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Sustainable Purification of Butanol from a Class of a Mixture Produced by Reduction of Volatile Fatty Acids

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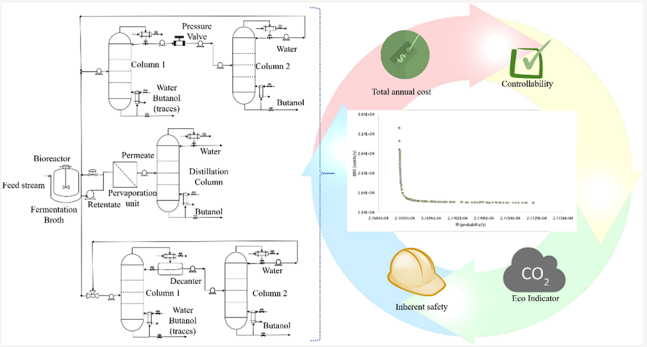
ABSTRACT: There has been an increasing interest in the conversion of biomass to biofuels, energy, and chemicals due to an increase in meeting environmental demands and price and decrease in the potential availability of crude oil. Among the biofuels postulated as viable alternatives due to their physicochemical characteristics is butanol. Given its high energy content, it is projected as a potential substitute for ordinary gasoline. However, butanol production process through fermentation of lignocellulosic material has shown some disadvantages. Another way of producing butanol is by reduction of volatile fatty acids (from waste streams of organic matters) with hydrogen. An effluent with a high content of water and butanol is obtained. In that sense, thermodynamic interactions make the separation process challenging. On the other hand, current policies and needs have guided the proposals for chemical processes to meet various sustainability metrics, for example, high profit margins and low environmental impact, with inherent safety and robust operation in the presence of disturbances. With this in mind, this work proposes purification schemes to obtain butanol of high purity, from a butanol−water mixture, in the compositions generated by reduction of volatile fatty acids, using pervaporation, pressure swing distillation, and azeotropic distillation. Comparing the results obtained, the pervaporation scheme turned out to be the most promising alternative as it presents reductions in all the "green" indicators (compared to the other purification alternatives) in percentages between 27 and 52%. The general indices for such alternative were 0.0392 ($/kg$_{butanol}$), 0.0066 (ecopoints/kg$_{butanol}$), 8274, 2.772 × 10^{-04} (probability/year), and 0.4281 $/kg$_{butanol}$ regarding the total annual cost, ecological indicator 99, condition number, individual risk, and minimum selling price, respectively.



1. INTRODUCTION

Butanol is a four-carbon alcohol, which is conventionally produced from fossil fuels. Butanol is used as an intermediate chemical in the production of butyl acrylate, butyl acetate, butyl glycol ethers, and butyl esters.[1] A market report shows that the market value of *n*-butanol by 2022 is estimated to reach 5.58 billion USD worldwide.[2] Butanol can also be used as a direct fuel or fuel additive for cars—this contributes to the market size. The conventional production procedure of *n*-butanol is highly unsustainable as the fossil fuel resources are limited and depleting, and their exploitation has severe negative environmental impacts.[3] As a result of these concerns, the research and development of green, renewable, and sustainable ways to produce bio-butanol from bio-sources have intensified over the past decades. Biobutanol compared to bioethanol is superior because of its higher energy content, higher octane number, higher ability to blend with gasoline, being a direct substitute to gasoline, its ability to be transported in already existing pipelines, and that it is safer to handle.[4] The most common way of producing biobutanol is through the fermentation of carbohydrates such as glucose. The acetone−butanol−ethanol (ABE) fermentation is a well-known process and has been investigated and improved since its industrialization in 1916. However, ABE butanol always struggled to compete on a commercial scale with the later butanol produced synthetically due to feedstock cost issues, the relatively low-yield, and sluggish fermentations, as well as problems caused by end-product inhibition and bacteriophage infections.[5] For example, works have been reported where low final butanol concentrations by fermentation of 6.66[6] and 3.43 g/L[7] or low productivity values of 5[8] and 0.96 g/Lh,[6] just to mention some data. These figures cause the costs associated with the downstream process to be high, losing viability of this approach to butanol production.

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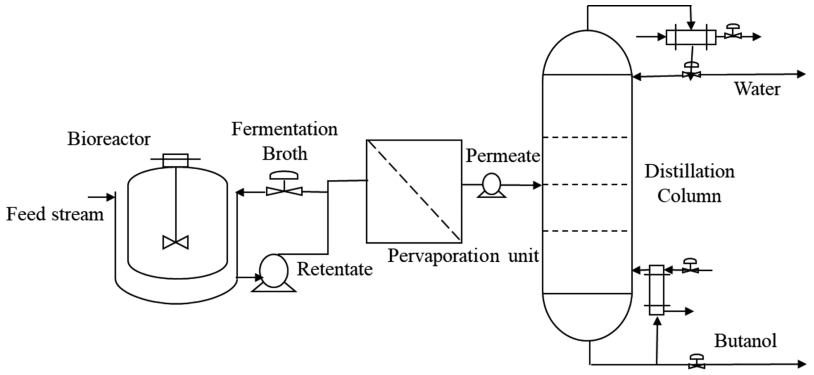

Figure 1. Pervaporation-distillation scheme.

An alternative way of producing butanol is by reduction of volatile fatty acids with hydrogen.[9] Lund[10] reported a project at The Technical University of Denmark in collaboration with Novozymes A/S. The project aims at developing a novel continuous fermentation process to produce butanol using hydrogen and waste streams of organic matters that are rich in butyric acid according to reported by Udugama et al.[11] The best-case scenario is expected to be that the culture will produce butanol at a concentration of 13 g/L as the only alcohol in a binary mixture consisting of water and butanol.[10] This way of producing butanol has several advantages because the organic matter from the waste streams is abundant compared to conventional biomass types, it is low cost compared to the cost of biomass, and it is a way of treating and handling waste—making it a waste-to-value production and thereby creating a sustainable production.[11] In several studies, it has been shown that alcohol production through volatile fatty acid reduction with hydrogen produces primarily butanol and water, as reported in Angenent,[12] Cardona and Sanchez,[13] Steinbusch et al.,[9] among others. The highest conversion efficiency of reactants to alcohol was observed and production of other components in very small amounts. Additionally, the bioconversion of butyric acid to butanol by *Clostridium saccharoperbutylacetonicum*, a fermentative process, was able to produce a binary mixture of butanol and water. The binary mixture was obtained with different proportion of butyric acid and a nutrient medium.[14] Therefore, this new technology to produce butanol requires a systematic evaluation separation processes in such a way that an environmentally friendly and economically profitable process can be generated for a possible industrial application. Although the separation of the butanol−water binary mixture has been widely studied, as far as the authors are aware, no study has been reported on the purification of the aforementioned mixture in the compositions obtained in the process of reduction of volatile fatty acids. Furthermore, no study has been reported on the separation processes regarding their sustainability using indicators such as: environmental impact, inherent safety, dynamic behavior, and economic profitability.

This work will focus on purification of butanol for two applications: high purity applications (99.9 mol % butanol), referred to as a chemical grade, and fuel grade applications (96.7 mol % butanol) using three separation processes: (i) pervaporation-distillation, (ii) azeotropic distillation, and (iii) pressure swing distillation. For each case, downstream processes will be designed and optimized with respect to the product specifications, and the economics, environmental index (eco-indicator 99), inherent safety, and control behavior of the downstream processes will be analyzed. A mixture consisting of the binary system water−butanol is studied for three representative case studies (compositions obtained in the process of reduction of volatile fatty acids[11]): (a) high-high being a scenario with high butanol concentration (1 mole%) in the feed stream and high butanol concentration (99.9 mole%) in the product stream, (b) high-low is high butanol concentration in the feed stream and low concentration (96.7 mole%) in product stream, and (c) low-low being a scenario with low butanol concentration (0.3 mole%) in the feed stream and low concentration (96.7 mole%) in the product stream.

2. DOWNSTREAM PROCESSES

The mixture studied in this work is at the liquid phase and consists of two components: water and butanol. Despite being a binary mixture, the case study analyzed in this paper appropriately represents alcohol production through reduction of volatile fatty acids. The physical feasible separation techniques identified by Lund[10] are pervaporation-distillation, azeotropic distillation, and pressure swing distillation.

2.1. Pervaporation-Distillation. Pervaporation is a processing method for the separation of mixtures of liquids by partial vaporization through a nonporous or porous membrane. The membrane acts as a selective barrier between the two phases: the liquid-phase feed and vapor-phase permeate. Pervaporation is a separation technology that is not limited by the liquid−vapor equilibria and involves a low energy consumption as compared to conventional distillation.[15] Typically, the upstream side of the membrane is at ambient pressure and the downstream side is under vacuum to allow the evaporation of the selective component after permeation through the membrane.[16] Thus, pervaporation has been combined with distillation to produce the so-called hybrid distillation-pervaporation systems, which can avoid the use of entrainers.[15] Commonly, in hybrid distillation-pervaporation systems, the pervaporation unit is externally located to the distillation column (Figure 1). Therefore, the azeotropic conditions can only be overcome inside the pervaporation unit while the performance of the distillation column is still limited by liquid−vapor equilibria.[15] Although pervaporation has many advantages, it still has some limitations, such as the high cost of materials of the membrane and its selection.[16]

Been retentate, the part of the feed that does not pass through the membrane, while the permeate is the part of the feed that does pass through the membrane.

2.2. Azeotropic Distillation and Pressure Swing Distillation. The azeotropic distillation process (Figure 2) is

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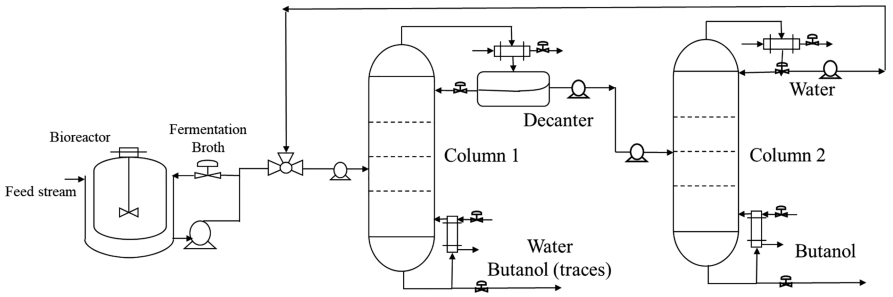

Figure 2. Azeotropic Distillation.

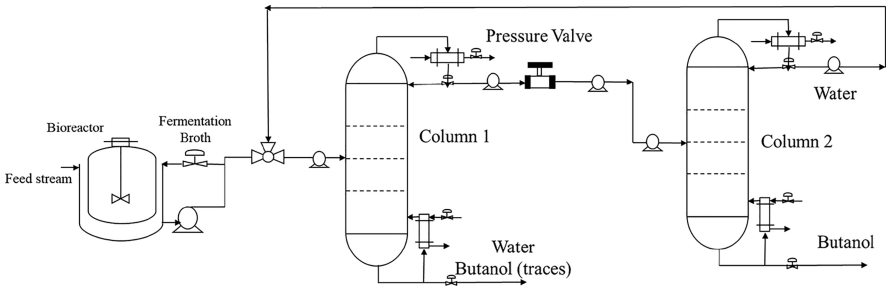

Figure 3. Pressure swing distillation.

Table 1. Feed Characterization for Each Case Study (in the Case of Pervaporation Is Feed Composition in the Distillation Column)

	pressure swing			azeotropic distillation			pervaporation	
mass flow (kg/hr)	low-low	high-low	high-high	low-low	high-low	high-high	low-high 500	low-high 2620
water	26205.1	26361.7	26190.1	53208.5	49988.9	49733.4	267.464	1401.5
butanol	346.48	1095.6	1088.4	703.5	2077.5	2066.9	247.5	1297.1
butanol (%wt)	1.30	3.99	3.99	1.30	3.99	3.99	48.07	48.07

widely used to separate non-ideal binary mixtures into their constituent pure components. A minimum-boiling azeotrope can be formed by the introduction of an azeotrope-forming compound (entrainer) to an existing azeotropic mixture or close-boiling mixture for which separation by conventional distillation is not feasible.[17]

Depending on the number of phases present in the new azeotrope, the azeotropic distillation will be homogeneous or heterogeneous. In both cases, it is essential to know the vapor−liquid (or vapor−liquid−liquid) equilibrium data to be able to properly design a distillation sequence.[18] The design of azeotropic distillation requires careful selection of a suitable solvent, and it is specifically challenging since the feasibility and optimality of the processes require consideration of the closed-loop design including solvent recovery. However, in this particular case, it does not require any solvent. The absence of a solvent means that costs do not increase. In other words, from the point of view of the total annual cost, considerable savings are being generated by the energy requirements associated with solvent recovery. Considering that energy expenditure represents an important percentage of the total annual cost, being able to carry out the separation without the use of solvent is an economic and operational advantage.

On the other hand, pressure swing distillation is an effective method of separating azeotropic mixtures when the composition of azeotrope varies greatly with the change of operating pressure.[19] Pressure swing distillation uses two columns operating at two different pressures to separate azeotropic mixtures by taking high-purity product streams from one end of the columns and recycling the streams from the other end with compositions near the two azeotropes (Figure 3).

Pressure swing distillation can be applied to both the minimum-boiling and maximum-boiling homogeneous azeotropic mixtures. Therefore, we would expect that less pressure sensitivity of the azeotropic mixture would be required to make the pressure swing configuration in a maximum-boiling system economical than in a minimum-boiling system.[20] Overall, the pressure swing distillation is a very robust and not so highly sophisticated method compared to multicomponent distillation or membrane processes, but the energy demand is in general higher. Also, the investment cost of the distillation columns is higher due to the pressure inside the vessels and feed composition strongly impacts the economics but not the basic process topology and operating conditions.[21]

3. CASE STUDY

The mixture, in this work, is assumed to be completely free of any solid particles, and to be at equilibrium at 101.33 kPa and 308.15 K; hence, the mixture is nonreactive. The mixture type is classified as an azeotropic, organic, polar, and non-electrolyte mixture, and the Wilson method predicts the vapor−liquid equilibrium as expected. By using the computer programs ICAS and PRO/II and the online database Dortmund Data Bank, pure component properties of water and butanol are reported in Lund.[10] In the present work, three different technologies were considered: pressure swing, azeotropic distillation, and pervaporation, each of them with a butanol−water feed from a process of reduction of volatile fatty acids with hydrogen. The

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feed streams considered, as well as the concentrations of butanol in each scenario, are shown in Table 1. Lund[10] reported a project at the PROSYS Research Center at The Technical University of Denmark in collaboration with Novozymes A/S. The best-case scenario is expected to be that the culture will produce butanol at a range concentration between 1.30 and 3.99 (the minimum and maximum concentrations reached) as the only alcohol in a binary mixture consisting of water and butanol.[10] The feeds considered, as well as the concentrations of butanol in each scenario, are shown in Table 1. For the case studies analyzed, the minimum and maximum composition reported for the production of butanol was taken. The flowrates shown for each experiment were those obtained experimentally according to Lund.[10] A point to highlight is that this volatile fatty acid-reducing renewable fuel production process does not require carbohydrates like fermentable sugars but uses biomass with high water content or low sugar content that is unsuitable as feedstock for current fermentation processes. This so-called low-grade biomass is abundantly present and is economically very attractive feedstock for the production of biofuels. Also, in the study presented by Lund,[10] the best-case scenario is expected to be that the culture will produce butanol at the concentration of 13 g/L as the only alcohol in a binary mixture consisting of water and butanol. According to Steinbusch et al.,[9] these are the typical characteristics of the butanol production process from reduction of volatile fatty acids.

In the particular case of pervaporation, the feed shown in Table 1 is from the membrane and is fed directly to the distillation column. On the other hand, the numbers 500 and 2620 refers to the number of m^2 of the membrane used. According to Fan et al.[22] and Chang,[23] the membrane has the best compromise of selectivity and flux properties, for separation of a 1.5 wt % butanol−water mixture. Fadeev et al.[24] reported that this is also the case for 1 wt % feeds. For the composition in the case study, it is fair to assume that the flux and selectivity will apply in this case also. The membrane is operated at 343.15 K as this provides the highest selectivity and flux, with a selective layer thickness of 22 μ and a downstream pressure at 0.27 kPa. The membrane has a flux performance of J = 1030 g/m^{2}h.

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The pressure swing distillation process utilizes the pressure sensitivity of the azeotropic composition of the mixture. The pressure sensitivity is shown in Table 2. By having two distillation columns in series, it is possible to "jump" the azeotrope and do the desired separation. Attending your observation, in this new version, a new paragraph and table have been added.

Table 2. Pressure Sensitivity Analysis of the Azeotropic Composition

pressure (kPa)	azeotropic composition (x_1)
10.13	0.83
20.66	0.81
50.66	0.79
101.66	0.77
1013.3	0.73
2000	0.73
4500	0.73

4. SUSTAINABLE INDICES

A sustainable design is inspired by the concept of sustainable development, and its purpose is to minimize the environmental, economic, and social impacts at an early stage of the design process.[27] According to concepts reported by Jiménez-Gonzalez et al.,[25] incorporating "green metrics" when designing a process toward the broader goal of environmental sustainability should be considered. Among those green metrics, required in the evaluation of sustainable processes, the indices of environmental, economics, safety, and process control should be highlighted. In the same sense, modification in the topology for the same downstream process can also modify sustainable indices.[26,27] This work attempts to bridge the gap between selection and the process design and sustainable indices and generate green processes.

4.1. Economical Index. As it has been described, for economic purposes, all designs were compared by means of the total annual cost (TAC) and the selling price. To calculate the total annual cost (TAC), the method published by Turton[28] was used (see the Supporting Information for more details). The economic study performed considers 10 years as the recovery period. The plant is assumed to run 8500 h/year. In addition, the following heating and cooling costs were taken into account: high-pressure (HP) steam (42 bar, 254 °C, \$9.88 GJ^{-1}), medium-pressure (MP) steam (11 bar, 184 °C, \$8.22 GJ^{-1}), low-pressure (LP) steam (6 bar, 160 °C, \$7.78 GJ^{-1}), and cooling water (\$0.72 GJ^{-1}).[20] Furthermore, considering a wider economical point of view, the evaluation of this project was also performed using other economic measure, the selling price (for details, see the Supporting Information).

4.2. Environmental Index. The Eco-Indicator 99 (EI99) was used to evaluate the sustainability of the processes and quantify the environmental impact due to the multiple activities performed in the process. This methodology is based on the life-cycle assessment. The approach was proposed by Goedkoop and Spriensma.[29] The EI99 has proven to be an important method for evaluating the overall environmental impact related to chemical processes. Some authors, such as Guillén-Gosálbez et al.[30] and Quiroz-Ramírez et al.,[31] among others, have demonstrated that applying the EI99 during the design and synthesis phases can lead to important improvements and reductions of wastes. The index was applied successfully in screening different alternatives for biofuels purification giving as results the optimal configuration with the lowest environmental impact and cost by Contreras-Vargas et al.[32] The eco-indicator 99 is calculated as follows

$$\mathrm{EI99} = \sum_{b} \sum_{d} \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (1)$$

where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage

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caused in category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d, and δ_d is the normalization factor for damage of category d (additional details in the Supporting Information).

4.3. Inherent Safety Index. Process safety was quantified by the individual risk (IR) index. The IR can be defined as the risk of injury or decease to a person in the vicinity of a hazard.[33] The main objective of this index is the estimation of likelihood affectation caused by the specific incident that occurs with a certain frequency. The IR does not depend on the number of people exposed. The mathematical expression for calculating individual risk is as follows

$$\mathrm{IR} = \sum f_i P_{x,y} \tag{2}$$

where f_i is the occurrence frequency of incident i, whereas $P_{x,y}$ is the probability of injury or decease caused by the incident i. In this work, an irreversible injury (decease) is used for which more data are recorded. The calculations of IR can be carried out through quantitative risk analysis (QRA), which is a methodology used to identify incidents and accidents and their consequences. The QRA starts with the identification of possible incidents. For distillation, columns are identified as continuous release and instantaneous releases. A continuous release is produced mainly by a rupture in a pipeline or partial rupture on process vessel causing a leak. The instantaneous release consists of the total loss of matter from the process equipment originated by a catastrophic rupture of the vessel. These incidents were determined through a hazard and operability study (HAZOP). The frequencies for each incident (f_i) were taken according to the previously reported values by the American Institute of Chemical Engineers (AIChE)[33] and using the event tree diagrams obtained with all probabilities of instantaneous and continuous incidents, along with their respective frequencies. Accordingly, instantaneous incidents are as follows: boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire, and toxic release, whereas the continuous release incidents are as follows: jet fire, flash fire, and toxic release. Once the incidents have been identified, the probability $P_{x,y}$ can be calculated through a consequence assessment, which consists of determining the physical variables as the thermal radiation, the overpressure, and the concentration of the leak originated by incidents and their respective damages. The calculations of the physical variables were realized according to the equations reported by AIChE.[33] The worst scenario was considered for calculating the dispersion, as well as a wind speed of 1.5 m/s and atmospheric stability type F[34,35] (for details, see the Supporting Information).

4.4. Control Properties Index. One of the basic and most important tools of modern numerical analysis is the singular value decomposition (SVD). There are numerous important applications of the SVD when quantitative and qualitative information is desired about linear maps. One important use of the SVD is in the study of the theoretical control properties in a chemical process. One definition of SVD is

$$G = V\Sigma W^H \tag{3}$$

Here, G is the matrix target for SVD analysis, Σ is a diagonal matrix, which consists of the singular values of G, V is a matrix, which contains the left-singular vector of G, and W is the matrix composed by the left-singular vectors of G (more details about mathematic fundaments in Klema and Laub,[36]).

In the case where the SVD is used for the study of the theoretical control properties, two parameters are of interest: the minimum singular value (σ_*), the maximum singular value (σ^*), and its ratio known as a condition number (γ)

$$\gamma = \frac{\sigma^*}{\sigma_*} \tag{4}$$

The minimum singular value is a measure of the invertibility of the system and represents a clue of potential problems of the system under feedback control. The condition number reflects the sensitivity of the system to uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with higher minimum singular values and lower condition numbers are expected to show the best dynamic performance under feedback control.[36−38] The SVD technique requires a transfer function matrix (G) around the optimum design of the distillation sequences and registering the dynamic responses of product composition. Vázquez-Castillo et al.[39] and Cabrera-Ruiz et al.[40] have recently demonstrated the use of the condition number as an index of dynamic performance and even as an objective function in a process of simultaneous optimization design-control.

For the case of pervaporation, studies concerning the impact on membrane target functions have been omitted. The reason for the omission is that a robust safety analysis requires an analysis of the probability and frequency data of possible catastrophic events associated with the use of membranes. In the case of the columns, the probability and frequency data are supported by several studies conducted by various authors over a considerable period. Therefore, the results shown in section 6 have the bias associated with the impact of the membrane on the objective functions.

5. OBJECTIVE FUNCTION AND OPTIMIZATION PROCEDURE

Considering the performance indices previously described, the objective function to be minimized is presented below

$$\mathrm{Min}(\mathrm{TAC},\ \mathrm{EI99},\ \gamma,\ \mathrm{IR}) = f(N_{tn},\ N_{fn},\ R_{rn},\ F_{rn},\ F_{ln},\ F_{vn},\ D_{cn},\ P_{cn},\ \mathrm{FC}_{cn}) \tag{5}$$

subject to $\vec{x_m} > \vec{y_m}$ where N_{tn} is the total number of column stages, N_{fn} is the feed stage in a column, R_{rn} is the reflux ratio, F_{rn} is the distillate/bottoms flux, F_{ln} is the interconnection liquid flow, F_{vn} is the interconnection vapor flow, and D_{cn} is the column diameter. Additionally, for the calculations of the inherent safety, it is necessary for various physicochemical properties such as heat of combustion, LC_{50}, flammability limits, etc. Furthermore, the limits established for the design variables were considered within the industrial values proposed by various authors.[41,42]

On the other hand, y_m and x_m are the vectors of required purities for the m_{th} components, respectively. The minimum purity targets were fixed as 99.9% and 96.7% mol for butanol according to previously explained scenarios in the feed stream. The recovery of butanol was set as 98% or above.

In the three case studies, optimization only of the distillation columns was considered. For each column, five variables to be optimized were considered. Table 3 shows the decision variables considered.

5.1. Optimization Procedure. To solve the objective function, as well as the model associated with the equipment, a

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Table 3. Decision Variables Used in the Multiobjective Optimization Process

type of variable		
parameter	process	search range
number of stages	discrete	5−100
feed stages	discrete	4−99
reflux ratio	continuous	0.1−75
distillate rate	continuous	0.1−10 (kmol h^{-1})
diameter	continuous	0.9−5 (m)

hybrid stochastic optimization algorithm, differential evolution with tabu list (DETL), was used. The use of this type of methodology is due to the nature of the model to be solved, that is, the model is highly nonlinear and potentially nonconvex. Additionally, these types of strategies have shown to be capable of solving these types of relatively complex problems.[43,44]

The DETL method has its basic foundations in the theory of natural selection. The method was not originally proposed as a hybrid method; differential evolution (DE) was initially proposed by Storn and Price[45] to solve single-objective problems, and later, it was adapted by Madavan and Field[46] to solve multiobjective problems. There are five essential steps in differential evolution: initialization, mutation, crossover, evaluation, and selection; all expressed by the equations described in the Supporting Information section.

On the other hand, the tabu concepts (tabu TL list and tabu TS search) were proposed by Glover.[47] The Tabu list avoids revisiting the search space by keeping a record of visited points; the TL is updated with each new generation of trial vectors. This tabu check is carried out in the generation step to the trial vector, and the new trial individual is generated repeatedly until it is not near to any individual in the TL. Both methods together increase computational efficiency; the first multiobjective version of this hybrid method was reported by Sharma and Rangaiah.[48] In the practical implementation, the hybrid method is written in visual basic within Microsoft Excel by means of DDE (dynamic data exchange), the numerical method exchanges input vectors (column stages, reflux ratio, etc.), and output (flows, thermal loads, etc.) with the process model (modeled in Aspen Plus). The stochastic method analyzes the values of the objective functions and proposes new values for the input vectors. On the other hand, the written code in visual basic also allows the link with Matlab, where it is possible to calculate the condition number as an objective function. The parameters used for the optimization process were as follows: 200 individuals, 800 maximum number of generations, a tabu list of 50% of total individuals, a tabu radius of 1×10^{-6}, and 0.8 and 0.6 for crossover probability and mutation factor, respectively. These parameters were obtained from literature and the tuning process via preliminary calculations.[44] Figure 4 graphically explains the optimization framework used in this optimization procedure.

6. RESULTS

According to section 5, the number of individuals evaluated was 160,000 for each of the study cases. Once the results were analyzed, no substantial improvement was observed among the last generations of vectors evaluated. Considering the above, it is assumed that the method has reached the necessary convergence and is in the region of the global optimum.

Various objective functions were considered in this optimization process, encompassing this optimization problem within a framework of sustainability. Taking this as a basis, an important aspect is to know if the optimization strategy can achieve all the stated objectives, or if there is antagonistic behavior between them.

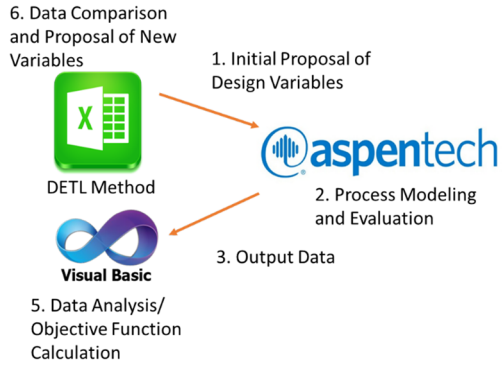

Figure 4. DETL Optimization framework.

To exemplify this situation, Figure 5 shows the behavior observed in the Paretos obtained in various case studies. The behavior was quite similar in all the analyzed schemes.

Although the joint evaluation of the four objective functions was carried out, the representation of a Pareto in two dimensions helps to understand the behavior between the objective functions.

Figure 5a shows the antagonistic behavior between the total annual cost and inherent safety, that is, the lower values of one objective function are related to larger values of the other. To understand the behavior of these objective functions, it is necessary to understand the model associated with each function. In the case of the TAC, its value is highly influenced by the costs of services and the capital cost; alternatively, the inherent safety depends largely on various physicochemical properties that potentially generate catastrophic events, for example, the explosive limits, the heat of combustion, the concentration of dangerous elements, the amount of matter inside the analyzed equipment, etc. Considering the above, it is clear that to decrease the TAC, it is preferable to design small equipment with low service costs. This justifies the use of intensified unit operations. In the particular case of service costs, these are directly influenced by the reboiler duty. Additionally, the reboiler duty has a direct connection with the reflux ratio, the greater the amount of condensed liquid that returns to the column in the form of reflux, the more energy must be invested for its reheating. Shortly, the design of low-cost equipment is associated, to mention a few, with small equipment, low energy consumption, and a low reflux ratio.

Due to the presence of water in the stream to be purified, it is clear that the reflux of each column causes a certain amount of water to be returned to the same column, resulting in a higher amount of internal water. As a result of that dilution, the potentially hazardous compound (butanol) is diluted and the potential hazard decreases. Certainly, to reduce the risk of accidents in a column, a high reflux ratio is preferred that allows the potentially dangerous compound to be diluted.

Considering the aforementioned, the antagonistic connection can be understood since on the economic side, small reflux ratios are preferred to decrease the cost of services and the TAC. Contrarily, decreasing the reflux ratio involves increasing the probability of risk. Therefore, the method must find a midpoint that allows you to decrease both objective functions. This midpoint is in the region where both objective functions find the smallest values.

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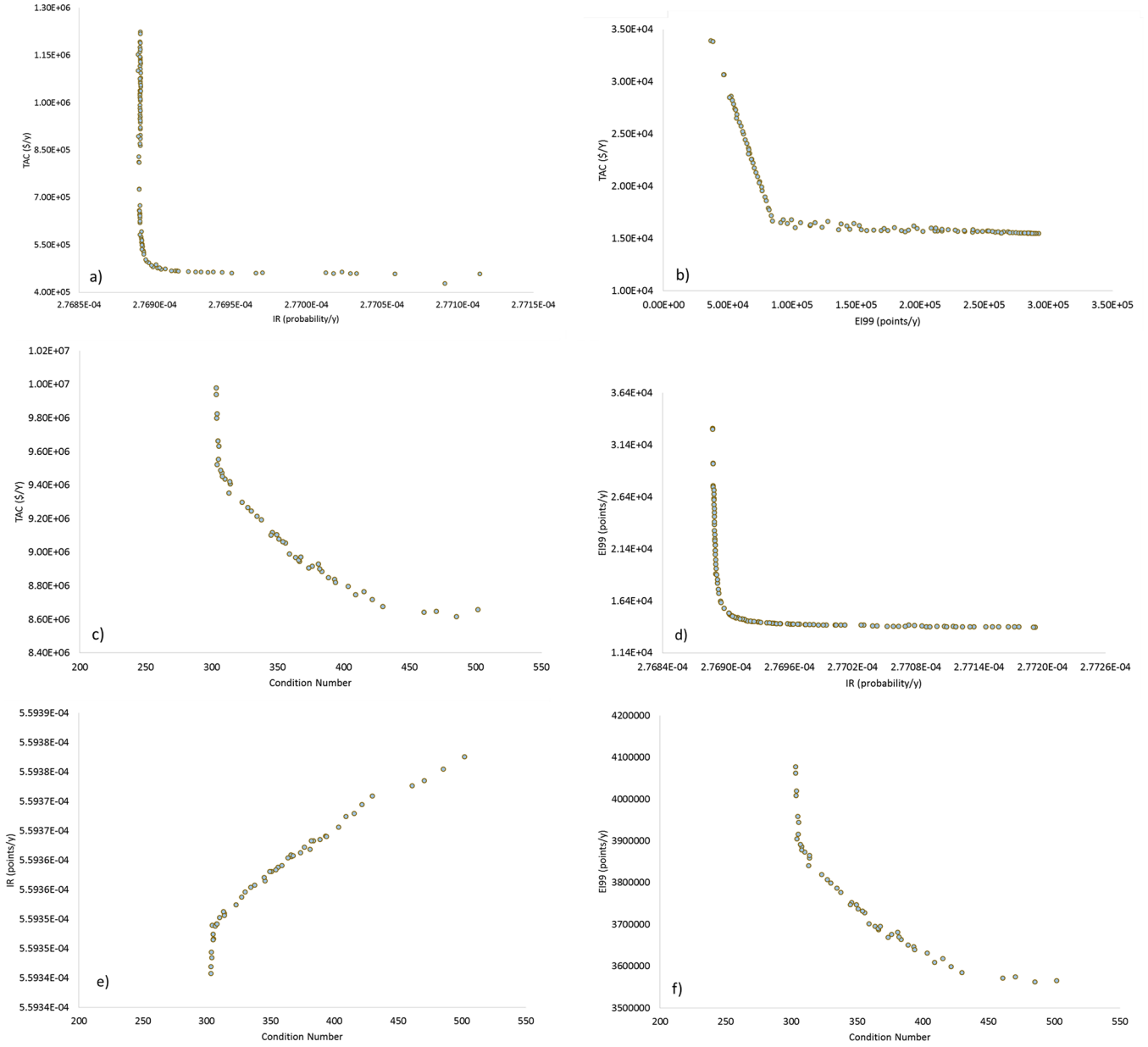

Figure 5. Pareto fronts evaluating all two-dimension alternatives for (a) pervaporation 2620, (b) pervaporation 500, (c) pressure swing high-high, (d) pervaporation 500, (e) pressure swing high-high, and (f) pressure swing high-high.

Figure 5b shows the antagonistic trend between TAC and IE99. As mentioned in section 4, the evaluation of the EI99 was carried out considering three aspects: the steam used for heating, the steel to build the equipment, and the electricity to pump cooling water. In this sense, it is clear that one direction to reduce the environmental impact is to design small and low-energy equipment. In the calculations of the TAC, the preferences are similar, small equipment with low energy consumption. Up to this point, it would seem that there is no antagonistic behavior between the objective functions. However, one must note that there is an inverse connection between the size of the equipment and the energy requirement. That is, small equipment (a few stages of equilibrium) will require a higher amount of energy, and equipment with larger dimensions (many stages of equilibrium) will require a lesser amount of energy to carry out the same purification process. Therefore, the design of the columns must consider a balance equipment not so small that it causes an increase in energy requirements, TAC and IE99, but neither very large equipment that impacts the capital cost, IE99, and energy.

By analyzing Figure 5c, the antagonistic behavior between the condition number and TAC is observed in the same way. The bottom line is that better dynamic behavior comes at a cost. After analyzing the convergence in the variables, it is observed that the small condition numbers are associated with large values of diameter and reflux ratio. A column with a relatively large diameter/reflux has better controllability as measured by the condition number. It is clear that large equipment with a high reflux ratio will generate a higher TAC. A midpoint should be sought avoiding affecting both objective functions, which causes antagonistic behavior in the objective functions.

Understanding the role that variables play in calculating the TAC, EI99, IR, and condition number, it is possible to understand the Paretos fronts formed in Figure 5d,f. It must

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Table 4. Objective Function for All Alternatives Studied and the Minimum Selling Price

technique	scenario	TAC ($/year $kg_{butanol}$)	EI99 (points/year $kg_{butanol}$)	cond. number	IR (Prob/year)	minimum selling price ($/kg)
azeotropic dist.	high-high	0.3432	0.1390	5.54	5.577×10^{-4}	0.6800
	high-low	0.3092	0.1223	18.75	5.590×10^{-4}	0.6289
	low-low	0.6992	0.2652	21.91	5.588×10^{-4}	1.6438
pervaporation	low-high 500	0.0392	0.0066	8274	2.772×10^{-4}	0.4281
	low-high 2620	0.0339	0.0066	2,066,538	2.772×10^{-4}	0.3297
pressure swing	high-high	0.9294	0.3841	42.49	5.594×10^{-4}	1.6038
	high-low	0.5864	0.2238	49.72	5.596×10^{-4}	1.1918
	low-low	1.5143	0.5735	485.34	5.584×10^{-4}	3.3773

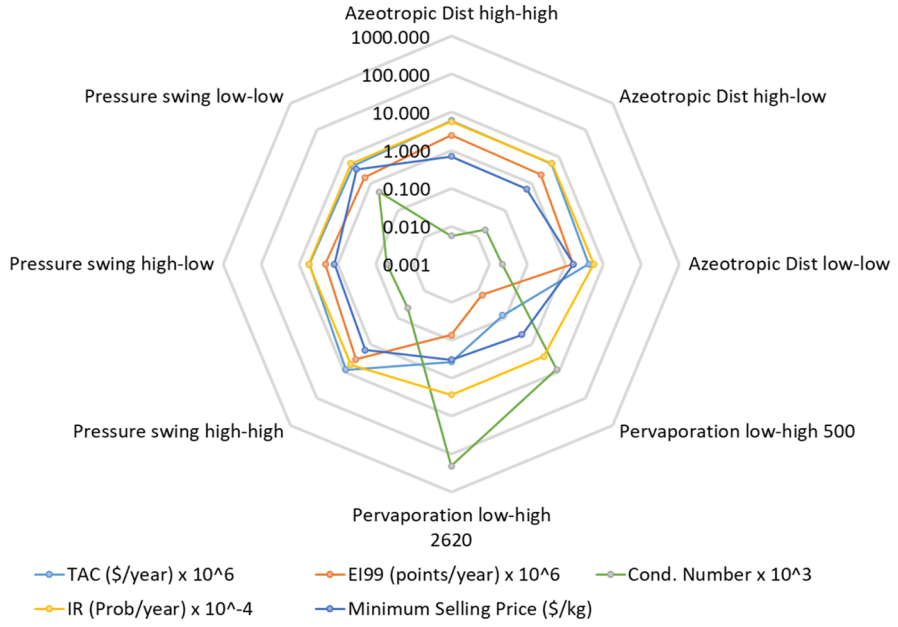

Figure 6. Comparison among the objective function of all case studies.

be considered that each design variable can cause different effects on the objective functions. For example, increasing diameter can benefit controllability; however, it has a detrimental effect on TAC. Alternatively, some other design variables have similar effects since they impact all the objective functions in various ways.

Finally, a relevant aspect to mention is what is observed in Figure 5e. Through the interaction of all the variables involved, it was possible to find a behavior where it can be observed that, with a lower number of conditions, it is possible to obtain a lower probability of accidents. This behavior is totally logical according to what is projected as a sustainable process. That is, from a green process perspective, processes that are not in tight control could produce more waste. In this case, the generation of waste is totally related to the continuous or instant release of potentially dangerous compounds, obviously increasing the inherent risk.

As a final product of the optimization process, Table 4 shows the objective functions obtained. Additionally, Figure 6 shows the global behavior of all the schemes analyzed in each of the objectives.

Table 5 and Figure 6 show how a significant amount of energy (reflected in the TAC) is required to increase purity from 96.7 to 99.9 mol %. For example, considering azeotropic distillation, the change in purity is reflected in a 10% increase in TAC per kg of butanol. For pressure swing distillation, this slight increase in purity has a cost of close to 40% in TAC per kg of butanol. In other words, some separation technologies require a greater energy investment to increase the purity of butanol.

Table 5. Design Parameters for the Distillation Column in Pervaporation

pervaporation	low-high 500 (C1)	low-high 2620 (C1)
number of stages	9	13
reflux ratio	0.346	0.347
feed stage	3	21
column diameter (m)	0.625	0.798
operative pressure (kPa)	101.353	101.353
distillate rate (kmol/h)	18.149	95.066
condenser duty (kW)	302.98	1588.05
reboiler duty (kW)	0.419	2.690

In the particular case of low-low feeding, the costs associated with purification rise considerably. For azeotropic distillation, as for pressure swing distillation, the increase in TAC per kg of butanol is more than double. This means that the cost associated with the production of high purity butanol from a relatively dilute fermentation broth (1.035% wt) is not economically viable compared to that slightly more concentrated one (3.99% wt).

While it is clear that the case studies do not consider the same feed stream because various scenarios are being considered, the normalized TAC value for each kilogram of butanol provides a fair comparison between each alternative.

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Table 6. Design Parameters for the Azeotropic Distillation Scheme

	high-high		high-low		low-low	
azeotropic distillation	C1	C2	C1	C2	C1	C2
number of stages	13	15	18	6	7	18
reflux ratio	1.229	0.204	0.604	0.107	0.364	1.3063
feed stage	11	12	17	4	4	13
column diameter (m)	1.371	1.478	0.837	1.189	1.046	1.078
operative pressure (kPa)	101.353	10.353	101.353	101.353	101.353	101.353
distillate to feed ratio	0.0348	0.756	0.037	0.728	0.009	0.731
condenser duty (kW)	2656.07	952.2	1392.6	755.06	209.32	527.68
reboiler duty (kW)	12177.43	993.46	11123.71	793.59	8432.57	541.58

Table 7. Design Parameters for the Pressure Swing Scheme

	high-high		high-low		low-low	
pressure swing	C1	C2	C1	C2	C1	C2
number of stages	6	25	10	18	19	8
reflux ratio	3.044	0.9	0.433	0.323	0.854	0.41
feed stage	5	4	7	13	10	4
column diameter (m)	0.806	0.9226	1.426	0.852	1.314	0.702
operative pressure (kPa)	101.353	10.3	101.353	10.3	101.353	10.3
outlet pressure in valve (kPa)		10.3		10.3		10.3
distillate to feed ratio	0.035	0.9227	0.033	0.925	0.0117	0.944
condenser duty (kW)	8674.93	4098.71	923.34	2827.59	648.35	1077.34
reboiler duty (kW)	18094.54	1628.11	10683.98	376.59	9088.68	220.02

In this sense, it is easy to observe that the process that involves membranes, pervaporation, is the one that generates the lowest total annual cost per kilogram of butanol produced. It is evident that the improvement in capital and service costs is due to the use of the membrane. Table 4 shows the advantage of feeding the column with a higher concentration of butanol compared to other technologies is clear. Additionally, this same technology produces alternatives with less environmental load, as well as safer and with a lower minimum selling price compared to the other alternatives. According to Table 5, the design parameters of the pervaporation schemes 500 and 2620 and the reboiler duty involved in the separation of the butanol−water mixture are less than the other alternatives. Even when the cost of membrane is already accounted, these alternatives are the most promising economic ones. Additionally, the correct combination of equipment size and energy requirements makes an environmental load of this equipment equally lower. In addition, considering only a single separation column reduces the probability of a catastrophic event by approximately 50% compared to the other alternatives.

However, the clear disadvantage of this pervaporation scheme is its controllability. According to Table 5, the condition number of the pervaporation is superior to the other alternatives. It is clearly observed that the diameters of other schemes, for example, azeotropic distillation, are greater than pervaporation. The number of conditions greater than the other technologies does not mean that it cannot be controlled; however, the dynamic effort to control that scheme when subjected to some disturbance is probably greater. In this way, the pervaporation scheme looks the best designer choice for industrial applications. Table 5 shows the design parameters required to reproduce this scheme.

Azeotropic distillation is the second best alternative in terms of TAC per kilogram of butanol, environmental load per kilogram of butanol, and the minimum selling price. In the case of controllability, it is evident that under a disturbance, the presence of the decanter dissipates its effects, and controllability is improved. Table 6 shows the design parameters for the azeotropic distillation system.

Finally, pressure swing distillation seems to be the worst alternative since performance indicators are the worst. Although, in inherent safety, this alternative is on par with azeotropic distillation, it is not a good option compared to the others. Tables 6 and 7 show the design parameters necessary to reproduce the best azeotropic distillation points and pressure swing columns.

Additionally, Figure 7 shows the stream information of each optimized scheme.

7. IMPLEMENTATION AND PRACTICAL CONSIDERATIONS

From a technology point of view, distillation is a tried and tested technology and can be rated at a technology readiness level (TRL) of 9;[49] as such from a commercialization point of view, distillation is an excellent process technology to carry out the separation process. It should also be noted that for a mixture such as Butanol and water, which has a significant difference in relative volatility, distillation would also likely be the most efficient method of carrying out this particular separation.[50] However, based on authors practical experience, the following aspects of this particular distillation process needs to be further investigated, and any key issues arising from this investigation should be addressed in full prior to commercial implementation.

The production of trace side components in both a fermentation and chemical-based reactions is a common occurrence and needs to be considered in both the design[51] and operation of the production process.[52−56] In addition, the "tight" separations such as the one proposed in this work can lead to compounds that are only present in (parts per million) range to be up concentrated and accumulate in a distillation column over time, creating potentially hazardous situations.[57] To this end, prior to commercialization, a detailed analysis of the

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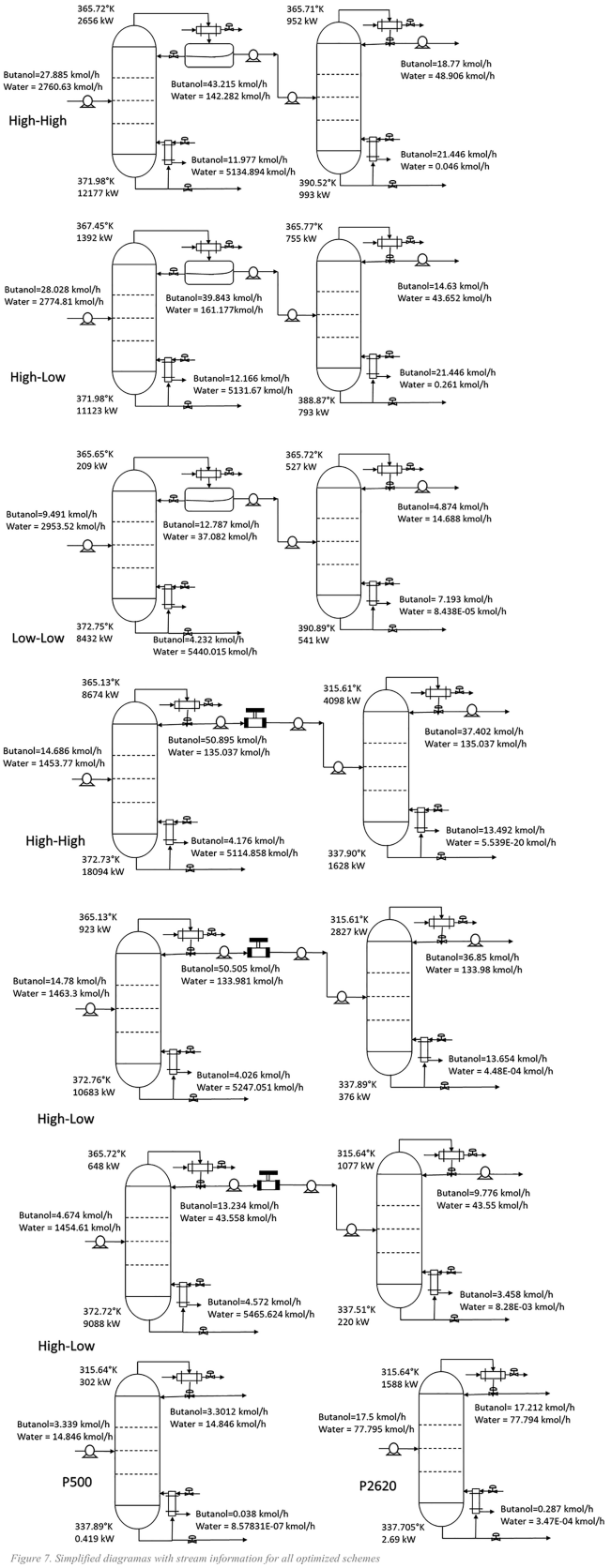

Figure 7. Simplified diagramas with stream information for all optimized schemes

Figure 7. Simplified diagrams with stream information for all optimized schemes.

fermentation broth that is produced in a bio-butanol process should be analyzed and appropriate measures taken to ensure trace components, in particular, middling boiling components (components with a volatility between water and butanol) are either not produced or if they are detected relevant changes to the design are made or monitored and managed during plant operations.

Similarly, the inherent nature of the fermentation process means variations in the broth leaving the fermenter as expected; to this end, there is a need to install an advanced control structure and enabling process measurement devices on the distillation process such that these variations can be dynamically compensated for. Monitoring of fouling (also due the trace level impurities found in a fermentation broth) must also be managed during the operation of this process; to this end, there is maybe a need to install a cleaning in place (CIP) system to allow for such a cleaning to be carried out. To this end, there is also a need to predict in advance the need for CIP as the distillation unit operations need to be taken "offline" to perform the CIP. Data-driven concepts can be employed for this requirement providing that there is sufficiently information-rich instrumentation (sensors) installed in the production process.[58−60]

8. CONCLUSIONS

In the present work, three different alternatives were evaluated for the separation of binary mixture water and butanol, in the compositions obtained in the process of reduction of volatile fatty acids. The evaluation of the sustainability metrics was carried out through the multiobjective optimization of the model using four objectives together. Comparing the results obtained, the pervaporation scheme turned out to be the most promising alternative. For example, the scenario low-high 500 reported values of 0.0392, 0.0066, 8274, 2772 × 10^{-4}, and 0.4281 of TAC/$kg_{butanol}$, EI99/$kg_{butanol}$, IR, condition number, and minimum sale price/$kg_{butanol}$, respectively. Regarding the scenario low-high 2620, the results were 0.0339, 0.0066, 2,066,538, 2772 × 10^{-4}, and 0.3297 of TAC/$kg_{butanol}$, EI99/$kg_{butanol}$, IR, condition number, and minimum sale price/$kg_{butanol}$, for the scenario low-high 2620, respectively. The use of the membrane allowed obtaining a more concentrated butanol feed, which places it in a more competitive position in all performance indicators. However, the other alternatives, pressure swing, for example, also showed a competitive minimum selling price compared to current butanol prices (27 and 52% of the cheapest option of pressure swing and azeotropic distillation, respectively). The effect of slightly increasing the concentration of butanol from the upstream process was observed. That is, from going up from 1.3 to 3.99% wt, there is a substantial improvement in various indicators. The results generated encourage the integration of a sustainable separation process to the process of reduction of volatile fatty acids for the generation of butanol in such a way that a possible industrial implementation is feasible in an environment of economic profitability and green engineering.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c06164.

Optimization procedure and objective function description (PDF)

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Notes

The authors declare no competing financial interest.

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