

Article

Energy Efficiency of Biorefinery Schemes Using Sugarcane Bagasse as Raw Material

Daissy Lorena Restrepo-Serna ¹, Jimmy Anderson Martínez-Ruano ^{1,2} and Carlos Ariel Cardona-Alzate ^{1,*}

¹ Departamento de Ingeniería Química, Instituto de Biotecnología y Agroindustria, Universidad Nacional de Colombia sede Manizales, Manizales 170003, Colombia; dlrestrepos@unal.edu.co (D.L.R.-S.); jiamartinezru@unal.edu.co (J.A.M.-R.)

² Escuela de Ingeniería Bioquímica, Pontificia Universidad Católica de Valparaíso, Valparaíso 23400000, Chile

* Correspondence: ccardonaal@unal.edu.co; Tel.: +57-6-8879300 (ext. 50417); Fax: +57-6-8879300 (ext. 50452)

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Abstract: The use of biomass to obtain value-added products has been a good alternative for reducing their environmental impacts. For this purpose, different studies have been carried out focused on the use of agro-industrial waste. One of the most commonly used raw materials has been bagasse obtained from the processing of sugarcane in high quantities in countries like Brazil, India, China, Thailand, Pakistan, Mexico, Colombia, Indonesia, Philippines, and the United States. From 1 ton of sugarcane, 280 kg of bagasse can be obtained. Sugarcane bagasse (SCB) is a waste that is rich in polysaccharides, which makes it a promising raw material for obtaining products under biorefinery concept. The objective of this work was to analyze from the energetic point of view, different biorefinery schemes in which SCB is employed as a raw material. The design and simulation of the different biorefinery schemes is performed in Aspen Plus software. From this software, it was possible to obtain the different mass and energy balances, which are used in the technical and energetic analysis. Exergy is used as a comparison tool for the energy analysis. These analyses allowed for the selection of the best biorefinery configuration from SCB.

Keywords: biorefinery; sugarcane bagasse; exergy analysis; energy analysis

1. Introduction

In the processing of agricultural products, different types of waste are generated. This represents an environmental problem in terms of their final disposal. In order to reduce the environmental impact that is caused by these wastes, different studies have been carried out to evaluate their potential to be used in different transformation processes, to obtain additional value-added products [1–4]. From these different renewable raw materials, several studies have been carried out that are focused on the use of agro-industrial waste [1,5]. One of the most commonly used raw materials is sugarcane bagasse (SCB), a residue that is obtained from sugar production [6,7]. From 1 ton of processed sugarcane, 280 kg of bagasse are generated [8]. Sugarcane has a high rate of production in countries such as Brazil, India, China, Thailand, Pakistan, Mexico, Colombia, Indonesia, Philippines, and the United States [9]. Between 2014 and 2015, the world production of sugarcane accounted for 175.1 million metric tons [10]. SCB is a residue that is rich in polysaccharides, and that is widely studied in the production of biofuels [11], and chemicals such as ethanol, xylitol, electricity, biopolymers, antioxidants, and lactic acid, among others [2,12,13]. SCB has a high potential for the generation of energy through the application of the gasification process [12]. Therefore, the development of biorefineries from SCB has been analyzed in many studies, with a great variety of configurations [14–16].

One of the variables to be considered in the design of processes is energy that is usually consumed in large quantities in biorefineries, due to the different processing stages that are involved [17]. A tool that allows for evaluation beyond the energetic changes in a process is the exergy analysis [18–20]. From thermodynamics, exergy is defined as the maximum amount of work that can be generated by a system (including mass and energy flows) once a thermodynamic equilibrium with the environment is achieved [21–24]. Compared to the energy, the exergy of a system is not conserved [25]. This fact is because of the entropy changes that are caused by physical and chemical conversions that are associated with irreversible processes. The calculation of these changes gives a more detailed idea of the phenomena that are involved in each processing unit, allowing for a deeper identification of the energy changes caused by each unit involved in a process [26]. Moreover, exergy analysis can be used to compare different technologies, or where appropriate, to compare similar processes with different raw materials.

SCB is a raw material with a high content of polysaccharides, which can be used in different transformation processes. According to the technology and the processing route used, it is possible to obtain a wide variety of products. From SCB, it is possible to obtain sugar monomers such as glucose and xylose, which can be used as platforms for obtaining different products. Both xylose and glucose can be used in the fermentation processes to obtain compounds such as butanol, ethanol, lactic acid, xylitol, succinic acid, arabitol, and poly-3-hydroxybutyrate (PHB), among others [7,8,13,27–32]. When xylose and glucose are used in the dehydration processes, furfural and hydroxymethylfurfural (HMF) are obtained, respectively [33–35]. These compounds can be used as platforms to obtain different products. Based on this information, an analysis of the energy efficiency of three biorefineries in which SCB is used as raw material is carried out in this work. For the energy analyses, the distribution of the energy flow at the input and output of each biorefinery is determined, in order to determine the quality of this energy. The latter is commonly known as the base for exergy analysis.

2. Methodology

2.1. Process Simulation

In the present work, three scenarios based on SCB as a raw material for obtaining products such as furfural, HMF, nonane, octane, syngas, and electricity are analyzed. The composition of SCB used in this work is described in Table 1. In the first scenario, the processes of acid pretreatment, detoxification, and enzymatic hydrolysis for the production of xylose and glucose are considered, which were transformed into furfural and HMF by dehydration processes. In the second scenario, the same processes used in scenario 1 are considered, but furfural and HMF are used to obtain octane and nonane, respectively. The third scenario is based on scenario 2, to which was added a cogeneration stage, in which syngas and electricity were obtained. Figure 1 shows the connection between the different processes that were used to obtain each of the products corresponding to each proposed scenario. The conditions and main equipment of each process are presented in Table 2. The simulation of each scenario is performed in the Aspen plus software (v 9.0, Aspen Technology, Inc., Houston, USA). The nonrandom two-liquid (NRTL) thermodynamic model was applied to calculate the activity coefficients of the liquid phase, and the Hayden-O'Connell equation of state was used to describe the vapor phase. In the case of the octane production, the Soave Redlich Kwong (SRK) equation of state was used. The raw material flow at high scale was 2.9 million metric tons, which represented the 6% of the world production of SCB between 2014 and 2015. For the purification of each of the components of interest, the corresponding phase balances were analyzed in order to determine the major separation process [33]. In the case of the distillation columns, the DSTWU short-cut method included in the Aspen plus software was employed, which uses an approximate method based on Winn–Underwood–Gilliland equations and correlations. With this module, an initial estimate of the number of theoretical stages, the reflux number, the location of the feed stage, and the distribution of the components can be obtained. The rigorous calculation of the separation units was

carried out in the RadFrac module. This module is based on the inside-out equilibrium method that uses the MESH equations (Mass balance equations, phase Equilibrium equations, Summation of the compositions, and Heat balance equations), which involves the simultaneous solution of the mass balance, phase equilibrium, summation expressions, and equations of heat balance of all components in all stages of the distillation column [30,36–38].

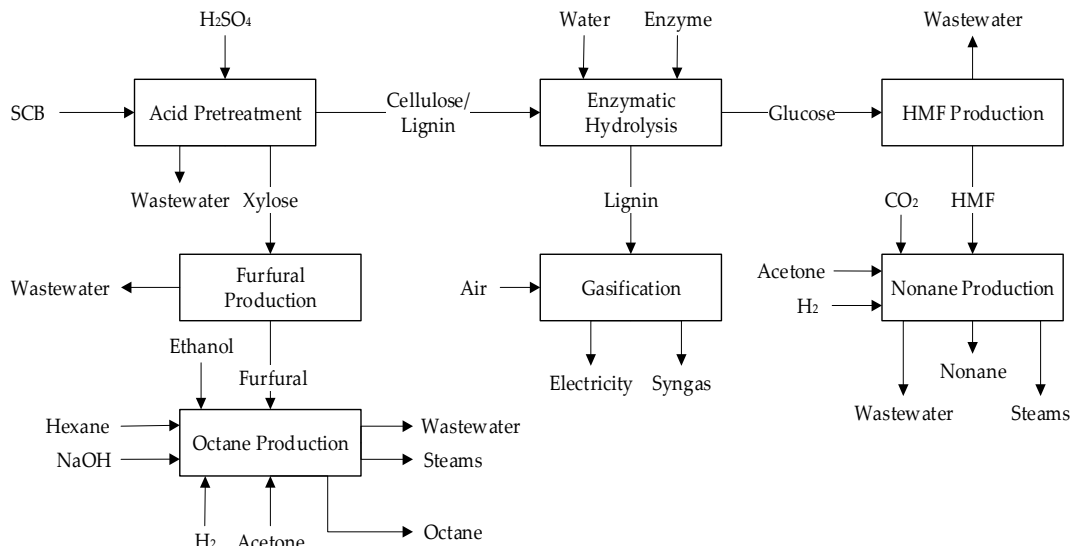


Figure 1. Flowsheet for SCB processing.

Table 1. Composition of sugarcane bagasse (SCB) employed in this work [39].

Component	Moisture	Cellulose	Hemicellulose	Lignin	Protein	Ash
Percent	50.00	23.70	12.05	11.70	2.40	1.15

Table 2. Conditions and main equipment used in each processing stage.

Stage	Purpose	Conditions	Reference
Acid hydrolysis			
Crusher	Size reduction to 0.5 mm	1 bar	[40,41]
Dilute acid reactor	Removal of hemicellulose as xylose	1 bar, 122 °C, 2% H ₂ SO ₄	
Filter	Separation of xylose from cellulose and lignin	1 bar	
Enzymatic hydrolysis			
Enzymatic reactor	Cellulose to glucose	1 bar, 50 °C, cellulose (25 IU/g)	[42]
Filter	Separation of glucose from lignin	1 bar	
Detoxification			
Detoxification reactor	Neutralizing the acid with Ca(OH) ₂	1 bar, 60 °C	[43]
Filter	Removal of salts present in the xylose solution	1 bar	
Furfural production			
Xylose dehydrator	Furfural production	10 bar, 170 °C	[44]
Decanter	Furfural concentration	1 bar, 25 °C	[45]
Octane production			
Aldol-condensation reactor	Aldol-condensation of furfural with acetone	1 bar, 85 °C, catalyzed by MgO/NaY	[46]
Mild-hydrogenation reactor	Mild-hydrogenation of aldol products	2.5 MPa, 140 °C, catalyzed by Pt/Co ₂ AlO ₄	[47]
Dehydration/hydrogenation reactor	Octane production	2.5 MPa, 170 °C	[47]
	Octane separation	One-column: 12 trays, 1.405 reflux ratio, total condenser, 4 bar Two-column: 29 trays, 1.224 reflux ratio, total condenser, 1 bar	
HMF production			
Glucose dehydrator	HMF production	10 MPa, 220 °C	[48]
Decanter	HMF separation	1 bar, 25 °C	[49,50]
Nonane production			
Aldol-condensation reactor	Aldol-condensation of HMF with acetone	1 bar, 50 °C, MgO/ZrO ₂ ad catalyst	[35]
Hydrogenation reactor	Hydrogenation of aldol products in supercritical carbon dioxide	12 MPa, 80 °C, Pd/Si-Al-MCM-41 as a catalyst	[34]
Dehydration/hydrogenation reactor	Nonane production	4 bar, 80 °C	[34]
Distillation column	Nonane separation	13 trays, 1.185 reflux ratio, total condenser, 1 bar	

Table 2. Cont.

Stage	Purpose	Conditions	Reference
Gasification			
Gasifier	Syngas production	6 MPa, 850 °C	[51,52]
Turbine	Electricity generation	1 bar	[53]

2.2. Energy and Exergy Analysis

The energy of a system is related to its transformation capacity. This relation is of great importance when it considers processes in which different transformations are carried out to obtain a range of value-added products [54,55]. The purpose of the exergy analysis is to identify the energy consumption in a system, as well as the nature of these consumptions. For this analysis, the energy balances obtained from the Aspen Plus software v 9.0 are used as input data. This information is used to gradually perform the energy balance for each unit into the biorefinery.

From the analysis of energy, and especially that of the exergy, the identification of the zones of the process, in which the main energy changes occur. In this way, it is possible to take measures in order to obtain maximum yields in terms of conversion or separation processes and above all, the energy yields involved in each stage [56–58].

Equation (1) describes the exergy balance for a system in a steady state, which considers the exergy transfer that is associated with the mass flows of the system, and the heat and work flows. In addition, it considers the exergy that is destroyed during the process, which is associated with the irreversibilities of the process [59,60]:

$$\frac{dEx}{dt} = Ex_Q - Ex_W + Ex_{flow} - Ex_{dest} \quad (1)$$

For a system in a steady state, in which there are no variations in properties over time, Equation (3) (obtained by equating the Equation (1) to zero) represents the exergy balance, where the terms associated with the flow of exergy by mass, heat, and work can be calculated by using Equations (5), (11) and (12), respectively. In this way, it is possible to determine the term of destroyed exergy (Equation (4)) using Equation (3):

$$0 = Ex_Q - Ex_W + Ex_{flow} - Ex_{dest} \quad (2)$$

$$Ex_{dest} = Ex_Q - Ex_W + Ex_{flow} \quad (3)$$

The exergy change associated to mass flows is divided into four main components: physical, chemical, potential and kinetic exergy [60–62]:

$$Ex_{flow} = Ex^{ph} + Ex^{ch} + Ex^{ki} + Ex^{po} \quad (4)$$

Some authors report that the contributions made by the terms of kinetic and potential exergy are very low compared to the contributions made by the terms of physical and chemical exergy [17,60–62]. Then, these terms can be ignored, so Equation (4) is reduced to:

$$Ex_{flow} = Ex^{ph} + Ex^{ch} \quad (5)$$

Physical exergy is defined as:

$$Ex^{ph} = \sum_i n_i ex_i^{ph} \quad (6)$$

$$ex_i^{ph} = (h_j - h_o) - T_o(s_j - s_o) \quad (7)$$

The differences $(h_j - h_o)$ and $(s_j - s_o)$ can be calculated from Equations (8) and (9):

$$(h_j - h_o) = \int_{T_o}^{T_j} C_p dT \quad (8)$$

$$(s_j - s_o) = \int_{T_o}^{T_j} \frac{C_p}{T} dT - R \ln\left(\frac{P}{P_o}\right) \quad (9)$$

While physical exergy considers temperature and pressure deviations, chemical exergy refers to deviations in the chemical composition of the system with respect to the environment. These deviations mainly involve the calculation of chemical reactions (reactive exergy), and mixing and separation processes (non-reactive exergy). The chemical exergy (Equation (10)) is calculated to take into account the standard exergy of each component (ex_i^{ch}), which can be found in the literature (see Equation (10)) [63,64].

$$Ex^{ch} = \sum_i n_i \left(ex_i^{ch} + RT_o \ln\left(\frac{n_i}{\sum n_i}\right) \right) \quad (10)$$

The exergy associated with the transfer of energy in the form of heat depends on the temperature at which it is produced in relation to the temperature of the reference in a stable environment. Thus, the heat exergy is determined as employed the Equation (11). The exergy transfer associated with the work is determined to be equal to the mechanical work that is supplied per stage (Equation (12)) [65].

$$Ex_Q = \int_{T_1}^{T_2} \left(1 - \frac{T_o}{T} \right) \delta Q \quad (11)$$

$$Ex_W = W_{1,2} \quad (12)$$

Using Equations (3), (5)–(12), the flow of exergy that is destroyed in each of the equipment that is involved in each transformation process was determined. These values were used to determine the amount of exergy destroyed in each process stage. The reference conditions were used to perform the calculations were 25 °C and 1 bar.

3. Results

3.1. Process Simulation

In the present work, a SCB flow of 357,300 kg/h is considered, with the composition being presented in Table 1. The main components of SCB (cellulose, hemicellulose, and lignin) are considered as the basis for obtaining value-added products. Through the acid pretreatment process, the xylose fraction is obtained, which is used for the production of furfural, being this a platform to obtain products such as octane. From the enzymatic hydrolysis of the cellulose (component of the solid fraction obtained in the acid hydrolysis) glucose is obtained. It can be transformed into HMF, and at the same time, this is transformed into nonane. The remaining solid (lignin) is subjected to a gasification process, resulting in the production of syngas, which by pressure, can be used to generate electricity. Considering the composition of the SCB used, and the process conditions presented in Table 2, glucose, xylose, and lignin flows of 80,782, 29,033, and 41,414 kg/h are obtained, respectively. The transformation of glucose and xylose into HMF and furfural resulted in flows of 55,196 and 16,573 kg/h of HMF and furfural, respectively. Then, the transformation of these platforms allowed flows of 38,527 and 10,135 kg/h, of nonane and octane to be obtained, respectively. The gasification of the lignin with air as a gasifying agent in a ratio of 1:3 generated a flow of syngas of 88,992 kg/h, which was used in electricity generation to produce 0.48 kW per kg of syngas processed. Based on the flows obtained under the analyzed conditions, SCB has a greater potential for obtaining glucose than obtaining xylose. This is because this raw material presents a greater composition of cellulose compared to the composition of hemicellulose, showing the potential of SCB to obtain products derived from glucose, such as HMF, nonane, ethanol, lactic acid, and others [30–32].

Based on the composition presented by SCB, other raw materials such as empty fruit bunches, oil palm rachis, and coffee cut-stems could have similar yields to the ones obtained above [37,66,67]. If the SCB (raw material) is changed to rice husks, the yields that could be obtained from both nonane and octane would be nearly the same, since this raw material has a similar composition of cellulose and hemicellulose [66].

3.2. Energy and Exergy Assessment

To present the energy balances obtained, Sankey diagrams are used. The results obtained are presented in Figure 2. The diagrams consider at the input the energy potential of the raw material (SCB) and the energy requirements, which consider the energy that is present in each of the utilities used in the respective process. The outputs of the Sankey diagram show the percentage of energy, present in each of the products obtained in each scenario, in the totality of the waste generated. Based on the energy balance, the energetic losses in each scenario are determined.

From the energy balances, the energy flows required in each of the scenarios are calculated, giving as results 13.10, 14.80 and 14.87 MJ per kg of SCB processed. A comparison between scenarios 1 and 2 shows that the use of scenario 1 products (furfural and HMF) as platforms for obtaining octane and nonane leads to an increase in the utility flows. This additional energy is required in each of the equipment that is used in the corresponding processes of transformation and purification of octane and nonane. With regard to the distribution of energy at the outlet, it can be seen that scenario 2, presenting a greater number of processing stages, evidences a high-energy content (but also producing a higher quantity of waste). These wastes represent more than 50% of the energetic potential of the process. On the other hand, the transformation structure of scenario 2 contributes to the reduction of the energy losses of the process. The wastes obtained in both scenario 1 as in scenario 2 present the same amount of solids (SCB which did not react and lignin obtained during enzymatic hydrolysis), salts (generated during detoxification process), and water. The difference between the energy content of these scenarios resides in the additional quantity of wastes that are generated in scenario 2 during the production of octane and nonane. In scenario 1, in addition to the previously mentioned residues, water (product of the processes of concentration and purification of furfural and HMF), xylose, and glucose that did not react in the respective processes are mainly wasted. In addition to all the residues mentioned above, in scenario 2, acetone, ethanol, and different intermediary products generated during the transformation processes of furfural and HMF into octane and nonane are discarded, respectively. Based on these results, it is evident that there is a need to implement processes that allow the transformation of these wastes into other value-added products, where the transformation processes implemented contribute to the reduction of the energy potential that is present in the wastes of the processes analyzed.

When comparing scenarios 2 and 3, no considerable variation in the percentage distribution of the energy content of the raw material and process utilities is evident. The similarity in the values is caused by the gasification process itself, which has a tendency to be a process that can provide its own energetic needs, so that it does not contribute to a significant measure to increase the energetic requirements of the global process. The addition of this process to scenario 2 contributes to decrease the amount of generated waste, as well as the amount of energy losses from the process. The above confirms that the use of a biorefinery scheme to use the largest amount of raw material components to be upgraded into value-added products allows for a more efficient use of the energy potential present in the raw material to be obtained.

In order to provide a more detailed analysis of the energy, the exergy is calculated at each stage of the process to obtain the flow of exergy destroyed in each of the scenarios analyzed. The exergy flows destroyed in MJ/h in scenarios 1, 2, and 3 are 28,533, 33,672, and 43,831, respectively. The change in the exergy flows in scenarios 1 and 2 results as a consequence of the increase in the energy requirements of the process. In addition, it also results as a consequence of the chemical exergy resulting from the transformation processes carried out for the conversion of furfural and HMF into octane and nonane,

respectively. Moreover, scenario 3 has the highest flow of exergy that is destroyed by a greater use of the raw material. In each of the scenarios analyzed, the increase in destroyed exergy is correlated to the irreversibilities that are associated to the different transformation processes, as well as the inefficiencies presented in each case. Among the inefficiencies highlighted are the energy losses in each process, as well as the conversions below 100%.

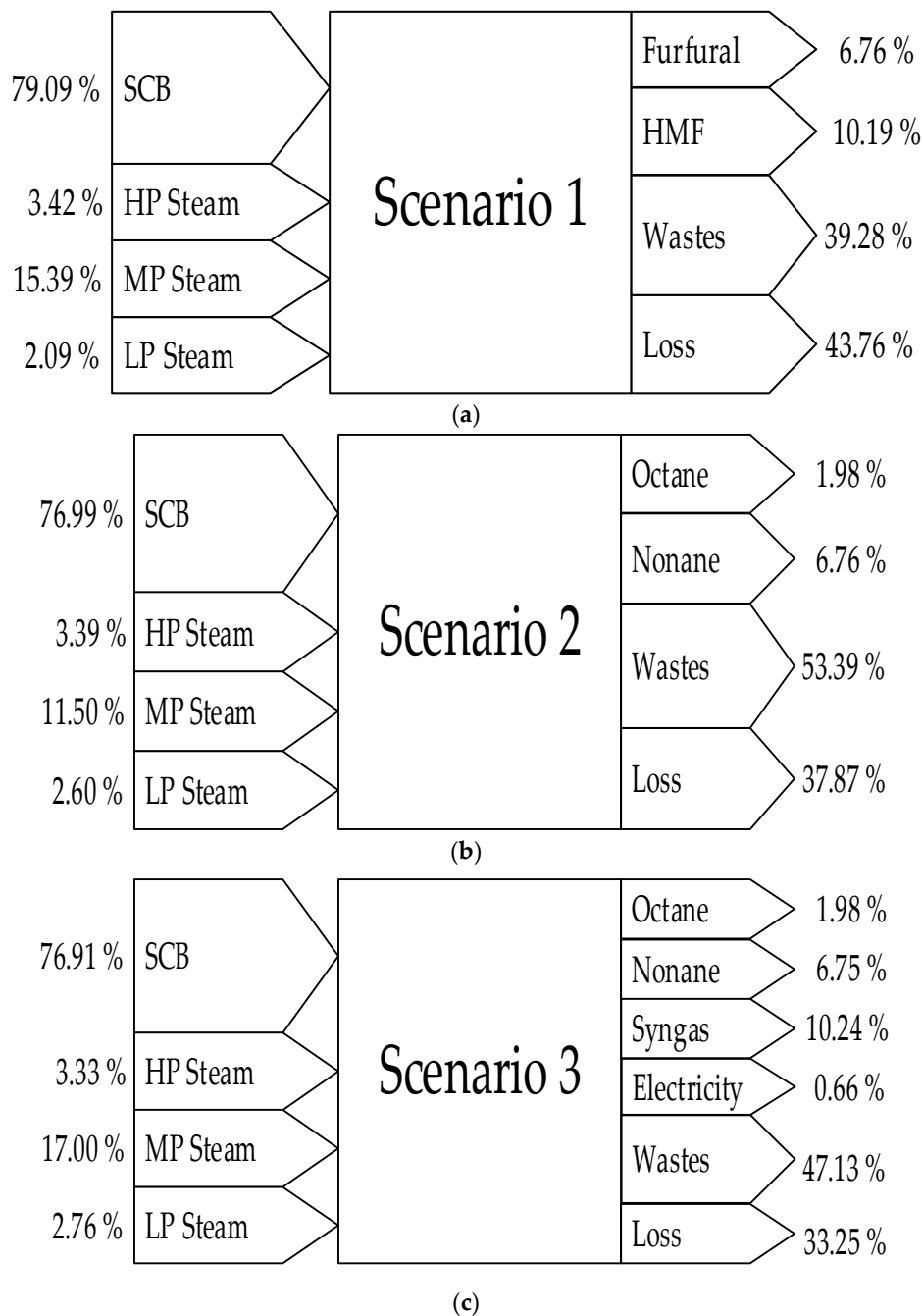


Figure 2. Sankey diagrams for the energy distribution of scenarios 1, 2, and 3. (a) Energy distribution in the scenario 1; (b) Energy distribution in the scenario 2; (c) Energy distribution in the scenario 3.

Through the analysis of the exergy, the stages that presented the highest contributions to the value of the destroyed exergy in each scenario are determined. The contribution to the total value of exergy destroyed in each scenario for each stage is presented in the Table 3. Stages such as detoxification, furfural production, and gasification presented the greatest contributions to the destroyed exergy

value in each case, with values of 7572, 7537 and 10,159 MJ/h, respectively. The detoxification process mainly involves the neutralization of the acid that is used in the acid hydrolysis stage, which leads to the formation of a salt with high irreversibility, due to the stability of the products obtained. The production process of furfural (obtained by the dehydration of pentoses such as xylose) has a high-energy consumption from the operating conditions that is used. The contribution of the energy used in the process is reflected in the term Ex_q . Finally, the process of gasification constitutes the destruction of the solid compounds structure to result in the formation of different gases. Since the phenomena are involved in both the production of furfural and the gasification process, the term physical exergy contributes greatly to these values. Here, the term that presents the greatest relevance is the entropy, evidencing the irreversibilities of these processes. Together with these same reasons and the low yields in the transformation processes, these are the causes of the decrease in the exergy flow when using both furfural and HMF as chemical platforms.

Table 3. Exergy efficiency by stage in each scenario.

Stage	Scenario 1	Scenario 2	Scenario 3
Acid hydrolysis	17.75	15.04	11.55
Detoxification	26.54	22.49	17.28
Enzymatic hydrolysis	20.98	17.78	13.66
Furfural	26.41	22.38	17.20
HMF	8.32	7.05	5.41
Octane	-	8.86	6.81
Nonane	-	6.40	4.92
Gasification	-	-	23.18

An energy comparison of the three scenarios shows that from scenario 3, it is possible to obtain a more efficient use of the energy present in the SCB. The scenarios 1, 2, and 3 presented an exergy of 0.08, 0.09, and 0.12 MJ per kg SCB. Scenario 3 presents a higher energy quality than the other two scenarios, i.e., it presents a higher value of exergy per kg of processed SCB. Thus, it shows that with the transformation of glucose and xylose into other products, the exergy of the process does not show considerable variations. Nevertheless, with the addition of the gasification stage, the exergetic flow presents a considerable increase, because this process allows the generation of electricity, which contributes to has a higher utilization of the energy that is present in the raw material. This can be observed in the exergetic efficiencies of each stage for each scenario, which are present in Table 3.

In order to evaluate each one of the transformation routes that are presented for the SCB from an exergetic perspective, the cumulative exergy is determined as the sum of the flow of exergy of each of the stages that are involved in the transformation route to obtain a product. The results obtained in this work are presented in Figure 3. This figure shows three possible transformation routes for SCB: the first (line continue) follows the gasification process, the second (dotted line) follows the process of obtaining and transforming xylose, and the third (discontinuous line) follows the process of obtaining and transforming glucose. The processes of obtaining octane and nonane presents a similar value of accumulated exergy, so from an exergetic point of view, it is not possible to select one transformation route or another. However, which of the two transformation routes has the best exergetic behavior could be determined, by evaluating different transformation alternatives for each case. With regard to the gasification process, it is evident by the nature of this process that it exhibits the highest value of cumulative exergy. Therefore, the SCB has a higher potential to be used in thermochemical processes such as gasification over chemical and biochemical processes [68–70]. The main reason for this are the low yields that can be obtained in these last two types of processes.

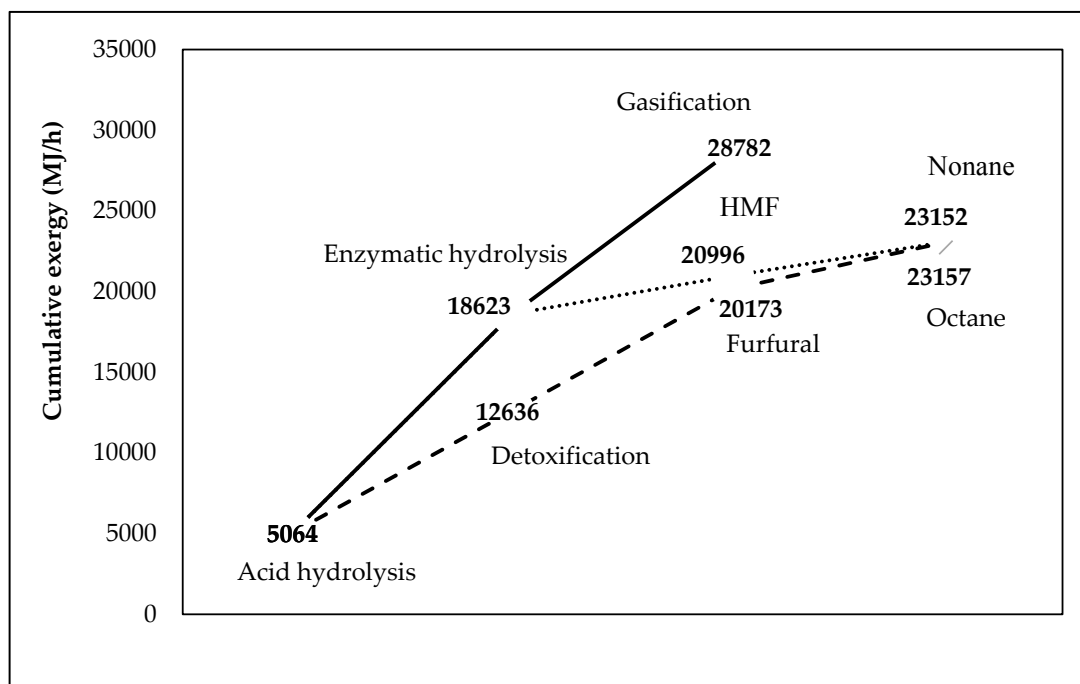


Figure 3. Cumulative exergy based on the transformation route.

4. Conclusions

The addition of processing stages can lead to a reduction in the energy losses of the process. However, this causes an increase in the energy potential of the process waste by increasing its mass flow. In order to identify the best transformation route in both technical and energy terms, it is necessary to evaluate different transformation alternatives.

As is demonstrated in this work, the exergy analysis allows for an understanding of the process possibilities. This means the prediction of the energy yield, as well as the efficiency of the process. These analyses allow for the identification of inefficient energy zones in the process, and which of these can be optimized through technological improvements, enabling the maximization of operational efficiency. In this sense, the exergy analysis is presented as a tool for the formulation of solutions to the techno-economic problems that are presented in industrial processes.

Among the possible transformation routes that can be presented for SCB, the route proposed in scenario 3 is presented as the best alternative transformation in terms of energetics, considering the options of transformation that are evaluated.

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