [18].
<i>Physicochemical</i>		
LHW	Removal of hemicellulose making enzymes accessible to cellulose [14].	Long residence time, less lignin removal [14].
Steam explosion	Includes hemicellulose degradation and lignin transformation; Cost-effective; Steam pretreatment with addition of a catalyst is the technology that has been claimed to be closest to commercialization [16].	Includes destruction of a portion of the xylan fraction; Incomplete disruption of the lignin-carbohydrate matrix, and generation of compounds that might be inhibitory to microorganisms used in downstream processes [16].
AFEX	Economic, fast, and highly efficient. Ammonia after pretreatment can be recycled for further applications [19].	Handling of ammonia solution for the pretreatment at large scale is a problem due to environmental concerns [19].

1.1.4. Physicochemical pretreatment

LHW is a hydrothermal pretreatment that uses water at high pressures to maintain the liquid state at high temperatures and causes alterations in the structure of the lignocellulose. It does not require any catalyst or chemical and usually involves temperatures of 150–230 °C for variable residence times from seconds to hours. High variability in the pretreatment results is attributed to the different feedstock. During LHW pretreatment, most of the hemicellulose is solubilized, making cellulose more accessible. Cellulose and lignin are not significantly affected and remain in the solid phase. Lignin is partially depolymerized and solubilized but complete delignification is not possible by hot water alone because of the recondensation of soluble components originated from lignin [23].

Steam explosion is a physicochemical pretreatment in which the biomass is subjected to pressurized steam for a given period of time, and then suddenly depressurized. This process makes the materials undergo an explosive decompression. One major feature of the steam explosion method is related to reaction time, from several seconds to a few minutes before the material is exposed to atmospheric pressure. The most important factors affecting the effectiveness of steam explosion are particle size, temperature, residence time, and the combined effect of both temperature and time. Sugarcane bagasse requires operating temperatures of 188–243 °C and reaction time ranges between 0.5 and 44 min [25].

AFEX (ammonia fiber explosion) is a process in which lignocellulosic biomass is exposed to liquid aqueous ammonia under moderate or high temperature and pressure for a period of time,

and then the pressure is suddenly reduced [19]. Typically, operating conditions (Table 1) of the AFEX process include aqueous ammonia dosage, 1–2 kg NH₃/kg dry biomass, and pH values of less than 12 [18]. Ammonia has a marked effect on lignocellulose causing swelling and physical disruption of biomass fibers, partial decrystallization of cellulose, and breakdown of lignin-carbohydrates linkages.

AFEX produces a solid pretreated material because during the pretreatment only a small amount of the material is solubilized and most of the biomass components remain in the solid fraction. Thus, since considerable hemicellulose is retained in the pretreated material, both celluloses and hemicelluloses will be required in the enzymatic hydrolysis process [23].

The typical operating conditions for the most promising pretreatment methods to be commercialized for the biofuel industry are shown in Table 1.

A comparison of various pretreatment processes for lignocellulosic biomass, and their advantages and disadvantages, are summarized in Table 2.

2. Description of processes

The selected pretreatment technologies studied in this paper are: Steam Explosion, Organosolv, Liquid Hot Water, and a combined SE and LHW pretreatments. These processes are the most used as pretreatment methods when sugarcane bagasse is the feedstock [2,17,27,28]. The properties of the components of the lignocellulosic material were obtained from the databank for biofuel components developed by NREL [29].

Table 3
Feedstock characterization [29].

Molecular formula	Component	Molecular weight (kg/kmol)	Solid enthalpy of formation (kJ/kmol)
C ₆ H ₁₀ O ₅	CELLULOSE	162.14	−976,362
C ₅ H ₈ O ₄	HEMICELLULOSE (Xylan)	132.12	−762,416
C _{7.3} H _{13.9} O _{1.3}	LIGNIN	122.49	−1,592,659

Table 4
Reactions and conversion rates for steam explosion pretreatment process.

Reactions	Yield (%)
C ₅ H ₈ O ₄ + H ₂ O → C ₅ H ₁₀ O ₅	61.4
C ₅ H ₈ O ₄ + H ₂ O → 2.5C ₂ H ₄ O ₂	9.2
C ₅ H ₁₀ O ₅ → C ₅ H ₄ O ₂ + 3 H ₂ O	5.1
C ₆ H ₁₀ O ₅ + H ₂ O → C ₆ H ₁₂ O ₆	4.1

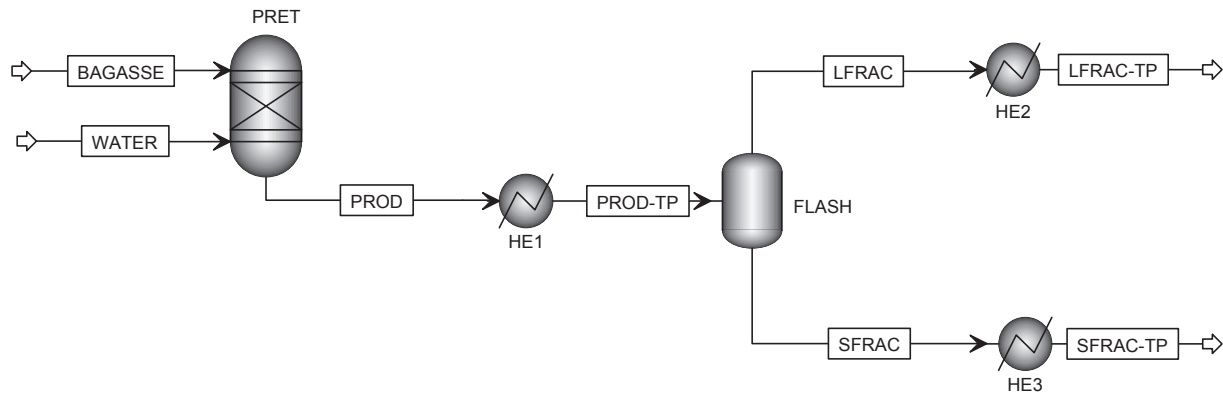


Fig. 4. Liquid hot water pretreatment process (Case C).

in rating or design mode. In the design mode, one can use the design specifications form to specify column performance parameters such as recovery yield.

On the other hand a yield reactor, RYield – nonstoichiometric, was chosen for simulating the liquid hot water LHW pretreatment performing the calculations based on the yield. In this case, the steam consumption rate of 18,000 kg/h was considered based on [33]. Furthermore, a temperature of 200 °C and a pressure of 5 MPa were adopted as operating parameters, with 88% xylose yield recovery [17].

The RYield model in Aspen Plus® simulator is used to represent reaction results in a product distribution with a known yield, as shown in the scheme of LHW pretreatment technology, Fig. 4. Hence, RYield calculates the product stream flow rates based on yield distributions.

In view of achieving the effective pretreatment, a combined steam explosion and liquid hot water pretreatment configuration is proposed, Case D. Combined physicochemical methods can enhance the sugar conversion from biomass and can improve the performance compared to a unique pretreatment. Fig. 5 shows a schematic of this configuration. The operating conditions defined for this case are illustrated in Table 9.

2.3. Exergy analysis

Using exergy analysis, it is possible to evaluate the performance of energy conversion processes not only on the basis of thermodynamics but also by including economic and environmental aspects and impacts of the processes considered. This comprehensive approach of the energy resources utilization has, as one of its most important features, the identification of sustainable ways of utilizing energy resources [34].

The exergy analysis methodology proposal enables the identification of the steps and exergy flows with higher exergy

consumption involved in the bioethanol production from lignocellulosic material. This analysis also allows comparing scenarios and selecting suitable design processes for bioethanol production. The reference temperature, $T_0 = 298.15$ K, and pressure, $P_0 = 1$ bar, were used as actual environmental conditions. In order to compare all the pretreatment processes on the same basis input and output streams for all the cases were taken at reference conditions. The chemical exergies of the substances involved in the processes are listed in Table 5 based on values reported by Refs. [9,35].

The determination of the chemical exergy b_{CH} is usually based on several correlations [35–37]. They are used to correlate a given fuel elementary composition to its LHV (lower heating value). Alternatively, b_{CH} calculation for each component and for the whole stream can be evaluated by using Eq. (1).

$$b_{CH} = \sum x_i b_{CH}^{\text{specific}} + RT_0 \sum x_i \ln x_i \gamma_i \quad (1)$$

where b_{CH}^{specific} represents the chemical exergy of the i th substance [kJ/kmol], x_i the mole fraction of the i th substance, R , universal gas constant [J/mol K], T_0 the temperature [K], and γ the activity coefficient.

In this study, the influence of (γ) was evaluated for each compound permitting to observe that it provides values close to one. For this reason, γ was considered equal to one, an ideal solution, in mixtures for chemical exergy calculations.

3. Results

Tables 6–9 show the values of some parameters used in the evaluation of the pretreatment technologies studied for bioethanol produced from sugarcane bagasse.

In the exergy analysis performed, the destroyed exergy rate and the exergy efficiency were calculated for each case. Destroyed exergy rate or irreversibility rate represents the rate of available

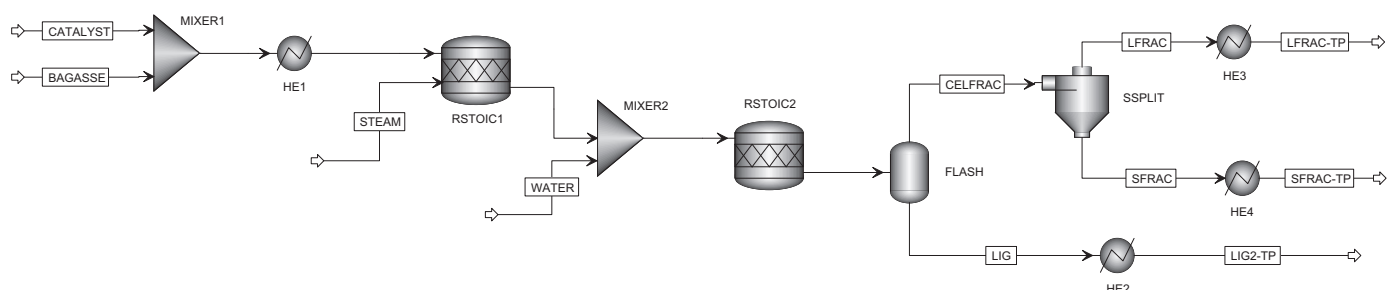


Fig. 5. Combined steam explosion and liquid hot water pretreatment process (Case D).

Table 5
Specific chemical exergy of the substances studied in the processes.

Formula	Substance	Aspen Plus® component identification	$b_{\text{CH}}^{\text{specific}}$ kJ/kg
$\text{C}_6\text{H}_{10}\text{O}_5$	CELLULOSE	CELU	18,875
$\text{C}_5\text{H}_8\text{O}_4$	HEMICELLULOSE	HEMI	19,177
$\text{C}_{7.3}\text{H}_{13.9}\text{O}_{1.3}$	LIGNIN	LIGN	37,133
CO_2	CARBON DIOXIDE	CO2	451
$\text{C}_2\text{H}_6\text{O}$	ETHANOL	C2H6O-2	29,471
$\text{C}_6\text{H}_{12}\text{O}_6$	GLUCOSE	C6H12-01	17,583
$\text{C}_5\text{H}_{10}\text{O}_5$	XYLOSE	C5H10-01	17,583
$\text{C}_2\text{H}_4\text{O}_2$	ACETIC ACID	C2H4O-01	17,583
$\text{C}_3\text{H}_8\text{O}_3$	GLYCEROL	C3H8O-01	19,667
$\text{C}_5\text{H}_4\text{O}_2$	FURFURAL	C5H4O-01	24,437
SO_2	SULFUR DIOXIDE	O2S	4897
SiO_2	SILICON DIOXIDE	SiO2	59*
H_2O	WATER (L)	H2O	50
$\text{C}_6\text{H}_6\text{O}_6$	ORGANIC ACIDS	C6H6O-01	14,275

*To determine the specific chemical exergy of SiO_2 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 Ref. [38].

work destroyed due to irreversible processes that take place inside the control volume. The exergy analysis of the different process stages was based on the concept of exergy efficiency η_B defined by Eq. (2) [34].

$$\eta_B = \frac{\text{Exergy of useful products}}{\text{Feeding exergy}} = \frac{B_{\text{products}}}{B_{\text{inputs}}} \quad (2)$$

A performance comparison in terms of exergy efficiency and destroyed exergy rate of the cases studied is summarized in Table 10.

Four sugarcane bagasse pretreatment processes were simulated using two typical chemical compositions for this raw material. High exergy efficiency values were reported for all the pretreatment techniques considered; in cases studied using the raw material 1, cases A (SE), C (LHW) and D (SE + LHW) reaching 91.0%, 93.3% and 94.4%, respectively. However, an exergy efficiency of 83.3% was observed for case B, and this value is a consequence of the greatest irreversibility rate observed due to the exergy consumption for recycling the solvent, organic liquid, involved in the pretreatment process. Nevertheless, using the raw material 2 for the case studies A (SE), B (Organosolv), C (LHW) and D (SE + LHW), exergy efficiencies of 93.2%, 85.4%, 94.1% and 95.1% were found, respectively.

Similarly, when the raw material 1 was used the destroyed exergy rate was 13.5 MW for case A, 9.4 MW for case C and 8.5 MW for case D. On the other hand, a high destroyed exergy rate of 39.9 MW was achieved for case B. However, using the raw material 2 for the case studies A (SE), B (Organosolv), C (LHW) and D (SE + LHW) the results were 10.6 MW, 36.4 MW, 8.8 MW and 8.0 MW, respectively.

Table 6
Inlet and outlet parameters of mass flow rates of case A.

Streams	Raw material	Mass flow (kg/s)	T (K)	P (kPa)	h (kJ/kg)	b (kJ/kg)	B_{tot} (kW)
BAGASSE	1	13.89	298.15	101.3	−23,382	9856	136,900
	2				−23,561	10,570	146,817
CATALYST	1 and 2	1.39	298.15	101.3	−16,763	4944	6872
STEAM	1 and 2	7.64	463.15	1250.0	−13,131	900	6876
SFRAC-TP	1	5.98	298.15	101.3	−21,721	6109	36,532
	2				−21,815	6401	38,278
LFRAC-TP	1	16.94	298.15	101.3	−22,540	5938	100,590
	2				−22,659	6214	105,265

Table 7
Inlet and outlet parameters of mass flow rates of case B.

Streams	Raw material	Mass flow (kg/s)	T (K)	P (kPa)	h (kJ/kg)	b (kJ/kg)	B_{tot} (kW)
BAGASSE	1	13.89	298.15	101.3	−23,382	9856	136,900
	2				−23,561	10,570	146,817
SOLVENT	1	21.39	298.15	101.3	−16,305	4719	100,939
	2				−16,156	4767	101,966
WATER	1 and 2	19.08	298.15	101.3	−15,815	50	954
LIG2-TP	1	32.39	298.15	101.3	−20,035	3204	103,778
	2				−20,117	3567	115,535
LFRAC-TP	1	21.97	298.15	101.3	−22,325	4327	95,064
	2				−22,511	4450	97,767

A comparison between the exergy performance of pretreatment process A and B obtained in this study and the one obtained by Ojeda et al. [8] indicates that the difference of the destroyed exergy and exergy efficiency values were not higher than 4% and 1% for the raw material 1. Using the raw material 2 the results obtained were 6% and 3%, respectively. These authors studied the bioethanol production chain by enzymatic hydrolysis of sugarcane bagasse adopting an acid-catalyzed steam explosion pretreatment, pentose fermentation, Simultaneous Saccharification and Fermentation SSF for cellulose, distillation and rectification, and molecular sieves for anhydrous ethanol production. The reported exergy efficiency for the pretreatment method was 87.5%.

Palacios-Bereche et al. [39] 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, adopting steam explosion as the pretreatment technology, found a global plant exergy efficiency of 28% for the conventional process.

It is worth noting that the values of destroyed exergy rate obtained for the pretreatment processes analyzed are high compared to the input bagasse exergy rate: 9.9% for case A, 29.2% for case B, 6.8% for case C and 6.2% for case D, when using the raw material 1. However, using the raw material 2 for the case studies A (SE), B (Organosolv), C (LHW) and D (SE + LHW) the calculated results were 7.2%, 24.8%, 6.0% and 5.5%, respectively. These results show the variation of bagasse constituents and the ranges of exergy efficiency for each pretreatment process highlighting the relevance of such processes in the overall exergy efficiency of second-generation bioethanol production routes. It is evident that exergy efficiency and the destroyed exergy rate of pretreatment processes are a function of the chemical composition of the sugarcane bagasse.

4. Conclusions

Pretreatment technologies published in the literature were described in terms of the mechanisms involved, advantages and disadvantages. Tables 1 and 2 provide a summary of the main pretreatment routes and their major characteristics for a number of

Table 8
Inlet and outlet parameters of mass flow rates of case C.

Streams	Raw material	Mass flow (kg/s)	T (K)	P (kPa)	h (kJ/kg)	b (kJ/kg)	B_{tot} (kW)
BAGASSE	1	13.89	298.15	101.3	−23,382	9856	136,900
	2				−23,561	10,570	146,817
WATER	1 and 2	5.00	538.15	5100.0	−14,759	341	1705
SFRAC-TP	1	5.98	298.15	101.3	−21,095	6951	41,567
	2				−21,520	7598	45,436
LFRAC-TP	1	12.91	298.15	101.3	−22,313	6791	87,672
	2				−22,650	7306	94,320

Table 9

Inlet and outlet parameters of mass flow rates of case D.

Streams	Raw material	Mass flow (kg/s)	T (K)	P (kPa)	h (kJ/kg)	b (kJ/kg)	B _{tot} (kW)
BAGASSE	1	13.89	298.15	101.3	−23,382	9856	136,900
	2				−23,561	10,570	146,817
CATALYST	1 and 2	1.39	298.15	101.3	−16,763	4944	6872
STEAM	1 and 2	7.64	463.15	1250.0	−13,131	900	6876
WATER	1 and 2	5.00	538.15	5100.0	−15,815	341	1705
LIG2-TP	1	3.14	298.15	101.3	−20,873	2788	8754
	2				−20,902	2894	9087
SFRAC-TP	1	11.82	298.15	101.3	−21,223	5105	60,341
	2				−21,466	5502	65,034
LFRAC-TP	1	12.96	298.15	101.3	−22,775	5769	74,766
	2				−22,963	6182	80,119

parameters. The choice of the optimum pretreatment process is highly dependent on the objective of the biomass pretreatment since different products are yielded.

Nevertheless, the choice of a pretreatment method should not only be based on its potential yield, but also on the process exergy efficiency because this parameter is directly associated with economic assessment and environmental impact. This physical quantity allows a better analysis of the alternatives to improve a given production process; moreover, exergy analysis takes into account the quality of the energy conversion processes.

The use of steam explosion combined with liquid hot water pretreatment in series presents the case with the lowest exergy consumption and better exergy efficiencies. This arrangement takes advantage of the high exergy contents obtained in the outflow of SE process to LHW method. Although some positive results were achieved with these combined methods, conducting an economic assessment of the entire combined pretreatments and its demonstration on a pilot scale are steps required to obtain engineering data for industrial scale processing and sufficient refined products for characterization and exploration.

Steam explosion using sulfur dioxide, SO₂, as a catalyst proved to be an effective pretreatment technique. This method employs high-pressure saturated steam for treating the lignocellulosic biomass. In this process, the abrupt depressurization and cooling of the lignocellulosic biomass after a specified reaction conversion was implemented. Furthermore, the use of acid catalyst increases the recovery of hemicellulose sugars and decreases the production of inhibitory compounds.

The LHW method shows low exergy consumption due to the fact that it is operated at high pressures and high temperatures, Table 8. Liquid hot water penetrates the lignocellulose matrix and degrades hemicellulose into xylose with the least generation of inhibitors. Another advantage is eliminating the need for a final washing step or neutralization because the pretreatment solvent is water.

Finally, in the simulation of the Organosolv pretreatment process, the aqueous organic solvents as the working medium present the lowest exergy efficiency because of its dependence with the

lignin and hemicellulose performance recovery. This is a fundamental factor in order to improve the enzymatic hydrolysis in the production of bioethanol from lignocellulosic biomass.

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Table 10

Performance comparison of the simulated pretreatment processes.

Pretreatment	Raw material	Case A SE	Case B Organosolv	Case C LHW	Case D SE + LHW
Exergy efficiency (%)	1	91.0	83.3	93.3	94.4
	2	93.2	85.4	94.1	95.1
Destroyed exergy rate (MW)	1	13.5	39.9	9.4	8.5
	2	10.6	36.4	8.8	8.0

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