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EXERGY ANALYSIS OF PRETREATMENT PROCESSES OF ETHANOL PRODUCTION BASED ON LIGNOCELLULOSIC BIOMASS

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ABSTRACT

Ethanol produced from lignocellulosic biomass is a renewable option to decrease the fossil fuels demand. Lignocellulosic biomass is considered as the future feedstock for ethanol production because of its low cost and its availability. The production of ethanol from lignocellulosic biomass involves different steps of pretreatment, hydrolysis (saccharification), fermentation, and ethanol recovery. A number of pretreatments such as concentrated acid hydrolysis, dilute acid hydrolysis, alkali pretreatment, CO_2 explosion, steam explosion, liquid hot water (LHW), ammonia fiber explosion (AFEX), lime treatment and organic solvent (Organosolv) treatment have been used frequently to remove lignin and to improve the saccharification of the cell wall carbohydrates. In this work it is evaluated via exery analysis biomass pretreatment methods in order to prepare lignocellulosic biomass to ethanol production by using sugarcane bagasse as raw material. In this sense, three case studies for the following pretreatment technologies (A) Steam explosion, (B) Organosolv and (C) LHW are modeled and evaluated. The results show highest exergy efficiency in case A (Steam Explosion) and case C (LHW) reaching 93.27 % and 94.42 %, respectively. In contrast, the case B (Organosolv) presented lowest exergy efficiency (85.68 %). It is worthy to note that the obtained values of destroyed exergy rate for the three analyzed pretreatment process are high compared to the input bagasse exergy rate: 8.1% for case A, 55.5% for case B, and 5.6% for case C, highlighting the relevance of such process in the overall exergy efficiency of second-generation ethanol production routes.

KEYWORDS

Lignocellulosic biomass, Sugarcane, Pretreatment methods, Cellulosic ethanol (Second-generation ethanol).

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INTRODUCTION

Second-generation ethanol production is not yet commercially available. Nowadays, different process configurations have been investigated in order to apply and develop efficient conversion processes using this technology [1, 2, 3]. In this context, based on exergy analysis, this work evaluates biomass pretreatment methods for second-generation ethanol production looking towards its implementation in the production process.

Recently, several articles have been published on this topic, with analyses of pretreatments and biochemical routes [4, 5, 6], for ethanol production from lignocellulosic materials. Another interesting application was the production of ethanol from bananas and their residues using exergy and renewability analysis [7, 8].

BIOMASS PRETREATMENT METHODS FOR 2ND GENERATION BIOFUELS

An important step in the production of biofuels from lignocellulosic biomass is the pretreatment method. Pretreatment affords the separation of the major biomass components, being these cellulose, hemicellulose and lignin and thus render the digestibility of lignocellulosic material. In this sense, pretreatments for lignocellulosic biomass include: biological, mechanical (physical), chemical methods and various combinations of these methods.

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 on a wide variety of feedstocks types, and there are recent review articles which provide a general overview of the field [13, 14, 15, 19].

Furthermore, a large number of articles have been published on biomass pretreatment methods with analyses of its advantages, limitations, disadvantages and economic assessment [5, 9, 10, 11, 12] looking towards illustrating the status and perspectives on production of bioethanol from sugarcane bagasse, as well as the trends in bioconversion of lignocellulose.

In addition, different studies analyzed the increase on second-generation ethanol production from sugarcane bagasse and trash taking into consideration standalone and integrated plants [1, 2, 3]. Moreover, different hydrolysis technologies, including improvements on hydrolysis yields, pentoses biodigestion and fermentation to ethanol production were studied. One of the most important evidence to implement pretreatment methods successfully to bioethanol production process is the removal of lignin and hemicellulose through a cost effective process. It is worth pointing out that physical pretreatment typically includes uncatalyzed steam explosion, liquid hot water pretreatment (LHW), mechanical comminution, and high-energy radiation.

LHW is a hydrothermal pretreatment that uses water at high pressures to maintain the liquid state at elevated temperatures and provokes 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 on the pretreatment results is attributed to the different feedstocks. During LHW pretreatment, most of the hemicellulose is solubilized, making the 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 through hot water alone, because of the recondensation of soluble components originated from lignin [15].

Steam explosion is a physicochemical pretreatment in which the biomass is subjected to pressurized steam for a period of time ranging and then suddenly depressurized. In this sense, one major feature of steam explosion method is related to reaction time, its variable range covers 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 (T) and time (t). Sugarcane bagasse requires operating temperature beyond 188°C to 243°C and reaction time ranges between 0.5 to 44 min [11].

Chemical pretreatments have the primary goal of improving the biodegradability of cellulose by removing lignin or hemicellulose, and to a lesser degree, decreasing the polymerization (DP) and crystallinity of the cellulose component. In this sense, the organosolv methods lead to good performance. It uses organic solvents such as methanol, ethanol, acetone, ethylene glycol, triethylene glycol, tetrahydrofurfuryl alcohol, glycerol, aqueous phenol, aqueous n-butanol [12]. It has values of ethanol concentration of 35-70% (w/w), pH of liquor might range from 2.0 to 3.8 and liquor to solids ratio ranging from 4:1 to 10:1 (w/w) [9]. The main fractions obtained after pretreating biomass are: cellulosic fibers; solid lignin, obtained after removal of the volatile solvent; 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 to enzymatic hydrolysis and fermentative microorganisms. Organosolv pretreatment produces a highly digestible cellulose substrate from almost all kind of feedstock, and lignin with the potential of high-value utilization can be recovered after pretreatment [15].

Ammonia Fiber Explosion (AFEX) is a process in which lignocellulosic biomass is exposed to liquid. Typically, operation conditions of AFEX include aqueous ammonia dosage, 1-2 kg NH_3/kg dry biomass, and pH values < 12.0 [12]. 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 cellulases and hemicellulases will be required in enzymatic hydrolysis process [15].

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 acid (H_2SO_4) and hydrochloric acid (HCL), which had 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 the most interest in such studies as it is inexpensive and effective. Two types of dilute-acid pretreatment processes are typically used [9]: High-temperature (T > 160 °C), continuous-flow process for low solids loadings (weight of substrate/weight of reaction mixture: 5-10%); Low-temperature (T < 160 °C), batch process for high solids loadings (10-40%).

The typical operating conditions for the categories selected are shown in Table 1. The most promising pretreatment methods to be commercialized for the biofuel industry were evaluated in this work.

Table 1. Comparison of biomass pretreatment processes

	Pretreatment Methods	*Operating Conditions*	*References*
PHYSICAL	Steam Explosion	T: 160-260°C P: 0.6-4.8 MPa Rt: 2 min	[9] [9] [10]
	Liquid Hot Water (LHW)	T: 190-230°C P > 5 MPa Rt: 1-46 min Sl < 20%	[10] [11] [11] [11]
CHEMICAL	Organosolv (Organic solvents)	T: 150-200°C P: 2 MPa Rt: 30-90 min	[12] [5] [9]
	Ammonia Fiber Explosion (AFEX)	T: 90°C P: 1.1-1.3 MPa Rt: 30 min	[9] [9] [9]
	Acid Pretreatment (Acid Hydrolysis)	T >160°C Rt: 2-10 min	[11] [11]
	Alkaline Pretreatment	*diluted NaOH* *Ca(OH)$_2$* T: 60°C T: 120°C Rt: 24h Rt: 4h	[11]

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

Table 2. Advantages and disadvantages of pretreatment methods

Pretreatment Methods	*Advantages*	*Disadvantages*
PHYSICAL		
Steam explosion	Include the 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 [9].	Include 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 [9].
LHW	Removal of hemicellulose making enzymes accessible to cellulose [14].	Long residence time, less lignin removal [14].
CHEMICAL		
Organosolv	Relatively pure, low molecular weight lignin is recovered as a by-product [12].	Solvents need to be drained, evaporated, condensed and reused [14].
AFEX	Produces negligible inhibitors for the downstream biological processes, so water wash is not necessary; Requires no particle size reduction [12].	Not efficient for biomass with high lignin content [14].
Acid pretreatment	Significantly higher xylose yield. Using batch dilute sulfuric acid pretreatment process, xylose yield showed to approach 80%-90% of theoretical value [12].	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 [12].
Alkaline	Removal of lignin and hemicellulose increases accessible surface area [14].	Long residence time; irrecoverable salts formed [14].

PROCESSES DESCRIPTION

The selected pretreatment technologies are: Steam Explosion, Organosolv and Liquid Hot Water. This processes are modeled and evaluated through Aspen Plus®[16] simulator. The properties of the components of the lignocellulosic material were obtained from the databank for biofuels components developed by NREL [17].

Raw material

Sugarcane bagasse is the feedstock considered in the performed simulations. Table 3 shows some the characteristics of cellulose, hemicellulose and lignin taken into account in the simulations. Furthermore, this lignocellulosic material is assumed to have the following typical chemical composition (w/w): Cellulose (47.5%), Hemicellulose (20%), Lignin (30%), and Ash (2.5%).

Table 3. Feedstock characterization

Molecular Formula	Component	Molecular weight (g/mol)	Solid enthalpy of formation (kJ/kmol)	Specific chemical Exergy (kJ/kmol)
$C_6H_{10}O_5$	CELLULOSE	162.14	-976,362	3,404,400
$C_5H_8O_4$	HEMICELLULOSE	132.12	-762,416	2,826,640
$C_{7.3}H_{13.9}O_{1.3}$	LIGNIN	122.49	-1,592,659	3,449,500

Reactor models

Stoichiometric reactor (RStoic model) is used in the simulator to represent the reactions involved in the steam explosion process. Table 4 shows the reactions and conversion yields considered in pretreatment reactor, according to [18]. Equations 1 to 4 indicate the formation of the main components in the pretreatment reactor: xylose ($C_5H_{10}O_5$), acetic acid ($C_2H_4O_2$), furfural ($C_5H_4O_2$) and glucose ($C_6H_{12}O_6$).

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

Reactions	Yield (%)	Equation
$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5$	61.4	(1)
$C_5H_8O_4 + H_2O \rightarrow 2.5\ C_2H_4O_2$	9.2	(2)
$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3\ H_2O$	5.1	(3)
$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$	4.1	(4)

The operating conditions defined for the steam explosion pretreatment were T = 190°C, and P = 1.25 MPa. The evaluated steam consumption was 27,500 kg/h, based on experimental data reporting the range of 0.55 to 0.65 kg of steam/kg moist bagasse for moisture bagasse contents in the range of 38.6 to 65.5% [20]. Hence, in this case it was used 0.55 kg of steam/kg moist bagasse for a moisture bagasse of 50%. Additionally, it was adopted the use of SO_2 catalyst in the reactor with a rate of 2% w/w, according to the pretreatment parameters for sugarcane bagasse reported by [19].

In the simulation of the Organosolv pretreatment process the solvent was the solution [w(ethanol) 34% and w(water) 66%] according to [5]. It must be pointed out that the Organosolv model proposed was based on Organosolv pretreatment parameters for sugarcane bagasse reported by [22]. The operating conditions defined for this case were T = 185°C, and P = 2 MPa in the first stage of the process (stream PROD), with 90% lignin yield recovery in the separator (SEP1 in Figure1).

The liquid phase obtained in the two filters (SEP1 and SEP2 in Figure1) containing dissolved lignin in the Organosolv solvent, these streams are fed into the distillation column for solvent recovery as illustrated in Figure 1. In addition, it was adopted a RadFrac column distillation type to represent this equipment in the simulation operating at P = 0.5 MPa.

On the other hand it was chosen a yield reactor (RYield) in the simulation of the LHW pretreatment. In this case, it was evaluated the steam consumption rate of 18,000 kg/h based on [21]. Furthermore, it was adopted T = 200°C, and P = 5 MPa as operating parameters, with 88% xylose yield recovery [10].

The RYield model in Aspen Plus® simulator is used to represent reactions results in a product distribution with a known yield. Hence, RYield calculates the product stream flow rates based on yield distributions.

Figure 1 shows simplified schemes of the pretreatment technologies for ethanol production from lignocellulosic biomass, for selected cases (A) Steam explosion, (B) Organosolv and (C) LHW. Steady-state reaction conditions are prevalent for all cases.

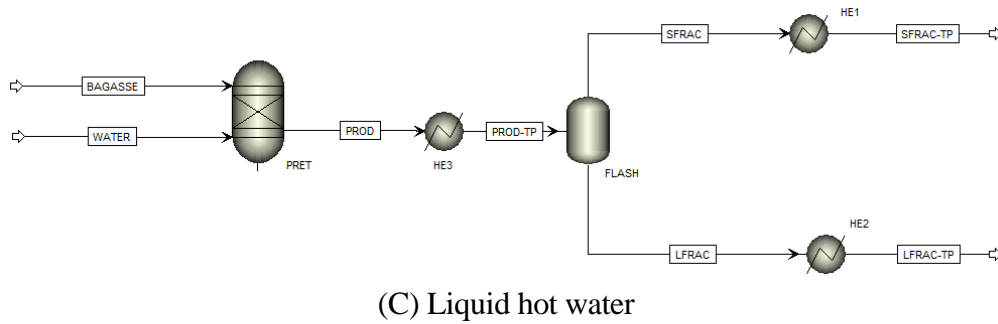(A) Steam Explosion

(B) Organosolv

(C) Liquid hot water
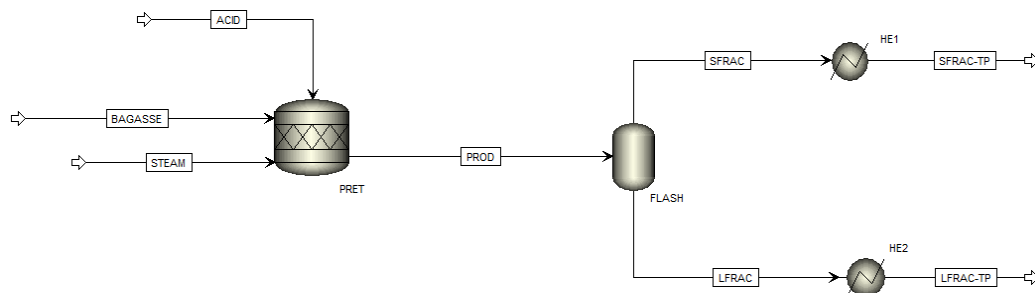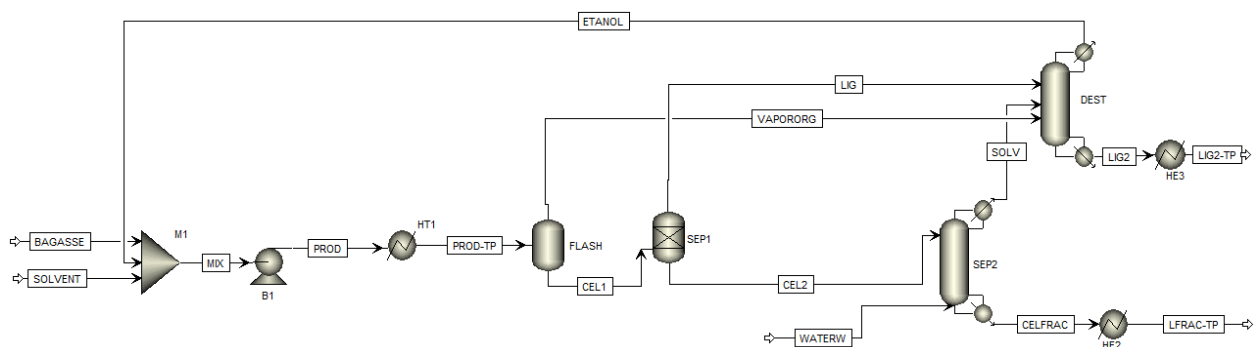
Figure 1. Schemes of pretreatment technologies modeled on Aspen Plus® software

EXERGY ANALYSIS

Exergy analysis methodology enables the identification of the steps and exergy flows with higher exergy consumption involved in the ethanol production from lignocellulosic material. This analysis also permits comparing scenarios and selecting suitable design processes for biofuels production. The reference temperature is T_0=298.15 K, and the pressure is P_0=1 bar were used as actual environmental conditions, and in order to compare all the pretreatment process in a same basis, input and output streams for all cases were evaluated at reference conditions. The chemical exergies of the different components involved in the processes are listed in Table 5, based on values reported by [6] and [23].

Table 5. Specific chemical exergy of the different components

Formula	Component	Component ID Aspen Plus	$b_{CH}^{specific}$ kJ/kmol
$C_6H_{10}O_5$	CELLULOSE	CELU	3,404,400
$C_5H_8O_4$	HEMICELLULOSE	HEMI	2,826,640
$C_{7.3}H_{13.9}O_{1.3}$	LIGNIN	LIGN	3,449,500
CO_2	CARBON DIOXIDE	CO2	19,870
C_2H_6O	ETHANOL	C2H6O-2	1,250,900
$C_6H_{12}O_6$	GLUCOSE	C6H12-01	2,793,200
$C_5H_{10}O_5$	XYLOSE	C5H10-01	1,835,300
H_2SO_4	SULFURIC ACID	H2SO4	108,600
$C_2H_4O_2$	ACETIC ACID	C2H4O-01	908,000
$C_3H_8O_3$	GLYCEROL	C3H8O-01	1,705,600
$C_5H_4O_2$	FURFURAL	C5H4O-01	2,338,700
SO_2	SULFUR-DIOXIDE	O2S	313,400
SIO_2	SILICON-DIOXIDE	SIO2	1,900
H_2O	WATER (L)	H2O	900

The composition used to calculate the chemical exergy (b_{CH}) is usually based on several correlations that can be found in [24] or [25]. It is used to correlate a fossil fuel elementary composition to its LHV. Alternatively, b_{CH} calculation for each component and for the whole stream can be evaluated as using Eq. (5).

$$b_{CH} = \sum x_i b_{CH}^{specific} + RT_0 \sum x_i \ln x_i \gamma_i \qquad (5)$$

Where $b_{CH}^{specific}$, represents the chemical exergy of the ith substance [kJ/kmol]; X_i, mole fraction of the ith substance; R, universal gas constant [J/mol K]; T_0, temperature [K]; and γ the activity coefficient. The influence of (γ) was evaluated for each compound, being observed that it provides values close to 1. For this reason, it was considered γ equals to 1 in mixtures chemical exergy calculations.

Results

Tables 6 to 8 show the values of some parameters used in the evaluation of the studied pretreatment technologies.

Table 6. Parameters of case A (steam explosion)

Streams	Mass Flow (kg/s)	T(K)	P(kPa)	h(kJ/kg)	b_{ch}(kJ/kg)	B_{tot}(kW)
BAGASSE	13.89	298.15	101.325	-24,151,100	2,574	35,752
ACID	1.39	298.15	101.325	-4,633,400	4,944	6,872
STEAM	7.64	463.15	1250	-13,110,000	50	382
SFRAC-TP	5.98	298.15	101.325	-21,813,800	1,269	7,588
LFRAC-TP	16.94	298.15	101.325	-23,051,900	1,920	32,524

Table 7. Parameters of case B (Organosolv)

Streams	Mass Flow (kg/s)	T(K)	P(kPa)	h(kJ/kg)	b_{ch}(kJ/kg)	B_{tot}(kW)
BAGASSE	13.89	298.15	101.325	-24,151,100	2,574	35,752
SOLVENT	21.39	298.15	101.325	-20,906,400	4,767	101,966
WATERW	19.08	298.15	101.325	-15,857,000	50	954
LFRAC-TP	21.97	298.15	101.325	-20,399,700	1,599	35,130
LIG2	32.39	298.15	101.325	-27,134,000	2,584	83,695

Table 8. Parameters of case C (LHW)

Streams	Mass Flow (kg/s)	T(K)	P(kPa)	h(kJ/kg)	b_{ch}(kJ/kg)	B_{tot}(kW)
BAGASSE	13.89	298.15	101.325	-24,151,100	2,574	35,752
WATER	5.00	538.15	5100	-15,032,000	50	250
SFRAC-TP	12.91	298.15	101.325	-14,660,000	1,751	22,605
LFRAC-TP	5.98	298.15	101.325	-8,695,900	1,904	11,385

In the exergy analysis performed in this paper, the exergy destroyed rate and the exergy efficiency were calculated for each case. Exergy destroyed rate represents the loss of quality of materials and energy. An efficiency comparison, in terms of exergy output/total exergy input, and exergy destroyed rate of the studied cases is summarized in Table 9.

Table 9. Performance comparison of the simulated pretreatment processes

	Case A	*Case B*	*Case C*
Pretreatment	*Steam Explosion*	*Organosolv*	*LHW*
Exergy Efficiency (%)	93.27	85.68	94.42
Destroyed exergy rate (MW)	2.89	19.84	2.01

High exergy efficiency values were reported for all cases. However, an exergy efficiency of 85.68% was observed for case B, and this value is a consequence of the greatest irreversibility rate observed due to the amount of organic liquid (aqueous ethanol solution) involved in pretreatment process. As can be observed in Table 9, cases A and C have exergy efficiencies close to 94%.

The destroyed exergy rate was 2.89 MW for case A and 2.01 MW for case C. On the other hand, high destroyed exergy rate (19.84 MW) was achieved for case B. A comparison between the exergy performance of pretreatment process A and B obtained in this study with [5] indicates that the difference of the destroyed exergy and exergy efficiency values was not higher than 6% and 2%, respectively.

It is worthy of note that the obtained values of destroyed exergy rate for the three analyzed pretreatment process are very high compared to the input bagasse exergy rate: 8.1% for case A, 55.5% for case B, and 5.6% for case C, highlighting the relevance of such process in the overall exergy efficiency of second-generation ethanol production routes.

CONCLUSIONS

Pretreatment technologies published in literature were described in terms of the mechanisms involved, advantages and disadvantages. Tables 1 and 2 give a summary of the main pretreatment routes and their major characteristics for a number of 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, economic assessment and environmental impact, but also on the process exergy efficiency. This physical quantity allows a better analysis of the alternatives to improve a given production process, moreover the exergy analysis takes into account the quality of energy conversion processes.

In this study, three sugarcane bagasse pretreatment processes were simulated. The results show high exergy efficiencies in cases A (Steam Explosion) and C (LHW) reaching 93.27% and 94.42%, respectively. Steam explosion using SO_2 as a catalyst proved to be an effective pretreatment, which is mainly attributed to the use of acid catalyst that increases the recovery of hemicellulose sugars and decreases the production of inhibitory compounds. The LHW method, the one with the lowest exergy consumption, has also the advantage of eliminating the need for a final washing step or neutralization because the pretreatment solvent is water.

NOMENCLATURE

T: Temperature (°C);
P: Pressure (MPa);
Rt: Reaction time (min);
Sl: Solids loading;
w/w: Weight/weight (%).

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