Comparison of Biobutanol Production Pathways via Acetone–Butanol–Ethanol Fermentation Using a Sustainability Exergy-Based Metric

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ABSTRACT: The incorporation of sustainability aspects into the design of chemical processes has been increasing since the last century. Hence, there are several proposed methodologies and indicators to assess chemical facilities through process analysis techniques. A comprehensive assessment involving economic, environmental, safety, and exergy parameters of two alternatives for butanol production from Manihot esculenta Crantz (cassava waste) is presented in this study. The modeling of process topologies involved using Aspen Plus software. Topology 1 generated a product flow rate of 316,477 t/y of butanol, while this value was 367,037 t/y for topology 2. Both processes used a feed flow of 3,131,439 t/y of biomass. This study used seven technical indicators to evaluate both alternatives, which include the return of investment, discounted payback period, global warming potential, renewability material index, inherent safety index, exergy efficiency, and exergy of waste ratio. Otherwise, this study implemented an aggregate index to assess overall sustainability performance. The results revealed that topology 2 presented higher economic normalized scores for evaluated indicators, but the most crucial difference between these designs came from the safety and exergetic indexes. Topology 1 and topology 2 obtained weighted scores equaling to 0.48 and 0.53; therefore, this study found that the second alternative gives a more sustainable design for butanol production under evaluated conditions.

1. INTRODUCTION

Fluctuating prices and the exposure to risks in the supply of fossil resources, along with an increase in the demand for liquid fuels, led to a keen interest in developing novel ways to generate fuels and value-added chemicals from renewable resources. Furthermore, emission of chemicals into the environment derived from the economic activities of many sectors, along with the overuse of nonrenewable resources, has pressured the society to fulfill human necessities. The concept of sustainability and sustainable design emerges as a response to mitigate the effects generated by the traditional economy, seeking to ensure the current needs without compromising future generations. Jia et al. mentioned that the application of the sustainability framework involves efforts and strategies to minimize the consumption of goods and services to reduce releases and simultaneously raise profits and social assets. In terms of the chemical industry, energy, and manufacturing sectors, the challenge is on track for including sustainability concepts. Therefore, the sustainable design approach has come up as a return to the efforts made for achieving pollution prevention, reduction of greenhouse gases (GHG), and valorization of crop residues, among others. The above-mentioned point relates to the need for changing the conventional technologies to generate alternatives based on a more sustainable chemical processing. These include the sustainable use of lignocellulosic materials as well as agricultural wastes for large-scale production of biofuels such as ethanol, biodiesel, butanol, or chemical substances such as succinic acid, acetic acid, levulinic acid, and acetone, among others.

Biobutanol is considered as a substance that has the potential to replace fossil-based fuels because of its high energy content, relatively low volatility, and affinity with water mixtures. This chemical is mostly generated at industrial scale from petroleum-based derivatives through the exo process by using propylene. As aforementioned, recent efforts have been...
made to develop suitable designs for large-scale production of butanol via acetone–butanol–ethanol (ABE) fermentation by consuming residues and waste biomass. This process has the potential to be a more sustainable alternative than fossil-based process. Butanol production via ABE fermentation has attracted much interest because this technology generates three main products, taking lignocellulosic biomass as a suitable feedstock for its processing. There are many ways to produce biobutanol through ABE fermentation, so many investigations have shown interest in studying technical aspects about this type of process. Jiang et al. described perspectives on butanol production using lignocellulosic materials, indicating that the solventogenics Clostridium beijerinckii and Clostridium acetobutylicum cannot be directly employed on this type of feedstock. Al-Shorgani et al. investigated the Clostridium acetobutylicum cannot be directly employed on the expected behavior addressed by other studies. Another relevant aspect of ABE fermentation processing is the requirements of downstream technologies, considering the complex equilibria between gases and solvents formed during the bioreactions. Contreras-Vargas et al. evaluated alternatives for ABE purification, including hybrid sequence, liquid−liquid extraction, and distillation columns. Sánchez-Ramírez et al. optimized alternatives of biobutanol purification topologies counting total annualized costs (TAC). Integrated batch fermentation and in situ gas stripping configuration was assessed, considering kinetics and rigorous phase equilibria.

There are limitations regarding biobutanol production associated with the inhibitory effect of fermentation reactions, the requirement of a pretreatment stage to extract reduced sugars, or the design of complex downstream processing as a result of the chemical affinity between the byproducts, and the tendency of these to form azeotropes in water mixtures. Therefore, the selection of processing stages in the production of biobutanol from lignocellulosic biomass becomes a crucial aspect as it allows generating alternatives that are feasible and environmentally friendly. Furthermore, the application of computer-aided process analysis instruments provides decision-making assets that allow the identification and selection of the most suitable routes. In this line, Kumar et al. implemented a techno-economic assessment of a biobutanol production pathway based on ABE fermentation from the transformation of cellulose and noncellulosic-based materials. Patrašcu et al. included energetic aspects for performing biobutanol separation technologies and proposed a new intensified configuration via vapor recompression to reduce energy consumption. A scheme of ABE fermentation was simulated via Aspen Plus, demonstrating the advantages of modeling this topology for further analyses.

Current tendencies regarding sustainability and cleaner production are showing that the notion of traditional chemical processes is shifting in response to the demand for the development of novel technologies. Such changes include the design of topologies that represents lower environmental effects, higher efficiencies in terms of energy, and more reliable and safe operations. Likewise, process analysis tools offer a useful framework for incorporating the concept of sustainability in the design of chemical production topologies. Several methods and indicators have been used for assessing processes in terms of sustainability. Li et al. presented a sustainability assessment of biofuel production processes incorporating exergy and inherent safety analyses. Sidar et al. discussed the application of different types of aggregate indicators into a single sustainability index for the evaluation of chemical processes. Yang et al. evaluated a coal/biomass Fischer–Tropsch process for fuel production using a multidimensional set of metrics considering economics, environmental, and societal aspects. Smith et al. used the GREENSCOPE indicators for sustainable computer-aided process analysis for the oxidation of toluene, establishing best and worst-case limits. Ruiz-Mercado et al. used Green Chemistry principles with process engineering foundations to assess and design chemical processes in sustainability terms.

The application of a weighted indicator for simultaneous evaluation of projects and alternatives has attracted recent interest. El-Halwagi presented the sustainability weighted return on investment metric (SWROIM), which integrates the conventional return of investment (ROI) estimation with technical indicators in order to show a value that is easy to read by the decision makers. Guillon-Cuevas et al. proposed a novel weighted indicator by incorporating safety and sustainability indicators in conceptual design via ROI. This index, called the safety and sustainability weighted return on investment metric (SASROIM), uses the normalization of technical indexes and weighting factors to generate a single indicator that allows the straightforward selection of evaluated alternatives. Moreno-Sader et al. addressed an integrated approach for evaluation of safety, sustainability, reliability, and resilience via the return on investment metric, introducing the safety, sustainability, reliability, and resilience weighted return on investment metric (S2R2WROIM). Table 1 summarizes relevant contributions regarding this topic to establish the gap between the reported literature on process analysis under sustainability aspects and this study.

As described, an essential advantage of the application of aggregate or weighted sustainability indexes is that these allow a better interpretation of obtained performance by the
application of several technical indicators. Besides, analyzing in detail previous contributions, it is palpable that many of these did not consider the relevance of including exergy aspects in the evaluation of process sustainability. Therefore, the opportunity of counting the effects associated with exergetic analysis and exergy concept might involve the knowledge of the real effective energy/work generated or consumed within a process (and sources of irreversibilities), which remains as a crucial aspect under the sustainable design approach. Taking into account the vast potential for the use of food crops in the generation of biobutanol, the availability of several processing pathways and the extensive set of technical metrics for the measurement of chemical processes, this study presents a comparison of two ABE fermentation topologies by using an aggregate sustainability metric. The abovementioned fact as an intent to seek process improvements allows the valorization of the autochthonous residual material from North Colombia. In this case, the metric includes the evaluation of exergy parameters, and the insights offered by the chosen indicators help to determine if the modeled alternatives perform an adequate use of mass and energy streams. Also, the global evaluation considered economic, environmental, and process safety criteria.

### 2. RESULTS

Two ABE topologies were studied and compared based on a combination of rigorous process simulation, application of process analysis, and evaluation of sustainability under a weighted/aggregate metric. The results obtained from rigorous simulation, process evaluation, and quantification of overall sustainability are discussed in the following sections. A feedstock feed of 3,131,439 t/y of Manihot esculenta Crantz (cassava waste) was set for both process alternatives. Niño-López et al. reported the chemical composition of this residue, mainly composed of carbohydrates, ash, acetate, and water. Table 2 shows the corresponded mass fraction for Manihot esculenta Crantz.

#### Table 2. Chemical Composition of Manihot esculenta Crantz

| component      | formula          | mass fraction |
|----------------|------------------|---------------|
| cellulose      | C_{6}H_{10}O_{5} | 0.40          |
| hemicellulose  | C_{5}H_{10}O_{4} | 0.13          |
| lignin         | C_{6}H_{10}O_{12} | 0.12         |
| water          | H_{2}O           | 0.24          |
| ash            | CaO              | 0.05          |
| acetate        | [C_{3}H_{4}O_{2}]^{-} | 0.05   |

Topology 1 generates a total mass flow of biofuels equaling to 462,924 t/y, including butanol, ethanol, and acetone. Topology 2 produces 1,061,588 t/y of butanol, acetone, and ethylene glycol (in this case, taken as a biofuel). As the nature of this process is producing biofuels, this study employed the resource energy efficiency indicator ($\eta_\text{e}$), which relates the energy content of the product and the total material input energy, as follows in eq 1.

$$\eta_\text{e} = \frac{\text{energy content of product}}{\text{total input energy}}$$

The total energy consumed through topology 1 was 5,586.52 GJ/h; this value for topology 2 corresponded to 4,573 GJ/h. The energy content of the product associates the energy density or heating value of each substance multiplied for its corresponding mass flow. Table 3 summarizes the energy density of substances considered as products for both processes.

#### Table 3. Reported Energy Value of ABE Products

| component      | energy content (MJ/t) | reference |
|----------------|-----------------------|-----------|
| butanol        | 33,000                | 33        |
| acetone        | 29,592                | 34        |
| ethanol        | 20,000                | 33        |
| ethylene glycol| 13,201                | 35        |

Data reported in Table 2 allowed us to estimate the output energy content for each evaluated ABE topology. Topology 1 showed a total mass-energy intensity of 14,707,753.11 GJ/t, and topology 2 presented 24,155,962.23 GJ/t. Based only on the abovementioned results, it is evident that the second process would generate higher energy in the case of the combustion of its product streams. Therefore, eq 1 was implemented to both verify the energy sustainability of the process and identify the alternative with the best produced energy performance. The $\eta_\text{e}$ for topology 1 was 0.29 GJ of energy produced per GJ of energy consumed, while this value for topology 2 was 0.60. This finding confirmed that topology 2 could potentially provide a higher energy content than topology 1. It is worth to mention that values for $\eta_\text{e} > 1$ might indicate that the process is not sustainable under the energy viewpoint, so the implementation of process optimization to reduce energy requirements (mainly in separation sections) can make this process more energy-sustainable.

#### 2.1. Economic Evaluation

An economic evaluation of ABE topologies was developed. This analysis began with the estimation of the total capital investment costs (TCIs) and the annualized fixed cost (AFC). The equipment cost, selection of equipment, and sizing were made by using the Aspen Process Economic Analyzer. Also, a plant life of 15 years was assumed. Besides, the analysis also involved estimation of the annualized operating cost (AOC). The cost and selling prices of the main raw material and products were consulted in the literature. In this sense, this study considered information provided from the United States Department of Energy and the Department of Agriculture, along with reported market prices from vendors and economic analytic web pages. Table 4 shows a range of the current market prices of the main products.

#### Table 4. Current Market Prices for ABE Products

| component      | price range ($/t) | reference |
|----------------|-------------------|-----------|
| butanol        | 800–1000          | 39,40     |
| acetone        | 750–1200          | 34,42     |
| ethanol        | 350–750           | 43,44     |
| ethylene glycol| 500–850           | 45        |

The prices reported in Table 4 correspond to the peak and lower values for the main products for the second semester of 2019 and the first semester of 2020. This study took the values for January 2020, which correspond with the upper limits for the listed prices. Besides, this study implemented a sensitivity analysis of the biobutanol selling price on the profit after taxes to show how fluctuating prices might affect the economic
behavior of the plants. Figure 1 depicts the sensitivity of profits after taxes (PAT) from variations on the butanol market price.

![Figure 1. Sensitivity on profits after taxes by changes of the butanol selling price for ABE topologies.](image)

The outcomes shown in Figure 1 indicates that the break-even point for topology 1 was close to 0.78 $USD/kg or 780 $USD/t, while this value for topology 2 corresponded to 0.58 $USD/kg or 580 $USD/t. The break-even price for topology 1 remains very close to the lower price, according to the range reported in Table 4. Otherwise, it is palpable that topology 2 can hold more significant fluctuations in the butanol selling price, and its break-even value indicates that the process remains profitable even for the reduction of the butanol selling price up to 42%.

On the other side, the utility costs were estimated for Colombian economic conditions, along with the full corporative tax rate (39%) and interest rate (9%) specific for this country. For topology 1, the utility cost was 25.50 USD per ton of main feedstock, while for topology 2, this value corresponded to 22.50. In this case, companies need to estimate the corporate rate, including the basic tax rate (33%), along with other issues associated with Colombian taxation policies. These other rates include the minimal alternative tax rate (1.5% reduced from 3.5% from 2019), payroll tax (9%), and social security tax for those employees that earn more than ten minimal wages, municipal tax (varies from 0.5 to 1.2%), and registration fees (0.3−0.7%). Therefore, this study sets 39% for the corporative rate considering the current rates and the discounts offered by the government for tax rate deduction.

Regarding Latin American countries, Colombia remains like one of the countries with the highest tax rates of value-added and business. However, it is worth mentioning that current policies are aimed at gradually reducing such rates to encourage business development and the creation of entrepeneurships. Table 5 summarizes assumptions made for developing process economic evaluation of ABE topologies.

It should be mentioned that the basis for the calculation of raw material cost and economic assessment parted from the availability of 3,131,439 t/y of Manihot esculenta Crantz. Likewise, topology 1 showed a feedstock cost of 69.19 $USD/t that comprised the main raw material, sulfuric acid, and sodium hydroxide. In contrast, topology 2 presented a corresponding feedstock cost of 152.03 $USD/t, including the same reagents used for topology 2, along with ethylene oxide. This compound increased the feedstock cost of topology 2 since its specific purchased cost. Table 6 displays the TCI, while Table 7 shows the detailed production costs for both topologies.

### Table 5. Main Assumptions for Economic Analysis of ABE Topologies

| parameter | topology 1 | topology 2 |
|-----------|------------|------------|
| process capacity (t/y) | 462,924 | 1,032,918 |
| mass flow of raw material (t/y) | 3,262,496.24 | 3,516,719.52 |
| raw material cost ($/t) | 69.19 | 152.03 |
| plant life (y) | 15 | 15 |
| salvage value | 10% depreciable | 10% depreciable |
| construction period (y) | 3 | 3 |
| location | North of Colombia | North of Colombia |
| tax rate | 39% | 39% |
| type of process | novel | novel |
| contingency percentage | 20% | 20% |
| utilities | steam, water, gas, electricity | steam, water, gas, electricity |
| process fluids | solid−liquid−gas | solid−liquid−gas |
| depreciation | lineal | lineal |

### Table 6. Estimation of TCI for Topology 1 and Topology 2

| cost of capital investment | topology 1 ($ USD) | topology 2 ($ USD) |
|---------------------------|---------------------|---------------------|
| delivered purchased equipment cost | 22,264,680.00 | 27,978,240.00 |
| purchased equipment (installation) | 6,679,404.00 | 8,393,472.00 |
| instrumentation (installed) | 2,671,761.60 | 3,357,388.80 |
| piping (installed) | 6,679,404.00 | 8,393,472.00 |
| electrical (installed) | 4,230,289.20 | 5,315,865.60 |
| buildings (including services) | 11,13,340.00 | 13,989,120.00 |
| services facilities (installed) | 8,905,872.00 | 11,191,296.00 |
| direct fixed capital investment | 62,563,750.80 | 78,618,854.40 |
| land | 2,226,468.00 | 2,797,824.00 |
| yard improvements | 8,905,872.00 | 11,191,296.00 |
| engineering and supervision | 11,577,633.60 | 14,548,684.80 |
| equipment | 2,226,468.00 | 2,797,824.00 |
| construction expenses | 7,569,991.20 | 9,512,601.60 |
| legal expenses | 222,646.80 | 279,782.40 |
| contractors’ fee | 4,379,462.56 | 5,503,319.81 |
| contingency | 13,358,808.00 | 16,786,944.00 |
| indirect fixed capital investment | 50,467,350.16 | 63,418,276.61 |
| fixed capital investment | 113,031,100.96 | 142,037,131.01 |
| working capital | 90,424,880.76 | 113,629,704.81 |
| start-up | 11,303,110.10 | 14,203,713.10 |
| TCI | 214,759,091.82 | 269,870,548.92 |

With the information provided by Tables 6 and 7, economic indicators are estimated for each ABE fermentation pathway. Topology 1 obtained an AOC and AFC equal to 414.10 MM USD/y and 6.80 MM USD/y, while topology 2 shows 922.51 MM USD/y and 922.51 MM USD/y, respectively. From the abovementioned results, the PBP and ROI were calculated for each simulated butanol production process. Likewise, it was obtained a discounted payback period for topology 1 of 7.64 y, while for topology 2, this value is 6.75 y. In the case of return on investment metric, the first pathway shows 19.34% and the second one shows 38.04%.

#### 2.2. Environmental Evaluation.

From the environmental viewpoint, process topologies for butanol production are evaluated by calculating the global warming potential (GWP) and renewability indexes. The first one counts the amount of CO₂ equivalent (CO₂e) that is generated by a bounded system per mass of products. This parameter is linked with
greenhouse gas emissions that are emitted by a process.\textsuperscript{50} Aspen Plus has a feature in the simulation user interface that shows an estimation of such a parameter for a simulated process. Topology 1 shows total emissions corresponding to a generation of 2,976,768.62 t/y of CO$_2$e, while topology 2 posted 3,967,296.87 t/y of CO$_2$e. For both processes, the boundaries of the modeled processes.\textsuperscript{51} In topology 1, among as long as the scope of this assessment only includes the during farming, harvesting, and transportation of raw materials, but this analysis does not include emissions that occurred and electricity, among other aspects. It is worth highlighting that this analysis does not include emissions that occurred during farming, harvesting, and transportation of raw materials, as long as the scope of this assessment only includes the boundaries of the modeled processes.\textsuperscript{21} In topology 1, among 27% corresponds with contributions because of mass flows of the process, while the remaining 73% belongs to equivalent CO$_2$ by utility requirements. Otherwise, the proportion for topology 1 is 20% contribution from mass flows and 80% from process utilities. For more details of CO$_2$ emissions of both processes, please check supplementary files. Figure 2 shows a comparison of CO$_2$ emissions from both ABE topologies.

The second evaluated parameter shows the relative use of renewable resources (as feedstock) considering the total mass input of the plant, where better and broader use of available and renewable resources indicates that a process is more sustainable over time.\textsuperscript{23} For both evaluated topologies, the total inlet feed flow of renewable resources is the same (Manihot esculenta Crantz). Different performances are obtained for each ABE fermentation pathway because of the specific input requirements of processing units. For example, topology 1 uses acid dilute pretreatment, which required a defined inlet flow of H$_2$SO$_4$, while topology 2 employs Steam Explosion, which does not need the use of an acid catalyzer. Table 8 shows the obtained results for the estimated environmental performance parameters.

### Table 7. Estimation of Operational Expenses for Topology 1 and Topology 2

| cost of operational expenses               | topology 1 ($ USD) | topology 2 ($ USD) |
|--------------------------------------------|--------------------|--------------------|
| raw materials                              | 225,642,615.41     | 534,638,371.41     |
| utilities                                  | 83,193,654.21      | 79,126,189.28      |
| maintenance and repairs                    | 5,651,555.05       | 7,101,856.55       |
| operating supplies                         | 847,733.26         | 1,065,278.48       |
| operating labor                            | 397,800.00         | 397,800.00         |
| direct supervision and clerical labor      | 59,670.00          | 59,670.00          |
| laboratory charges                         | 39,780.00          | 39,780.00          |
| patents and royalties                      | 1,130,311.01       | 1,420,371.31       |
| direct production cost (DPC)               | 316,963,118.93     | 623,849,317.03     |
| depreciation                               | 7,386,975.53       | 9,282,620.47       |
| local taxes                                | 3,390,933.03       | 4,261,113.93       |
| insurance                                  | 1,130,311.01       | 1,420,371.31       |
| interest/rent                              | 2,147,590.92       | 2,698,705.49       |
| fixed charges                              | 14,055,810.49      | 17,662,811.20      |
| plant overhead                              | 238,680.00         | 238,680.00         |
| total manufacturing cost                   | 331,257,609.42     | 641,750,808.23     |
| general expenses                           | 82,814,402.36      | 160,437,702.06     |
| total product cost (TPC)                   | 414,072,011.78     | 802,188,510.29     |

#### 2.3. Process Safety Evaluation

The measurement of safety performance of modeled topologies involves the implementation of the inherent safety index (ISI). This analysis included the assumption of the worst possible condition for each assessed subindex. The abovementioned fact allows the evaluation of unknown situations as the maximum associated risks that can be caused by a process.\textsuperscript{52} The ISI index counts the contributions of the chemical inherent safety (CIS) and the process inherent safety (PIS). Such parameters required much information about chemical substances and operational conditions. The CIS evaluates the exothermic grade of reaction performed in the process by estimating the heats of reaction. For topology 1, three main reactions (for the whole process) were identified corresponding to one of these to each process unit (except in the separation stage). Conversion of xylose to butanol in the fermentation system [see eq 22] is the most exothermic reaction for this pathway, showing a heat of reaction equaling $-6536.16$ J/g. In the case of topology 2, the same reaction was found to be the most exothermic. In both process topologies, several side reactions are developed, obtaining that conversion of xylose to acetic acid [see eq 25] is the most exothermic side reaction with an enthalpy equaling $-6507.75$ J/g. Chemical safety also assesses the risky properties of dangerous substances. This evaluation quantifies flammability, explosivity, and toxicity of handled chemicals. In the case of toxicity, the reported threshold limit values (TLV) inform about the harmfulness of such substances.\textsuperscript{53} Explosivity and flammability involve the upper and lower explosivity limits (UEL and LEL, respectively) and the flashpoint of substances. Table 9 shows the main features and properties of dangerous substances identified in both ABE fermentation topologies.

The knowledge of these properties helps us with determining the unexpected and unwanted interactions between chemical substances with the equipment, the system, or between them. In the case of topology 1, the most dangerous interaction is formed by the blend of ABE solvents, which forms a highly flammable liquid mixture, representing a chemical interaction subindex ($I_{int}$) of 3. Regarding topology 2, the riskiest interaction is due to the handling of ethylene oxide (highly explosive) with ABE solvents in the separation stage, a
condition that represents an \( I_{\text{tox}} = 3 \). Data reported in Table 9 also allowed determining the hazardous substance sub-index, which counts the potential effects associated with toxicity, explosivity, and flammability sub-indexes of handled components of the processes. In this sense, the maximum sum of these variables (\( I_{\text{tox}} + I_{\text{exp}} + I_{\text{fl}} \)) provides the score for this chemical safety category. Through the analysis, it was determined that acetone was the riskiest component in

| chemical     | health | fire | reactivity | TLV (ppm) | UEL–LEL (%) | flashpoint (°C) |
|--------------|--------|------|------------|-----------|-------------|-----------------|
| acetic acid  | 3      | 2    | 0          | 10        | 15.20       | N/A             |
| sulfuric acid| 3      | 0    | 2          | 0.25      | N/A         | N/A             |
| furfural     | 4      | 2    | 1          | 2.04      | 17.20       | 60              |
| ammonia      | 3      | 0    | 0          | 50.25     | N/A         | N/A             |
| sodium hydroxide | 3 | 0    | 0          | 1.22      | N/A         | N/A             |
| butanol      | 2      | 2    | 0          | 100       | N/A         | 35              |
| acetone      | 2      | 3    | 0          | 1010.33   | 10.30       | −20             |
| ethanol      | 2      | 3    | 0          | 1000      | 15.70       | 15.5            |
| butyric acid | 3      | 2    | 0          | N/R       | 8.00        | 69              |
| ethylene oxide| 3    | 4    | 3          | 1         | 97.00       | −20             |
| ethylene glycol | 2 | 1    | 1          | 25        | 12.10       | 111             |

\( \text{N/A means not apply; N/R means not reported.} \)

Table 10. Description of Main Equipment for Topology 1

| unit type of unit | temperature (°C) | pressure (atm) | inventory (t) | material |
|------------------|------------------|----------------|---------------|----------|
| cassava waste storage | tank | 28 | 1 | 325 | stainless steel |
| biomass milling | crusher | 28 | 1 | 325 | stainless steel |
| steam generator | boiler | 268 | 13 | 228 | stainless steel |
| acid PT reactor | reactor | 190 | 13 | 917 | hastelloy-c 200 |
| flash cooler | separator | 103 | 1 | 917 | stainless steel |
| filtration 1 | filter/membrane | 103 | 1 | 343 | stainless steel |
| heat exchange 2 | heat exchanger | 40 | 1 | 209 | stainless steel |
| ion exchange | separator | 40 | 1 | 209 | resin-lined |
| neutralization | reactor/tank | 50 | 1 | 204 | stainless steel |
| filtration 2 | rotatory-drum | 50 | 1 | 203 | epoxy-lined |
| heat exchange 3 | heat exchanger | 90 | 1 | 3657 | stainless steel |
| lignin solubilization | reactor | 90 | 1 | 3657 | stainless steel |
| heat exchange 4 | heat exchanger | 28 | 1 | 3657 | stainless steel |
| separation | separator | 28 | 1 | 3657 | stainless steel |
| enzymatic hydrolysis | reactor | 45 | 1.66 | 2241 | stainless steel |
| filtration 3 | filter/membrane | 45 | 1 | 2241 | stainless steel |
| heat exchange 5 | heat exchanger | 37 | 1 | 505 | stainless steel |
| ABE fermentation | reactor | 37 | 1 | 771 | stainless steel |
| gas stripping | column | 100 | 1 | 771 | stainless steel |
| heat exchange 6 | heat exchanger | 28 | 1 | 200 | stainless steel |
| condenser 1 | separator | 3 | 1 | 229 | CO\(_2\)-stainless steel |
| heat exchange 7 | heat exchanger | 28 | 1 | 77 | stainless steel |
| heat exchange 8 | heat exchanger | 28 | 1 | 132 | stainless steel |
| beer column | column | 100 | 1 | 132 | stainless steel |
| heat exchange 9 | heat exchanger | 28 | 1 | 15 | stainless steel |
| acetone column | column | 75 | 1 | 110 | stainless steel |
| heat exchange 10 | heat exchanger | 28 | 1 | 89 | stainless steel |
| condenser 2 | separator | 37 | 1 | 21 | stainless steel |
| heat exchange 11 | heat exchanger | 28 | 1 | 15 | stainless steel |
| ethanol column | column | 42 | 1 | 89 | stainless steel |
| heat exchange 12 | heat exchanger | 28 | 1 | 2 | stainless steel |
| heat exchange 13 | heat exchanger | 70 | 1 | 108 | stainless steel |
| molecular sieves | molecular sieves | 192.4 | 1 | 2 | stainless steel |
| heat exchange 17 | heat exchanger | 28 | 1 | 2 | stainless steel |
| decantation | decanter | 70 | 1 | 108 | stainless steel |
| heat exchange 14 | heat exchanger | 28 | 1 | 53 | stainless steel |
| butanol column | column | 120 | 1 | 55 | stainless steel |
| heat exchange 15 | heat exchanger | 60 | 1 | 55 | stainless steel |
| heat exchange 16 | heat exchanger | 28 | 1 | 42 | stainless steel |
topology 1 with a dangerous substances sub-index of 7. In the case of topology 2, ethylene oxide presented the highest score for this category with a score of 13, because this substance might cause skin irritations and respiratory problems, is extremely flammable, and readily forms an explosive mixture with air.\textsuperscript{54} The data about operational conditions provides the platform to evaluate the PIS aspect in the ISI method, involving mass inventory, equipment, and secure process structure, identifying the maximum potential risk derived from the operation of the plant.\textsuperscript{55} Tables 10 and 11 reports the description of the equipment and the inventory for topology 1 and topology 2, respectively.

It is easy to realize that most of the used equipment required stainless steel as the construction material, but it is worth mentioning that a special alloy is needed for handling H\textsubscript{2}SO\textsubscript{4} in the pretreatment unit because this substance is highly aggressive with metal-based materials. Hastelloy c-200 was chosen, which is composed of nickel, chromium, and molybdenum.\textsuperscript{56} This condition corresponded to a corrosivity sub-index ($I_{corr}$) of 2 (in both cases) because a special material is used for construction of some equipment in both topologies. Using the information provided by Tables 10 and 11, inherent safety sub-indices for PIS calculation were set. For topology 1, the maximum operating pressure and temperature are 13 atm and 268 °C, the first one located in the pretreatment reactor during the second one in the steam generator unit. About topology 2, these values correspond to 36 atm and 220 °C, both found in the steam generator unit.

Inventory is a relevant parameter counted to estimate PIS. This indicator gives the amount of handled mass based on a retention time of 1 h for the inside-battery limits area (ISBL) equipment. For evaluation purposes, this study assumed that all process units and operations belong to ISBL, as long as at the conceptual design stage, the required information is not always available regarding additional equipment in the outside battery limits area (OSBL).\textsuperscript{57} Figure 3 shows the obtained performance for each evaluated sub-index for both topologies.

The final parameter evaluated in the PIS for the overall calculation of ISI was the secure structure sub-index. The estimation of this variable involves the current platform in Table 11. Description of Main Equipment for Topology 2

| unit                  | type of unit | temperature (°C) | pressure (atm) | inventory (t) | material            |
|-----------------------|--------------|------------------|----------------|---------------|---------------------|
| biomass milling       | crusher      | 28               | 1              | 354           | stainless steel     |
| steam generator       | boiler       | 220              | 36             | 859           | stainless steel     |
| steam explosion       | reactor      | 190              | 36             | 1513          | hastelloy-c 200     |
| flash cooling         | separator    | 115              | 1              | 1513          | stainless steel     |
| filtration 1          | filter/membrane | 115          | 1              | 258           | stainless steel     |
| heat exchange 1       | heat exchanger | 28             | 1              | 1255          | stainless steel     |
| heat exchange 2       | heat exchanger | 90             | 1              | 4155          | stainless steel     |
| lignin solubilization | reactor      | 90               | 1              | 4155          | stainless steel     |
| heat exchange 3       | heat exchanger | 28             | 1              | 4155          | stainless steel     |
| separation            | separator    | 28               | 1              | 4155          | stainless steel     |
| enzymatic hydrolysis  | reactor      | 45               | 1.66           | 2397          | stainless steel     |
| filtration 2          | filter/membrane | 45             | 1              | 2397          | stainless steel     |
| heat exchange 4       | heat exchanger | 37             | 1              | 505           | stainless steel     |
| ABE fermentation      | reactor      | 37               | 1              | 724           | stainless steel     |
| gas stripping         | column       | 100              | 1              | 724           | stainless steel     |
| heat exchange 5       | heat exchanger | 28             | 1              | 518           | stainless steel     |
| condenser 1           | condenser    | 3                | 1              | 206           | stainless steel     |
| heat exchange 6       | heat exchanger | 28             | 1              | 95            | stainless steel     |
| heat exchange 7       | heat exchanger | 70             | 1              | 111           | stainless steel     |
| decantation           | decanter     | 70               | 1              | 111           | stainless steel     |
| distillation 1        | column       | 100              | 1              | 53            | stainless steel     |
| reactive distillation 1 | column   | 197              | 1              | 90            | stainless steel     |
| reactive distillation 2 | column   | 197              | 1              | 32            | stainless steel     |
| distillation 2        | column       | 118              | 1              | 60            | stainless steel     |
| heat exchange 8       | heat exchanger | 28             | 1              | 44            | stainless steel     |
| heat exchange 9       | heat exchanger | 28             | 1              | 43            | stainless steel     |
| distillation 3        | column       | 54               | 1              | 59            | stainless steel     |
| heat exchange 10      | heat exchanger | 28             | 1              | 43            | stainless steel     |
| condenser 2           | condenser    | 33               | 1              | 16            | stainless steel     |
| heat exchange 11      | heat exchanger | 28             | 1              | 15            | stainless steel     |

Figure 3. Performance of evaluated ISI sub-indexes for ABE topologies.
which an evaluated system operates, analyzing how the interconnected units work together under a holistic-safety viewpoint.\textsuperscript{58} As both processes are designed on the same basis, and there are many common features; thus, the resulted secure index was the same. The corresponded score for this parameter was equal to 3, as long as these topologies handled vast corrosive, harmful, and explosive/flammable substances, so it is expected that the process operates above the neutral safety point. In summary, topology 1 presented a PIS, CIS, and ISI of 20, 14, and 34, respectively. In the case of topology 2, these values corresponded to 26, 14, and 40. It is worth noting that both cases CIS contributed the most in the obtained safety performance. Also, these results showed that ABE topologies would operate far from the neutral point, considering that this condition corresponds to an ISI of 24.\textsuperscript{59}

2.4. Exergetic Indicators. In order to evaluate the exergetic performance of modeled processes, the exergy analysis method\textsuperscript{60} was implemented to determine process irreversibilities and exergy flows, among others. This process analysis tool provides the needed data to estimate the proposed exergy-based indicators. In this sense, this study bounded main stages in ABE topologies to develop the exergy analysis. This allows determining sources of irreversibilities, establishing those units that require the implementation of optimization strategies. For topology 1, the classification involved the following stages: pretreatment, overliming, enzymatic hydrolysis, ABE fermentation, and separation. Otherwise, the hierarchy for topology 2 included the same described stages, excluding the overliming stage as long as this design does not demand neutralization of acid solvents. The calculation of exergy flows and balance involves the estimation of the chemical exergy of process streams. The literature reports the specific chemical exergy of many substances. The free energy of Gibbs ($\Delta G$) along with the specific exergy of constituent elements are used to estimate the chemical exergy of a compound ($\text{Ex}_{\text{fi}}$).\textsuperscript{61} Table 12 summarizes the specific chemical exergy of key components handled in both ABE topologies.

Moreover, calculation of exergy streams also includes estimation of other thermodynamic variables (entropy, Gibbs energy, work, and heat flows, among others), allowing determining the total physical, chemical, work, and heat exergy flows of an analyzed system. Besides, the exergy balance counts contributions from mass exergy inlet flow ($E_x^{\text{inlet}}$), utility inlet exergy flow ($E_x^{\text{utility}}$), irreversibilities ($E_x^{\text{irr}}$), exergy of waste ($E_x^{\text{waste}}$), and outlet product exergy ($E_x^{\text{out}}$) flow.\textsuperscript{62} The above data is quite relevant in the estimation of both exergy efficiency ($n_x$) indicator and exergy of waste ratio ($W_x$). Table 13 summarizes inlet and outlet exergy flows for hierarchized stages in topology 1, while Table 14 shows the same variables for topology 2. The supplementary file shows more details about the exergy balance of both ABE topologies.

Exergetic balance for topology 1 showed a total inlet exergy flow of 14,768.61 GJ/h. Also, this process presents a total irreversibility flow of 12,367.19 GJ/h, obtaining an overall exergy efficiency of 26%. Otherwise, topology 2 obtained a total inlet exergy flow of 19,999.76 GJ/h, with an exergy utility flow of 13,392.18 GJ/h and an exergy efficiency of 40%. Calculated exergy flows also allowed the estimation of the waste of exergy ratio index, which describes the amount of lost exergy with respect to the total inlet exergy flow. The best performance for this indicator necessarily involves small quantities of exergy loss by waste streams for a process to generate the products. Table 15 reports the main exergy flows for modeled topologies.

According to results reported in Table 15, topology 1 had an exergy of waste ratio of 26.43%, indicating an exergy flow of 3,270 GJ/h. Otherwise, topology 2 presented a lower $W_x$ of 19.10%, which corresponds to 2,845 GJ/h. It is palpable that topology 2 had better use of mass streams (in terms of exergy) than topology 1, but both processes might increase their global efficiency by the implementation of optimization techniques and mass integration methods.\textsuperscript{63}

2.5. Sustainability Weighted Indicator. Once all sustainability indicators were estimated for each modeled topology, a simultaneous weighted evaluation was performed through index normalization and an aggregate sustainability metric. The first step to assess the weighted aggregate indicator is developed by normalizing the evaluated technical metrics. It requires that target values for each indicator are set considering process performance (for exergy and environmental parameters) or employing well-established reported target values (for safety and economic indicators). The normalized scores were used in the final calculation of the aggregate sustainability metric [see eq 29]. As this index evaluates four different types of technical indicators, it needs the definition of the weighted factor. El-Halwagi\textsuperscript{25} mentioned that this coefficient involves the relative importance of the evaluated criteria compared to a defined parameter, which has traditionally counted economic profits in terms of the ROI metric. This study partially used

Table 12. Summary of Specific Chemical Exergy of Key Components in ABE Topologies

| chemical      | formula        | MW (g/mol) | $\Delta G$ (kJ/mol) | $E_x^{\text{in}}$ (kJ/kg) | $E_x^{\text{out}}$ (kJ/kg) |
|---------------|----------------|------------|---------------------|--------------------------|---------------------------|
| butanol       | $\text{C}_4\text{H}_{10}\text{O}$ | 74.12      | -150.7             | 5,083.38                 | 68,583.11                 |
| acetone       | $\text{C}_2\text{H}_4\text{O}$    | 58.08      | -151.3             | 2,684.98                 | 46,228.99                 |
| ethanol       | $\text{C}_2\text{H}_4\text{OH}$  | 46.07      | -174.8             | 589.40                   | 27,154.00                 |
| butyric acid  | $\text{C}_4\text{H}_8\text{O}_2$ | 88.11      | -360               | 4,435.60                 | 30,341.62                 |
| ethylene oxide| $\text{C}_2\text{H}_4\text{O}$    | 44.03      | -13.23             | 2,384.57                 | 54,157.85                 |
| ethylene glycol | $\text{C}_4\text{H}_8\text{O}_2$ | 62.04      | -301.8             | 3,001.88                 | 48,386.20                 |

Table 13. Exergy Balance of Topology 1

| stage                        | $E_x^{\text{inlet}}$ (GJ/h) | $E_x^{\text{out}}$ (GJ/h) | $E_x^{\text{irr}}$ (GJ/h) | $E_x^{\text{waste}}$ (GJ/h) |
|------------------------------|-------------------------------|---------------------------|----------------------------|-----------------------------|
| pretreatment                 | 2,728.27                      | 5,552.82                  | 8,281.09                   | 4,919.55                    |
| overliming                   | 1,302.34                      | 4,919.44                  | 6,221.78                   | 4,032.94                    |
| enzymatic hydrolysis fermentation | 3,334.09                    | 6,937.29                  | 10,471.38                  | 6,558.39                    |
| separation                   | 1,388.84                      | 4,736.49                  | 6,125.32                   | 3,218.96                    |

18717

https://dx.doi.org/10.1021/acsomega.0c01656
ACS Omega 2020, 5, 18710–18730
As mentioned, this study presents two different pathways for butanol production (along with other chemicals); thus, the role of the exergy performance becomes crucial if the main goal is to produce clean liquid fuels with the best possible energy performance. The weight factor for the exergetic criteria was fixed to be 1.0. Regarding engineering projects, process economics is always a key aspect for the construction of chemical plants; in fact, plant profitability has been the most implemented standard for the decision makers. In this case, the weighting factor equals to 1.5 times respect to the reference value, which is fixed to be 1.0. Environmental and safety performance are considered as highly essential aspects in process design, even the commonly used indicators in the evaluation of these parameters are closely related because both assess potential effects and consequences on the surroundings (biotic or abiotic) derived from the operation of a chemical plant. This study set a weighting factor of 1.0 for (biotic or abiotic) derived from the operation of a chemical plant; in fact, plant profitability has been the most implemented standard for the decision makers. In this case, the weighting factor equals to 1.5. Environmental and safety performance are considered as highly essential aspects in process design, even the commonly used indicators in the evaluation of these parameters are closely related because both assess potential effects and consequences on the surroundings (biotic or abiotic) derived from the operation of a chemical plant. This study set a weighting factor of 1.0 for (biotic or abiotic) derived from the operation of a chemical plant; in fact, plant profitability has been the most implemented standard for the decision makers. In this case, the weighting factor equals to 1.5. Environmental and safety performance are considered as highly essential aspects in process design, even the commonly used indicators in the evaluation of these parameters are closely related because both assess potential effects and consequences on the surroundings (biotic or abiotic) derived from the operation of a chemical plant. This study set a weighting factor of 1.0 for (biotic or abiotic) derived from the operation of a chemical plant; in fact, plant profitability has been the most implemented standard for the decision makers. In this case, the weighting factor equals to 1.5. Environmental and safety performance are considered as highly essential aspects in process design, even the commonly used indicators in the evaluation of these parameters are closely related because both assess potential effects and consequences on the surroundings (biotic or abiotic) derived from the operation of a chemical plant. This study set a weighting factor of 1.0 for (biotic or abiotic) derived from the operation of a chemical plant; in fact, plant profitability has been the most implemented standard for the decision makers.

Table 14. Exergy Balance of Topology 2

| stage                          | $E_{\text{in}}^\text{x}$ (GJ/h) | $E_{\text{ex}}^\text{out}$ (GJ/h) | $E_{\text{w}}^\text{out}$ (GJ/h) | $E_{\text{loss}}^\text{out}$ (GJ/h) | $n_{\text{w}}$ (%) | $W_{\text{w}}$ (%) |
|-------------------------------|-------------------------------|-------------------------------------|----------------------------------|-------------------------------------|-------------------|-------------------|
| pretreatment                  | 4,347.57                      | 5,050.17                            | 9,397.75                         | 4,010.87                            | 5,386.87          | 301.52            |
| enzymatic hydrolysis fermentation | 913.82                        | 8,771.28                            | 9,685.09                         | 1,855.66                            | 7,829.44          | 1,525.32          |
| separation                    | 2,921.87                      | 10,961.89                           | 13,883.76                        | 5,164.97                            | 8,718.79          | 1,525.32          |

The worst and best values for ROI are set according to target interest rates commonly acceptable in chemical processing. Otherwise, DPBP is established considering the plant life (15 years) as the worst possible result for this indicator. In the case of environmental metrics, the upper limit value for GWP represents the maximum possible waste generation as CO$_2$ emissions in a chemical plant (per kg of product). At the same time, RIM serves as a scale performance indicator through percentages (as same for exergy efficiency). The upper value of GWP for topology 1 was 81.59 kg of CO$_2$/kg of product, while 89.25 kg of CO$_2$/kg of product for topology 2. The worst value for the safety indicator is the maximum possible total score for the ISI in the analysis of a chemical process. Finally, the limit values for exergy of waste ratio correspond to the amount of exergy lost by the streams that outs the process as residual flows; likewise, the worst possible performance is obtained when the all-exergy flow that enters the process is missed by outlet waste streams (100%). This study is followed to normalize technical indicators of each sustainability criteria for further evaluation of the weighted sustainability of both ABE topologies. Table 17 displays the results of evaluated indicators and corresponded normalized scores for ABE topologies.

Figure 4 displays the obtained results for the aggregate sustainability metric for each modeled topology. According to the results shown in Figure 4, topology 2 presented the best performances for economic aspects (ROI and DPBP). Also, the normalized score for GWP was higher for this process. Otherwise, topology 1 better uses its available renewable

Table 15. Exergy Flows for Topology 1 and Topology 2

| process                      | $E_{\text{in}}^\text{x}$ (GJ/h) | $E_{\text{ex}}^\text{out}$ (GJ/h) | $E_{\text{w}}^\text{out}$ (GJ/h) | $E_{\text{loss}}^\text{out}$ (GJ/h) | $n_{\text{w}}$ (%) | $W_{\text{w}}$ (%) |
|------------------------------|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|-------------------|-------------------|
| topology 1                   | 14,771.15                       | 2,401.42                         | 12,369.63                        | 26                                | 26.43             | 1.00              |
| topology 2                   | 20,002.01                       | 5,105.72                         | 9,685.09                         | 1,855.66                          | 7,829.44          | 1,525.32          |

Table 16. Best and Worst Values for Sustainability Indicators

| indicator | unit   | best value | worst value |
|-----------|--------|------------|-------------|
| ROI       | %      | 40         | 0           |
| PBP       | yr     | 0          | plant life  |
| GWP       | kg CO$_2$/kg | 0 | all GWP waste released |
| RIM       | %      | 100        | 0           |
| ISI       | %      | 50         | 0           |
| $n_{\text{w}}$ | %      | 100        | 0           |
| $W_{\text{w}}$ | kg/kg | 0          | 100%        |

The worst and best values for ROI are set according to target interest rates commonly acceptable in chemical processing. Otherwise, DPBP is established considering the plant life (15 years) as the worst possible result for this indicator. In the case of environmental metrics, the upper limit value for GWP represents the maximum possible waste generation as CO$_2$ emissions in a chemical plant (per kg of product). At the same time, RIM serves as a scale performance indicator through percentages (as same for exergy efficiency). The upper value of GWP for topology 1 was 81.59 kg of CO$_2$/kg of product, while 89.25 kg of CO$_2$/kg of product for topology 2. The worst value for the safety indicator is the maximum possible total score for the ISI in the analysis of a chemical process. Finally, the limit values for exergy of waste ratio correspond to the amount of exergy lost by the streams that outs the process as residual flows; likewise, the worst possible performance is obtained when the all-exergy flow that enters the process is missed by outlet waste streams (100%). This study is followed to normalize technical indicators of each sustainability criteria for further evaluation of the weighted sustainability of both ABE topologies. Table 17 displays the results of evaluated indicators and corresponded normalized scores for ABE topologies.

Figure 4 displays the obtained results for the aggregate sustainability metric for each modeled topology. According to

Table 17. Results and Normalized Score for the Evaluated Indicator of ABE Topologies

| process          | ROI      | DPBP     | GWP       | RIM      | ISI      | $n_{\text{w}}$ | $W_{\text{w}}$ |
|------------------|----------|----------|-----------|----------|----------|----------------|----------------|
| topology 1       | 19.34%   | 7.64 y   | 6.43 kg CO$_2$/kg | 8.6%     | 34       | 26%           | 26.43%         |
| topology 2       | 38.04%   | 6.75 y   | 3.37 kg CO$_2$/kg | 7.05%    | 40       | 40%           | 19.10%         |
| normalized topology 1 | 0.48 | 0.49 | 0.92 | 0.09 | 0.32 | 0.26 | 0.74 |
| normalized topology 2 | 0.95 | 0.55 | 0.96 | 0.07 | 0.20 | 0.40 | 0.81 |
resources. These magnitudes for that indicators corresponded with normalized scores equaling to 0.48, 0.49, 0.92, and 0.09 for topology 1, while 0.95, 0.55, 0.96, and 0.07 for topology 2. These results might indicate that if the decision between these options has to be made from economic and environmental points of view, topology 2 emerges as the most suitable alternative. Otherwise, there is an evident difference regarding the results obtained from inherent safety and exergy evaluations.

For the first parameter, butanol topology 1 presented a better behavior for inherent chemical safety while the performance for PIS was similar for both designs. In the case of exergetic assessment, topology 2 is the modeled process with the best efficiency results showing higher performances from $n_{ex}$ and $W_{ex}$. Finally, the application of the aggregate sustainability index allowed the selection of the best alternative taking into account the results obtained from the evaluated indicators. In this case, topology 2 obtained the highest score (0.53) compared to the value posted by topology 1 (0.48). It is worth mentioning that according to the reported results, both evaluated alternatives represent qualified designs for a promising generation of biofuels (butanol and ethanol) and value-added chemicals (acetone and ethylene glycol) from the sustainable use of the lignocellulosic material.

3. CONCLUSIONS

Butanol production processes via ABE fermentation were presented. This work involved studying technical, economic, environmental, safety, and exergy indicators, along with the evaluation of an aggregate sustainability index. Results showed that topology 1 obtained a global production yield of 0.14 ton of ABE per ton of biomass, while topology 2 showed a corresponding yield of 0.16, along with a generation of 537,165 t/y of ethylene glycol as a byproduct formed from the reaction between water and ethylene oxide. Economic and environmental performances for both processes were quite similar, obtaining a corresponding normalized ROI of 0.928 for topology 1 and 0.944 for topology 2, while for GPW, the posted scores correspond to 0.997 and 0.83, respectively. The main difference between the simulated alternatives was found from the evaluation of safety and exergy indicators, because a contrary behavior between these indexes was found. The abovementioned point is related to the fact that topology 1 showed a better safety performance, while topology 2 is a more efficient process from thermodynamic and energy point of view. Finally, the application of the aggregate index allowed the development of a unified sustainability evaluation of modeled butanol processes and the further selection of topology 2 as the most adequate and sustainable alternative. For future works, more technical indicators can be included to get broader outcomes. These can include operational and economic uncertainty evaluations, health and occupational issues, and the potential of business development, among others. Also, analogous procedures can evaluate other types of aggregate indexes, allowing further comparisons.

4. PROCEDURE

Figure 5 displays a schematic of the methodology applied in this work. The first step encompasses the searching and screening of process inventory, taking into account the goals of the selected process. In this regard, information related to suitable technology pathways, processing capacity, suitable feedstock, and operational conditions, among other parameters are set. Data for process inventory are commonly collected from the literature, technical reports, and lab-scale experiments, among others. Besides, this process synthesis stage can be developed by hierarchical, mathematical, or hybrid methods. Therefore, for the evaluated case study (butanol biorefinery), the hierarchical approach was used.

The second step includes the modeling of screened and synthesized processing alternatives using rigorous process simulation. Therefore, the use of computer-aided tools requires setting several parameters and variables, which include aspects such as thermodynamic models and property estimation equations, type of process (steady-state or dynamic), selection of equipment, and downstream units, among others. In this study, the commercial software Aspen Plus was used for developing process simulations. Much data are then provided by such modeling; extended mass/energy balances, property estimation, azeotrope behavior, rigorous vapor–liquid equilibria, and overall and processing unit yields, among others. Such information is crucial for the development of process analysis, where these variables and parameters are needed for the evaluation of economics, environmental issues, process safety, and exergy/energy performance. According to Figure 5, the third stage refers to the establishment of target sustainability metrics based on economic, environmental, safety, and exergy parameters. There are several indicators for measuring the technical performance of a chemical plant. Thus, the proposed
sustainability assessment considers those metrics allowing the selection of the best alternative from a weighted simultaneous evaluation of sustainability parameters.

### 4.1. General Process Description

The case study presented in this study relates a large-scale production of butanol via ABE fermentation from lignocellulosic biomass.

Figure 6 shows a generalized block diagram displaying the main processing units required in this type of processing. According to Figure 6, the process starts in the handling and size reduction unit, where the biomass (primary raw material) is conditioned for further treatments. The process continues to the pretreatment unit, where the carbohydrates (cellulose and

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**Figure 6.** Generalized block diagram for butanol production from lignocellulosic biomass.

**Figure 7.** Process flowsheet diagram for butanol production in topology 1.

---

Raw material
- Lignocellulosic biomass

Process alternatives:
- Milling

Process alternatives:
- Dilute acid
- Steam explosion
- Organosolv
- Alkali

Process alternatives:
- Enzymatic

Process alternatives:
- Co-fermentation C5 and C6 sugars

Non-pure ABE products

Process alternatives:
- Distillation
- Gas stripping
- Absorption
- Membrane technologies
hemichellulose) and lignin are treated in order to break their molecular structure and allow separation/solubilization of reducer sugars. Several alternatives for performing this stage are reported in the literature; technologies such as dilute acid treatment, steam explosion, Organosolv, and alkali treatment, among others, have been widely used. At the end of this stage, solids and liquids streams are separated.

The process continues to the enzymatic hydrolysis unit (for saccharification of extracted cellulose), while pentoses (liquid stream) are directly sent to the fermentation unit. Before fermentation and enzymatic hydration reactions, lignin is separated from the reducer sugars to avoid inhibition processes. The saccharification unit allows the production of glucose, which is subsequently mixed with the extracted xylose, before entering the ABE fermentation reactor. In this stage, clostridia are used for the formation of acetone, butanol, and ethanol (along with other byproducts) by a complex reaction mechanism. The ABE fermentation reactions require large amounts of waters, and also, several byproducts are formed. A mechanism. The ABE fermentation reactions require large ethanol (along with other byproducts) by a complex reaction

4.2. Process Topology 1. Process topology 1 comprises a processing pathway to treat cassava waste to generate high-concentrated butanol, along with acetone and ethanol. Topology 1 includes milling, dilute acid pretreatment, enzymatic hydrolysis, fermentation, column, and downstream processing section. The separation/purification stage comprises the following units: gas stripping, beer acetone, ethanol, and butanol columns. The selection of these elements considered many criteria associated with reported high yield, implementation at industrial scale, and performance as an interconnect system. Figure 7 shows the process flowsheet diagram of the processing pathway described for topology 1.

This design involved dilute-acid pretreatment, considering that previous contributions have demonstrated promising results for the formation of reducing sugars. Lopez-Castrillon et al. reported a yield of 88% for the conversion of carbohydrates for this stage. Biomass feedstock entered the process already cleaned and available for sizing reduction in a crusher unit. The power required to perform this stage was 44.65 MJ/h, with a ratio of the cut-off size of 1.7 under Bond’s Law. Then, biomass flow is directed to the dilute acid reactor under a solid concentration of 42% wt. The pretreatment reactor operates under 190 °C and 1.2 atm, maintaining an acid concentration of 1.1% wt. A steam generator supplied the required energy to rise and maintain the temperature under the defined conditions and also generated the needed pressure to the system. The outlet reactor stream is separated through a flash cooler, reducing the moisture content (and pressure back to 1 atm) of the flow and separating physical phases. The condensate flow is filtered to separate remaining solid carbohydrates and solubilized sugars. Wooley et al. recommended implementing ion-exchanging to reject acid components from the carbohydrate liquid flow, with a yield of 88% for acetic acid and 100% for sulfuric acid. The process for the solid-phase pathway directed to neutralization and gypsum precipitation operations for stabilizing the pH of the mixture in a purge tank. A sequential step comprised of filtration and hydro-cyclone separation, which separated liquid fractions by 20% from the main solid stream. It is worth mentioned that the filter unit in this train operated (1 atm) with a solid load of liquid outlet of 0.47 and an efficiency of solid purification of 99%.

As lignin is well known as an inhibitory agent in hydrolysis and fermentation reactions, this topology included an extraction technology or delignification process. This stage comprised separation of lignin through the use of NaOH (2% wt) as the precipitator agent in a solid-liquid proportion of 1:10, reaching lignin solubilization at 90 °C and 1 atm. The following stage was the enzymatic hydrolysis after solubilized lignin separation through filter/membrane technology. Luo et al. demonstrated that enzymatic hydrolysis technology is cost-effective in biorefinery processing, reaching a fraction yield of 80% for the conversion of cellulose to glucose. Enzymatic hydrolysis reactor operated under 45 °C and 1.6 atm. After filtration of neither desired nor reactive components, both delignified and carbohydrates liquid stream are mixed before entering the ABE fermentation reactor. The fermentation stage is the main stage of the evaluated processes, which allows the formation of main products. Haigh et al. fractional conversions of glucose of 49.98% for butanol, 27.28% for acetone, and 5.30% for ethanol, under 35 °C and 1 atm. Other undesired components emerged in this stage, so the process continued to multiple separation stages for the extraction of ABE components. This stage is performed at a temperature of 37 °C and 1 atm of pressure, keeping a water proportion of 80%. In this topology, the configuration included an initial gas stripping unit for the removal of impurities and massive amounts of water. After condensation of solvents (letting rejection of most dissolved gases) performed at 3 °C and 1 atm, the main flow directs to the Beer Column for separation of CO₂. The following stages encompass distillation towers for the extraction of ABE products considering their boiling point. This purification/separation system first encompassed the acetone column to separate acetone from the other ABE solvents. The bottom of this tower that contains the two- and three-carbon primary alcohols is directed to the ethanol column. Separated ethanol is obtained in the distillate stream, while rich-butanol solution prevails in the bottom.

Because of the homogeneous azeotrope formed by water and ethanol, high purity of this alcohol is produced employing molecular sieve adsorption. This stage is developed at 110 °C and 1 atm, demanding an auxiliary steam flow 1.5 times the treated ethanol mass flow. Otherwise, butanol purification involved the addition of a decanter that operated at 70 °C and 1 atm, being this unit a fundamental operation for breaking the heterogeneous azeotrope formed by butanol and water. The decantation unit generated two outlet streams: (i) organic-rich and (ii) aqueous-rich, in which the first one is directed to the Butanol tower for final purification of this product. It is worth pointing out that the formation of heterogeneous and homogeneous azeotropes between alcohol-based components and water makes it challenging to develop purification stages, so these towers operate under severe operational conditions, which can cause the process to be cost-effective. Table 18 summarizes the specific operating conditions and features of separation columns for the purification of ABE products in topology 1.

This design involves performing several chemical and biochemical reactions that allow the generation of main products. Likewise, most of the performed reaction mechanisms depend on the specified operating conditions to reach.
high rates of formation. Following, eqs 2–17 show the different chemical equations developed by each process stage.

- Dilute acid pretreatment

\[
(Xylan)_n + nH_2O → nXylose
\]  
\[ (Xylan)_n → nFurfural + 2H_2O \]  
\[
(\text{Glucan})_m + mH_2O → m\text{Glucose}
\]

- Fermentation

\[
\text{Glucose} → \text{butanol} + 2CO_2 + H_2O
\]  
\[
\text{Glucose} + H_2O → \text{acetone} + 3CO_2 + 4H_2
\]  
\[
\text{Glucose} → 2\text{ethanol} + 2CO_2
\]  
\[
\text{Glucose} → \text{butyric acid} + 2CO_2 + 2H_2
\]  
\[
\text{Glucose} → 3\text{acetic acid}
\]

- Enzymatic hydrolysis

\[
6\text{Xylose} → 5\text{butanol} + 10CO_2 + 5H_2O
\]  
\[
3\text{Xylose} → 5\text{ethanol} + 5CO_2
\]  
\[
2\text{Xylose} → 5\text{acetic acid}
\]

Through the production process shown in Figure 3 and the assumed biomass inlet flow, a total mass flow of 316,477 t/y of butanol, 139,186 t/y of acetone, and 7,261 t/y of ethanol was synthesized. The abovementioned fact represents an overall production yield of 0.14 ton of ABE per ton of biomass. Table 19 summarizes the main mass streams of ABE topology 1.

### 4.3. Process Topology 2

As described for topology 1, this pathway involves processing the same lignocellulosic biomass feedstock to synthesize high concentrated butanol and further generation of commercial concentrated acetone and ethanol. The following stages comprised topology 2: milling, steam explosion, enzymatic hydrolysis, fermentation, gas stripping, decanter, reactive distillation (with ethylene oxide) column, butanol column, stripping column, and acetone-ethanol column. Figure 8 shows the process diagram for ABE topology 2. As described for topology 1, the biomass is available already clean and ready for processing in topology 1.

The first feature dissimilar of topology 2 compared to topology 1 is that the feedstock pretreatment, in this case, includes steam explosion technology. Wang et al.\(^{87}\) reported that the steam explosion could reach a similar yield showed by

### Table 18. Operating Conditions and Features of Separation Columns of Topology 1

| processing unit | variable | value |
|-----------------|----------|-------|
| gas stripping   | number of trays | 10    |
|                 | reflux ratio   | 3.00  |
|                 | type of condenser | none |
|                 | condenser pressure | none |
| beer column     | number of trays | 4     |
|                 | reflux ratio   | 1.5   |
|                 | type of condenser | partial-vapor |
|                 | condenser pressure | 1 atm |
| acetone column  | number of trays | 20    |
|                 | reflux ratio   | 15    |
|                 | type of condenser | partial-vapor |
|                 | condenser pressure | 0.5 atm |
| ethanol column  | number of trays | 50    |
|                 | reflux ratio   | 30    |
|                 | type of condenser | partial-vapor |
|                 | condenser pressure | 0.1 atm |
| butanol column  | number of trays | 12    |
|                 | reflux ratio   | 5     |
|                 | type of condenser | partial-vapor |
|                 | condenser pressure | 1 atm |

### Table 19. Summary of Main Streams of ABE Topology 1

| stream | mass flow (t/y) | temperature (°C) | pressure (atm) | cellulose | hemicellulose | lignin | ash | acetic acid | water | xylose | glucose | sulfuric acid | furfural | cellobiose | butanol | acetone | ethanol | carbon dioxide |
|--------|----------------|-----------------|---------------|-----------|--------------|--------|-----|------------|-------|--------|---------|---------------|----------|-----------|--------|---------|--------|----------------|
an acid-based process, without using acid solvents and further neutralization stage. Therefore, the extraction yields of eqs 2−17 are also different. Prior to entering the steam explosion reactor, the biomass flow is first sent to the crushing unit for particle size reduction under the same conditions described for topology 1. Steam explosion pretreatment was performed at 190 °C and 32 atm that allowed to break the carbohydrate structures present in the biomass. This stage involved the identical reactions developed in acid dilute pretreatment in topology 1. The outlet flow of the pretreatment reactor is cooled to 115 °C and 1 atm, separating much water and both dissolved and not dissolved carbohydrates. Further filtration made available solid and liquid flows for the following processing. Solids rich in cellulose followed to lignin extraction and enzymatic hydrolysis stages; these two operations performed under the same conditions described for topology 2. Otherwise, the liquid stream rich in solubilized sugars directs to the ABE fermentation unit. The ABE fermentation production implies the development of several chemical and biochemical reactions in order to synthesize butanol (high concentrated) along with byproducts. Most of the reactions for topology 2 are the same as described by topology 1 [see eqs 2−17]. Another differential aspect included in topology 2 is the use of reactive distillation units in the separation/purification of synthesized solvents. This stage involves performing the following chemical reaction.

\[
\text{Ethylene oxide} + \text{H}_2\text{O} \rightarrow \text{ethylene glycol}
\]  

The reaction in eq 18 allows us to break the mixtures between water−butanol and water−ethanol to form the heterogeneous and homogeneous azeotropes, so, if the water content of the mainstream is highly decreased, further downstream units are simplified. Therefore, the downstream processing of topology 2 remarkably differs from the described configuration for topology 1. In this pathway, the process started with a gas stripping column followed by condensation of the stripping distillate at 3 °C and 1 atm. At this point, this process added a decantation unit to break the butanol-water azeotrope, in this case, at a temperature of 90 °C and 1 atm. The rich-organic stream that exited from decantation followed to the first reactive distillation tower, otherwise, the rich-aqueous stream directed to the first distillation unit (multi-effect). Distillate flow of the multieffect tower is treated in the second reactive distillation that sensibly decreases water content, forming ethylene glycol. It should be mentioned that ethylene glycol is also generated, leaving the first reactive tower in the bottom stream. Both distillate streams of reactive distillation columns continued to a successive train of two
multieffect distillation columns and a final condensation unit (33 °C and 1 atm) for the full recovery of butanol and acetone. Table 20 shows the specific operating conditions and features of separation columns for the purification of ABE products in topology 1.

Table 20. Operating Conditions and Features of Separation Columns of Topology 2

| processing unit | variable       | value       |
|-----------------|----------------|-------------|
| gas stripping   | number of trays| 10          |
|                 | reflux ratio   | 3.00        |
|                 | type of condenser| none     |
| distillation column 1 | number of trays| 10          |
|                 | reflux ratio   | 1.00        |
|                 | type of condenser| partial-vapor |
|                 | condenser pressure| 1 atm      |
| reactive column 1| number of trays| 10          |
|                 | reflux ratio   | 12          |
|                 | type of condenser| partial-vapor |
|                 | condenser pressure| 1 atm      |
| reactive column 2| number of trays| 10          |
|                 | reflux ratio   | 10          |
|                 | type of condenser| partial-vapor |
|                 | condenser pressure| 1 atm      |
| distillation column 2 | number of trays| 10          |
|                 | reflux ratio   | 15.5        |
|                 | type of condenser| partial-vapor |
|                 | condenser pressure| 1 atm      |
| distillation column 3 | number of trays| 15          |
|                 | reflux ratio   | 10          |
|                 | type of condenser| partial-vapor |
|                 | condenser pressure| 0.3 atm    |

Summarizing, the modeling of topology 2 shows production of 398,953 t/y of butanol and 136,837 t/y of acetone. For this alternative, ethanol purification was not considered because of the low yield of this product, and also, it required further separation stages that do not compensate for the economic investment. Furthermore, topology 2 shows an overall ABE production yield of 0.16 tons per ton of processed biomass. Also, as uses ethylene oxide as reactive chemical and ethylene glycol is formed, this substance is considered as a by-product obtaining a total mass flow of 525,798 t/y at industrial grade. Furthermore, ethylene glycol is considered a third product in the economic evaluation of this topology to compensate for the high cost of ethylene oxide. Table 21 summarizes the main streams of ABE topology 2.

### 4.4. Economic Indicators.

The minimization of operational costs or maximization of profits is very often applied as criteria in decision-making regarding project alternatives for a chemical processing design. According to El-Halwagi, economic analysis should include an evaluation of two costs: the TCI and the total AOCs. Likewise, the annual fixed charges (AFC) of a chemical plant in include TCI (considering depreciation), property taxes, insurance, salaries, and other expenses. The sum of AFC and AOC gives the TAC. One of the most important indicators used for evaluating the profitability of an engineering project is the ROI, which is defined as follows.

\[
\text{ROI} = \frac{\text{annual profit}}{\text{TCI}} \times 100\%
\]  

Commonly, the ROI employs the annualized net income (after taxes), and it has units of percent per year. Also, this metric is analogous to interest rates from financial and investment companies in the economic market. Thus, this parameter measures and sets the performance (and target) for the evaluated designs. Another economic parameter used in this study is the discounted payback period (DPBP), which shows how fast the depreciable TCI can be recovered, considering non-discounted fixed capital investment (FCI) expenses and the value of money over time. The DPBP gives the time required to recover the depreciable FCI, using the

Table 21. Summary of Main Streams of ABE Topology 2

| stream | 1          | 11         | 12          | 28          | 43          | 46          | 54          | 56          |
|--------|------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|
| mass flow (t/y) | 3,100,125 | 375,950    | 1,676,718   | 6,460,471   | 385,164     | 140,634     | 136,837     | 398,953     |
| temperature (°C) | 28         | 115        | 115         | 37          | 28          | 28          | 28          | 28          |
| pressure (atm) | 1.00       | 1.00       | 1.00        | 1.00        | 1.00        | 1.00        | 1.00        | 1.00        |

| Mass Fraction |
|---------------|
| cellulose     | 0.40       | 0.03       | 0.62        | 0.01        | 0.00        | 0.00        | 0.00        | 0.00        |
| hemicellulose | 0.13       | 0.00       | 0.05        | 0.01        | 0.00        | 0.00        | 0.00        | 0.00        |
| lignin        | 0.12       | 0.01       | 0.20        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| ash           | 0.05       | 0.00       | 0.08        | 0.02        | 0.00        | 0.00        | 0.00        | 0.00        |
| acetic acid   | 0.05       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| water         | 0.24       | 0.74       | 0.04        | 0.73        | 0.00        | 0.00        | 0.00        | 0.00        |
| xylose        | 0.00       | 0.19       | 0.01        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| glucose       | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| sulfuric acid | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| furfural      | 0.00       | 0.02       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| cellooligos   | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| butanol       | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| acetone       | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| ethanol       | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| carbon dioxide| 0.00       | 0.00       | 0.00        | 0.12        | 0.00        | 0.00        | 0.00        | 0.00        |
| ethylene oxide| 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        | 0.00        |
| ethylene glycol| 0.00      | 0.00       | 0.00        | 0.00        | 0.00        | 1.00        | 0.99        | 0.00        | 0.01
discounted cash flow diagram. Therefore, the estimation of this parameter involves the application of graphical and interpolation means using the cumulative Net Present Value diagram.\(^\text{90}\) The selection of these indexes to assess economic aspects in the weighted sustainability metric comes from there are among the most used technical parameter in decision making (mainly ROI),\(^\text{25}\) setting threshold values which reflect the level of risk of an engineering project. Besides, the DPBP gives a more realistic approach to the needed years to recover the initial investment.\(^\text{91}\)

**4.5. Environmental Indicators.** Chemical processing requires the consumption of natural resources (which include raw materials and energy), resulting in a decrease and depletion of these sources over time. Also, industrial production commonly releases waste and gas emissions into the environment, which could intensify the effects of overuse of natural resources.\(^\text{92}\) Therefore, the minimization of waste discharge and gas emissions becomes a crucial goal to diminish the level of risk of an engineering project. Besides, the DPBP requires the consumption of natural resources (which include renewable resources to diminish the consumption of non-renewable materials and energy), resulting in a decrease and depletion of these sources over time. Also, industrial production commonly releases waste and gas emissions into the environment, which could intensify the effects of overuse of natural resources.\(^\text{92}\) Therefore, the minimization of waste discharge and gas emissions becomes a crucial goal to diminish the level of risk of an engineering project. Besides, the DPBP requires the consumption of natural resources (which include renewable resources to diminish the consumption of non-renewable materials and energy), resulting in a decrease and depletion of these sources over time. Also, industrial production commonly releases waste and gas emissions into the environment, which could intensify the effects of overuse of natural resources.\(^\text{92}\) Therefore, the minimization of waste discharge and gas emissions becomes a crucial goal to diminish the level of risk of an engineering project. Besides, the DPBP

\[
\text{GWP} = \frac{\text{total CO}_2 \text{ equivalents}}{\text{mass of products}} \quad (20)
\]

In this sense, the total CO\(_2\) equivalent metric describes different GHG in a standardized unit. So, for any kind of emission, the CO\(_2\) equivalent means the estimated amount of carbon dioxide that would present a corresponding GWP.\(^\text{94}\) Therefore, a certain quantity of any GHG corresponds to an amount of CO\(_2\) equivalent by multiplying its mass flow per emission factor. The United States Environmental Protection Agency (USEPA) recommended the use of the Tier I method for calculating corresponding GHG emission, eq 21 shows

\[
\text{GHG emission} = 0.001 \times \text{fuel usage} \times \text{HHV} \times \text{emission factor} \quad (21)
\]

HHV refers to the high heating value of a substance. These values can be obtained from the EPA’s GHG reporting program. The next step involves the conversion of tons of emissions to tons of CO\(_2\) equivalent, as described earlier.\(^\text{93}\)

Therefore, the application of this method allows us to estimate in a single number the total amount of emissions from diverse sources, including gas vents, energy generation, and steam production, among others. The second environmental indicator is associated with the quantification of the use of renewable resources to diminish the consumption of non-renewable materials in order to enhance process sustainability.\(^\text{22}\) Likewise, the renewability material index is estimated through eq 22.

\[
\text{RI}_\text{M} = \frac{\text{total renewable feedstock input}}{\text{total mass input}} \times 100\% \quad (22)
\]

The advantages of using these environmental-based metrics are that these can provide straightforward information about the impacts on atmosphere (in case of GWP) and the use of renewable resources in terms of percentage of entering mass flow, indicating the degree of commitment with the environmental sustainability. In the case of GWP, this indicator has been widely implemented as a standard to measure potential global warming impacts of different gases and allows comparison between different systems.\(^\text{96}\)

**4.6. Process Safety Indicator.** The measurement of safety and risks for a chemical plant is considered as a key aspect regarding process reliability and sustainability. Safety indicators are aiming to establish a performance framework considering potential hazards derived from construction, operation, and maintenance of chemical facilities.\(^\text{97}\) Also, these metrics are associated with the societal dimension in the sustainable development concept, where aspects such as chemical safety, equipment safety, the possibility of working accidents, among others, are taken into consideration for such type of analysis.\(^\text{98}\) Several methodologies and metrics for assessing social/safety aspects of chemical processes are reported in the literature. The Dow & Fire Safety Index, Prototype Safety Index, Explosion Hazard Index, or Mond Index are among the most used methods in industries for estimating safety performance.\(^\text{57}\)

Nevertheless, a lot of these safety metrics require information that is not available in the early stages of designs, so in order to overcome this limitation, the ISI is used in this study. This method measures internal aspects related to the intrinsic characteristics of a process, which include handling safer chemical components and operations. The approach aims to avoid and eliminate hazards through the quantification of process risks from technical data that is available in the conceptual design stage.\(^\text{58}\) The main goal of the inherent safety concept is to find the sources of potential hazards associated with substance properties and configuration of interconnected units, eliminating them (instead of controlling), which makes the process essentially safer.\(^\text{99}\) Likewise, coming from an inherently safer design, the task is to generate and evaluate process alternatives avoiding the use of hazardous materials and an application of a more straightforward engineering project. Heikkila\(^\text{59}\) introduced the ISI, which counts aspects from the CIS index and the PIS index, according to eq 23.

\[
\text{ISI} = \text{CIS} + \text{PIS} \quad (23)
\]

The calculation of eq 23 implies the estimation of several parameters and properties regarding chemical compounds handled through the process, divided into (i) chemical inherent aspects (exothermic degree of reactions, chemical interactions, hazardous properties, and corrosivity) and (ii) process aspects (inventory, operating pressure and temperature, equipment safety, and secure structure). Table 22 shows the chemical and process safety sub-indexes used for estimating the ISI.

Also, Table 1 gives corresponding scores for each inherent safety sub-index. The ISI is calculated by adding all evaluated sub-indexes, which result in a unified metric that allows making comparisons of safety performance for different process alternatives, as described by eqs 24 and 25.

\[
\text{CIS} = I_{\text{SR}} + I_{\text{MR}} + I_{\text{INT}} + (I_{\text{FLA}} + I_{\text{EXP}} + I_{\text{TOX}})_{\text{max}} + I_{\text{COR}} \quad (24)
\]

\[
\text{PIS} = I_{\text{I}} + I_{\text{T}} + I_{\text{P}} + I_{\text{EQ}} + I_{\text{ST}} \quad (25)
\]

where \(I_{\text{SR}}\) and \(I_{\text{MR}}\) is the sub-index for main and side reactions, \(I_{\text{INT}}\) is the chemical interaction sub-index, \(I_{\text{FLA}} + I_{\text{EXP}} + I_{\text{TOX}}_{\text{max}}\) is the maximum hazardous substance sub-index, which counts flammability, explosivity, and toxicity of most dangerous components.

https://dx.doi.org/10.1021/acsomega.0c01656
ACS Omega 2020, 5, 18710–18730
4.7. Exergy and Energy Efficiency Indicators. According to the second law of thermodynamics, it is well known that the natural processes have restrictions on the spontaneous direction of these, especially the driving forces involved in any physical phenomenon always vary from high to low potentials. Consequently, a process that exclusively transfers heat from a specific temperature to a higher one does not exist. Also, this law of physics restricts that there is no entity (e.g., a processing unit) that works in a certain way that its only effect is to produce work, the system and its surroundings will necessarily be affected. Therefore, for any chemical process, there is always a loss of energy (and work) associated with the process’s irreversibilities and the restriction mentioned above coming from the second law. Thus, exergy gives the maximum amount of theoretical work obtained between a well-defined system and its surroundings. The evaluation of exergy performance in a chemical process design becomes a key aspect in terms of production efficiency and energy supply settings due process irreversibilities along with a quantification of how far a system is from an ideal state. The exergy efficiency ($n_{ex}$) is a widely used indicator for measuring thermodynamic (and irreversibilities) performance in terms of exergy flow as follows

$$n_{ex} = 1 - \left( \frac{E_{in}}{E_{ex}} \right)$$

Equation 26 allows knowing the efficiency for a whole, section, or unit of a chemical process. $E_{in}$ is the total inlet exergy flow, and $E_{ex}$ is the total exergy loss. Irreversibilities represent the difference between the total inlet and total outlet product exergy flow ($E_{out}$). In order to determine the above variables, the exergy analysis is necessarily performed.

Another exergy efficiency parameter used in this study is the exergy of waste ratio ($W_{ex}$), calculated as follows

$$W_{ex} = \left( \frac{\text{exergy of waste streams}}{\text{total inlet exergy}} \right) \times 100\%$$

The exergy of waste ratio is an energy/thermodynamic performance metric that expresses the required amount of exergy lost because of outlet waste streams with respect to the total input exergy flow that enters a chemical process; therefore, it allows us to make easy comparisons between different alternatives even when these do not have the same baseline feed flow. Recent contributions have implemented the exergy efficiency as a metric to establish the overall energy performance of a chemical plant based on the Second Law of Thermodynamics, using it as a parameter to study whole processes or a section of them.

4.8. Sustainability Weighted Indicator. In order to compare the overall performance of the modeled butanol production alternatives, data regarding technical parameters need to be standardized. Therefore, each used indicator is normalized by expressing it as the difference between the current ($i_i$) and worst values divided by the difference between the best ($i_{b,w}$) and worst ($i_{w,w}$) values, as shown in eq 28

$$I_j = \frac{i_i - i_{b,w}}{i_{b,w} - i_{w,w}}$$

The normalized indicator $I_j$ varies in the range $[0, 1]$, where a higher number means a better sustainability performance. For developing this goal, process benchmarking is included, considering target values for best and worst performance of each technical parameter. Moreover, the analysis of the overall sustainability performance continued with the integration of an aggregate index, allowing the easy definition of the best alternative using a weighting of the evaluated indicators. This metric is presented as follows

$$S = \left( \prod_{j} w_j I_j^p \right)^{1/n}$$

$S$ relates the aggregate sustainability metric of a process alternative $p$, $I_j^p$ is the normalized indicator, $w_j$ is the weighting factor of indicator $j$, and $n$ is the number of evaluated indicators. Equation 29 provides an efficient (and straightforward) way to evaluate different topologies by using the geometric mean of the evaluated indicators.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01656.

Feed and outlet streams with corresponding CO$_2$ equivalent for topology 1, utility blocks with corresponding CO$_2$ equivalent for topology 1, feed and outlet streams with corresponding CO$_2$ equivalent for topology 2, utility blocks with corresponding CO$_2$ equivalent for topology 2, mass exergy balance of ABE topology 1, and mass exergy balance of ABE topology 2 (PDF)

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ACKNOWLEDGMENTS

The authors declare no competing financial interest.

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