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Multiobjective Optimal Acetone−Butanol−Ethanol Separation Systems Using Liquid−Liquid Extraction-Assisted Divided Wall Columns

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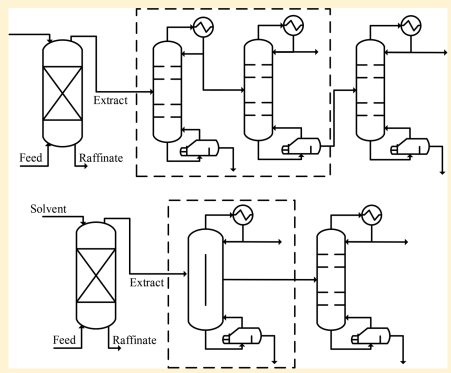
Supporting Information

ABSTRACT: Biobutanol is receiving great interest from both the academia and industry sectors, and some companies are already focusing on revamping bioethanol plants to produce biobutanol. The recovery of fuel grade butanol by distillation was proven not to be economically sustainable. On the other side, hybrid flowsheets, obtained with the combination of liquid−liquid extraction and distillation, were proposed as a more convenient alternative. Divided wall columns (DWCs), as one of the most promising intensified distillation alternatives, were here explored in combination with liquid−liquid extraction. A multiple-objective function, taking into account the economy, the environmental impact, and the process controllability, was defined to screen the alternatives. Among all the configurations considered, liquid−liquid extraction combined with a DWC equipped with two reboilers and a side rectifier, reached 22% and 18% reduction of the economy and environmental index, respectively. At the same time, also the controllability was improved compared to the hybrid liquid−liquid-assisted simple column distillation sequence considered as a reference.



■ INTRODUCTION

The acetone, butanol, ethanol (ABE) fermentation process, extremely popular in the time window between the World War I and the developing of the petrochemical industry, it is now coming back into the spotlight due to the properties of biobutanol. A comparison of the physical properties of bioethanol and those of biobutanol shows that biobutanol has a higher energy density and a lower tendency to absorb water; moreover, biobutanol/gasoline blends are less corrosive, making possible the use of the existing distribution infrastructures. Nevertheless, considering 1 kg of corn as feedstock, the yield of pure bioethanol is 0.30 kg and only 0.11 kg for the biobutanol production.[1] Taking into account the relevance of the feedstock's cost, the process yield could represent an issue in choosing between the two biofuels, and indicates the necessity of a higher research effort in improving the global efficiency of the biobutanol production.

As most of the alcohols obtained by fermentation, the biobutanol production process can be divided into three main sections: biomass pretreatment, fermentation, and product removal and purification.[2] The layout of the pretreatment stage depends on the biomass used, but in general its function is increasing the yield of fermentable sugars. Different technologies are available, varying from physical, physico-chemical, and chemical methods, to biological agents.[3,4] Recently, alternative methods, such as ionic liquids, ozonolysis, ultrasounds microwave, and supercritical carbon dioxide, have been proposed to reduce the energy consumption of the pretreatment section.[5] In the fermentation step, the conversion of the sugars is performed by the bacteria belonging to the genus Clostridium. Beyond the optimization of the fermentation conditions, metabolic engineering studies are the key approach to increase the production of butanol in the final fermentation broth.[6] A promising technique could be avoiding the ethanol production and promoting a AB fermentation process.[7] Studies on the product removal and purification section have been focused on the selection of the unit operations and their combination to perform the separation required with the lowest energy consumption. Distillation, as one of the most widespread separation methods, was initially applied for the separation of ABE mixtures. Marlatt and Datta[8] and Roffler et al.[9] proposed a three-column plus two-stripper configuration. Different alternatives have been successively proposed by van

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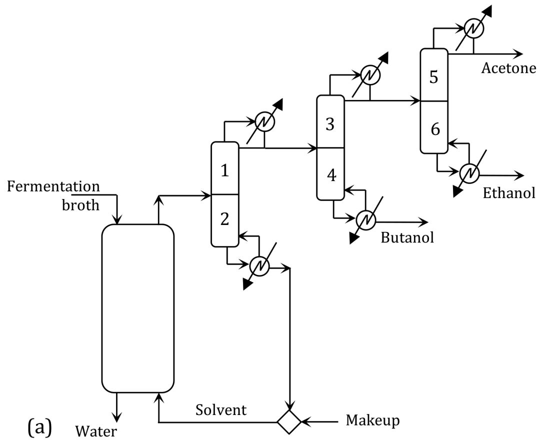

Figure 1. Liquid−liquid extraction-assisted simple columns: (a) liquid−liquid extraction-assisted indirect sequence (HLL-ISC), (b) liquid−liquid extraction assisted indirect−direct sequence (HLL-IDSC).

der Merwe et al.,[10] Lenz and Moreira,[11] and Qureshi and Blaschek[12] among the others.

For multicomponent mixtures, different alternatives are available to perform the separation by distillation ranging from simple column sequences, passing through thermally coupled, thermodynamic equivalent structures, heat integrated, intensified and divided wall columns (DWCs). The definition of all the alternatives is of paramount importance in the selection of the optimal configuration. This topic was approached during the years by different researchers, leading to different synthesis methodologies.[13−25] Nevertheless, since most of the alcohol mixtures obtained by fermentation are diluted and nonideal, their separation by distillation is too energy intensive, penalizing the whole process economic profitability. In particular, the ABE mixture has a homogeneous azeotrope between ethanol and water and a heterogeneous azeotrope between butanol and water and the combination of different unit operations appears the most efficient way to perform the separation. Liquid−liquid extraction-assisted distillation was proven to be an efficient combination for the ABE separation. At this point, it should be specified that liquid−liquid extraction can be combined into the bioreactor in order to reduce the strains butanol inhibition (extractive fermentation), or after the fermentation step (external solvent extraction).[26] The latter case is here considered.

When two or more unit operations are combined in the same "hybrid flowsheet", to accomplish the separation task, the generation and the evaluation of all the possible alternatives was not deeply explored. There are few exceptions, like the work of Kraemer et al.,[27] in which the authors developed an hybrid extraction-distillation flowsheet based on the optimal solvent selection. Liu et al.[28] used an algorithm method for process-network synthesis based on the P-graph. They considered gas stripping, distillation, and extraction as possible unit operations and, among all the alternatives predicted, only the hybrid extraction−distillation flowsheets resulted as competitive. In the present work the hybrid liquid−liquid extraction-assisted distillation flowsheets are considered, focusing on alternatives with divided wall columns (DWCs). DWCs were already proven to be an effective solution for biofuels separation. Torres-Ortega and Rong[29] proposed new DWC arrangements for the bioethanol purification reaching savings in the total annual cost of about 20%. Kiss[30] revised the application of DWCs for the production of bioethanol, biodiesel, and bioethers for industrial case studies, proving the possibility to reach energy savings up to 20−60%. However, DWC applications for the separation of biobutanol have not been fully explored. Yu et al.[31] examined a DWC configuration for the dehydration of *tert*-butanol reaching a 20% reduction of the total annual cost compared to the conventional distillation scheme. Okoli and Adams[32] studied the separation of biobutanol in a quaternary DWC, using the minimization of the total annual cost as design criterion. Even if useful information are included in both works, they only considered a specific configuration and a single objective function. In the present work a complete set of DWCs is presented and compared considering a multiobjective function obtained by the combination of three different indexes taking into account the economy, the environmental impact and the controllability of the alternatives. The present work contributes in defining a set of new hybrid alternatives obtained following a precise synthesis procedure avoiding any inventive generation activity. In the present work, conventional and nonconventional DWCs were examined.

■ HYBRID FLOWSHEETS SYNTHESIS PROCEDURE

The synthesis procedure is the essential tool used in the generation of the searching space that includes all the possible configurations to be explored. This step avoids the adaptation of known configurations to the specific case considered or any other activity that brings to the definition of an incomplete set of alternatives that eventually leads to ignore potentially optimal solutions. Sequential synthesis procedures, initialized by the simple column alternatives, were proven to be effective in the generation of complex multicomponent arrangements.[33] Simple column sequences are the simplest way to perform a separation by distillation and, for multicomponent mixtures, different arrangements are possible according to the components separation order. The number of sequences can be evaluated according to the formula reported by Thompson and King.[34] Following this modus operandi, liquid−liquid extraction assisted simple distillation columns, are considered first. In these hybrid flowsheets, the extract phase is fed to the distillation section. For the ABE separation case, this stream is expected to be a four-component mixture containing the solvent, the acetone, the butanol and ethanol; then five simple column sequences are possible. Two possible alternatives are reported in Figure 1; the hybrid liquid−liquid extraction

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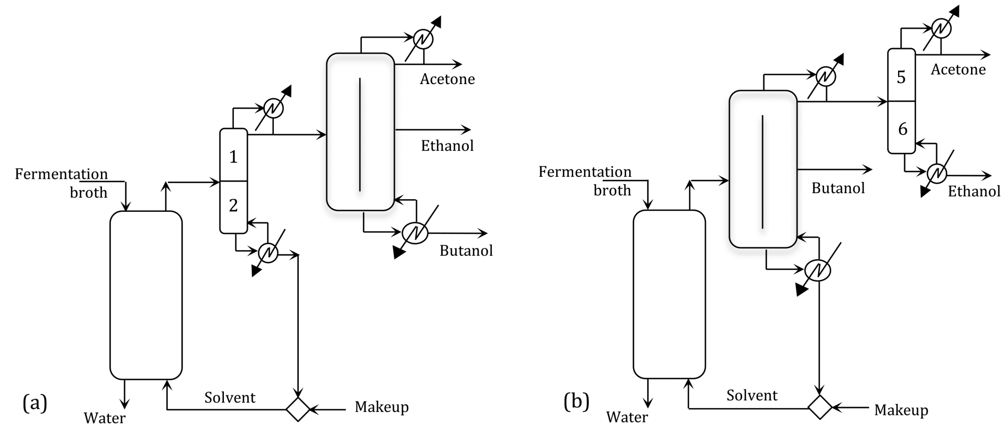

Figure 2. Liquid−liquid extraction-assisted conventional DWC configurations.

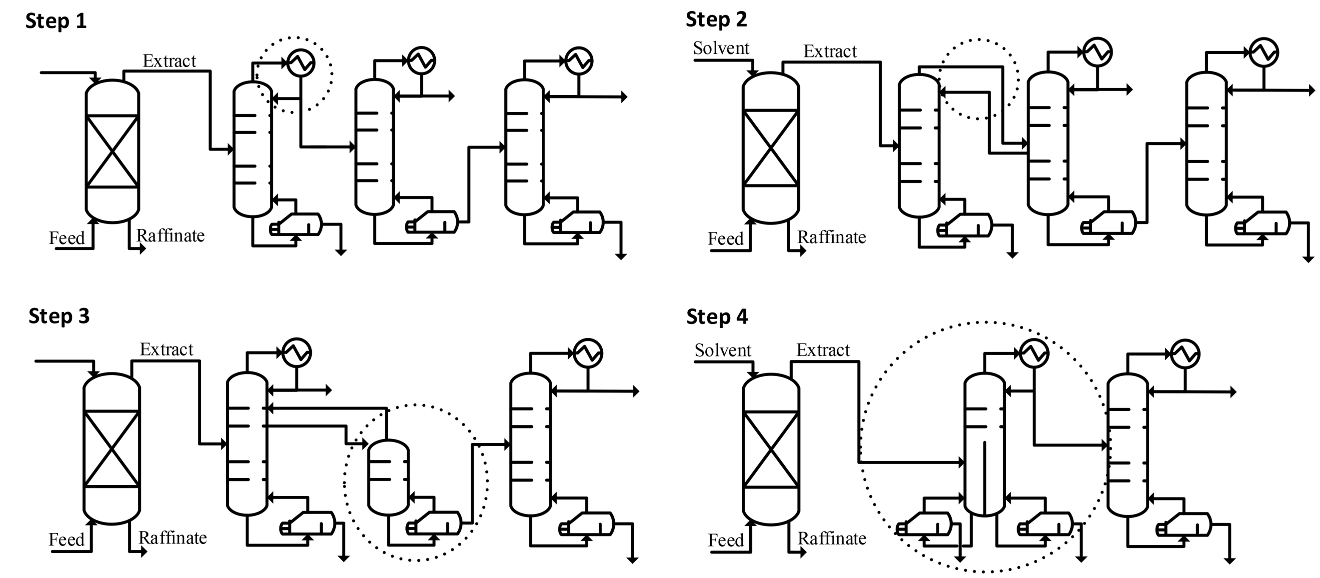

Figure 3. Liquid−liquid extraction-assisted nonconventional DWC configurations synthesis procedure.

indirect simple column configuration (HLL-ISC) and the hybrid liquid−liquid extraction indirect−direct simple column configuration (HLL-IDSC). For the generation of hybrid flowsheets in which liquid−liquid extraction is coupled with intensified distillation alternatives such as DWC, a distinction between conventional and nonconventional DWC was considered. Conventional DWCs are here defined, according to the schemes proposed by Kaibel,[35] as a single shell column equipped with a condenser, a reboiler, and a vertical partition in the central part. Three or four streams can be obtained, and the case of three streams is considered in this study.

Starting from a liquid−liquid-assisted simple column configuration, it is possible to substitute in a combinatorial process: two of the three columns with a ternary conventional DWC. Considering the HLL-ISC reported in Figure 1a, the resulting configurations are reported in Figure 2. The conventional DWC substitutes always two columns, the resulting hybrid flowsheet is then composed by a sequence of the liquid−liquid extractor, a simple column, and the DWC.

Differently from the case of conventional DWCs, to generate nonconventional DWCs a more structured systematic synthesis methodology is required. A nonconventional DWC is here defined as a column that could include multiple reboilers/condensers and/or intermediate reboilers and multiple walls.

A four-steps procedure able to generate a unique subspace of multicomponent nonconventional DWCs starting from simple column configurations was proposed by Rong.[36] The synthesis procedure is illustrated in Figure 3 using the hybrid indirect−direct simple column sequence as an example. The dotted circles evidenced the structural change done passing through the synthesis steps. In the first step, a simple column configuration is selected from the subspace including all the possibilities. In the second step, the original thermally coupled configurations are considered. These are obtained from the simple column configurations by elimination, in a combinatorial way, condensers and/or reboilers associated with nonproduct streams. Those exchangers are replaced by bidirectional thermally coupled vapor and liquid streams. In Figure 3 this step is accomplished by substitution of the first column condenser. The third step regards the generation of the thermodynamic equivalent structures from the corresponding original thermally coupled configuration by rearranging the column sections connected by thermal couplings. In Figure 3, this step brings to a configuration with a side stripper connecting the two remaining columns. In the last step, the multicomponent DWCs are obtained from the thermodynamically equivalent configurations by incorporating the single column section into its thermally linked column through a

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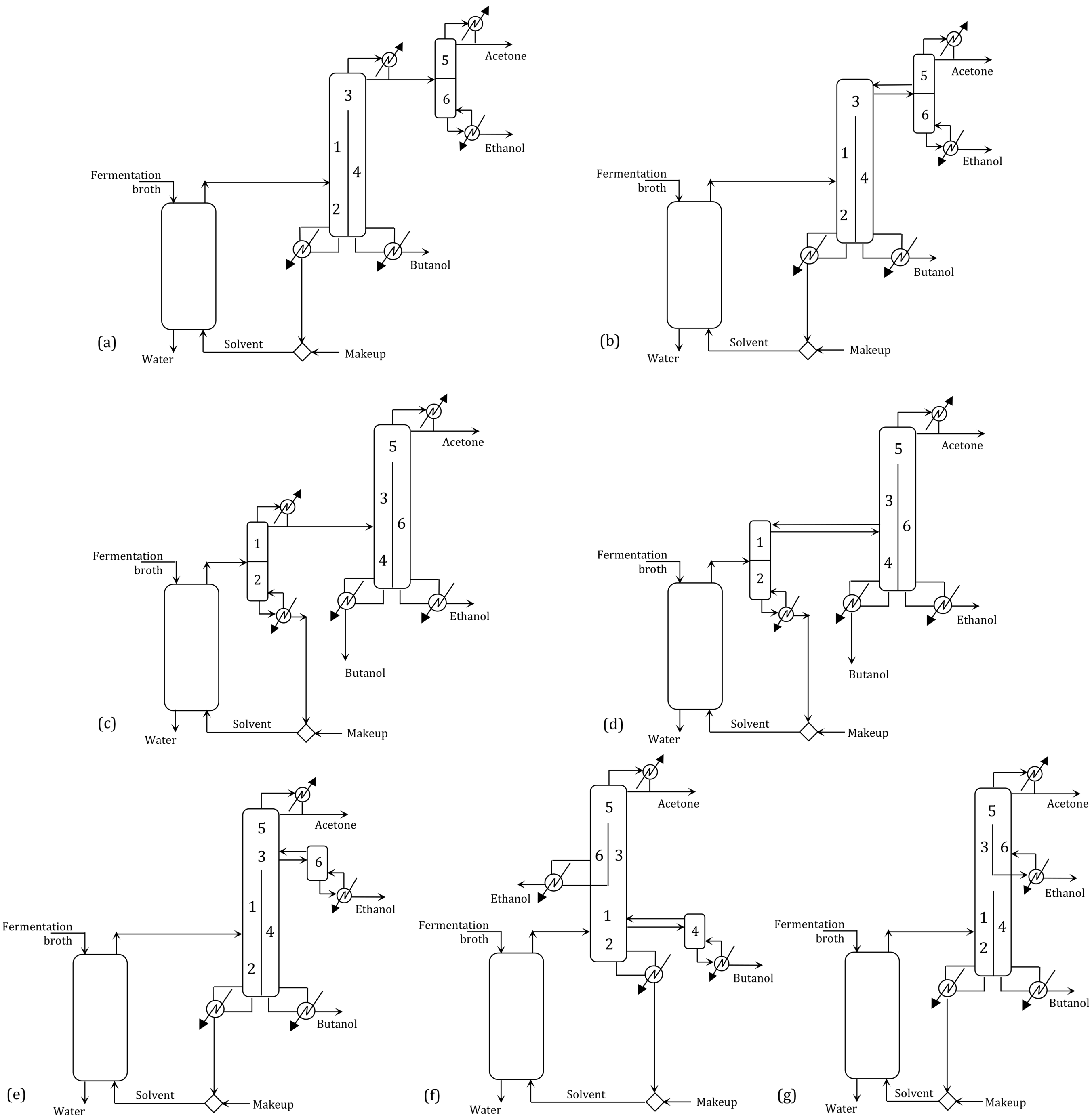

Figure 4. Liquid−liquid extraction-assisted nonconventional DWC configurations.

dividing-wall. In the example considered, the stripper section is implemented inside the column. As a result, the DWC with two reboilers is obtained. All the possibilities obtained from the HLL-ISC are summarized in Figure 4. Besides the generation of a complete new subspace of alternatives, this methodology has an important advantage compared to combinatorial-based methodologies. It is possible to establish a clear correspondence between each simple column configuration and the derived DWCs. Then, once the best simple column configuration is identified, only the DWCs derived from that sequence can be considered.

■ DESIGN PROCEDURE

The design of the hybrid liquid−liquid extraction-assisted distillation flowsheets was performed by minimizing an object function composed of the total annualized cost, the eco-indicator 99, and the condition number. The implementation of the controllability index in the design ensures the economical and smooth operation of the plant despite the influence of disturbance.[37]

Economic Index: the Total Annualized Cost (TAC). The total annualized cost is the index used in the objective function to take into account the economy of the process. It is evaluated as the sum of the annualized capital cost and the operating costs as reported in eq 1:

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$$\mathrm{TAC} = \frac{\text{capital costs}}{\text{project life}} + \text{operating costs} \quad (1)$$

The capital costs include the cost of the columns (shell and trays), kettle reboilers, and shell and tube condensers. The capital cost was annualized considering a project life equal to 10 years. The operating costs were obtained as the sum of the costs associated with the auxiliary fluids for the reboilers and condensers. The TAC evaluation was performed according to the correlations and data reported by Turton et al.[38] According to Dejanovic et al.,[39] the capital cost of the DWCs was increased by 20% to take into account the wall arrangement.

Environmental Indicator: Eco-Indicator 99 (EI99). The EI99 was used to quantify the environmental load of the flowsheets over the life cycle. In the EI99 methodology, 11 impact categories are considered aggregated into three major damage categories: human health, ecosystem quality, and resources depletion.

It was quantified following the procedure proposed by Goedkoop and Spriensma[40] as reported in eq 2:

$$EI99 = \sum_{b} \sum_{d} \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (2)$$

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 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.

Index of Process Controllability: Condition Number (CN). Since this study is focused on hybrid flowsheets where DWCs are included, the controllability of the system gains an important role in the alternatives selection. Choosing the condition number as controllability index, its definition is based on the numerical concept of singular value decomposition (SVD). The SVD of the matrix K in eq 3, results in three component matrices:'

$$\mathbf{K} = \mathbf{U}\Sigma\mathbf{V}^{\mathrm{T}} \quad (3)$$

where, $\mathbf{K}$ is an $n \times m$ matrix; $\mathbf{U}$ is an $n \times n$ orthonormal matrix called the "left singular vector"; $\mathbf{V}$ is an $m \times m$ orthonormal matrix called the "right singular vector"; $\sum$ is an $n \times m$ diagonal matrix of scalars called the "singular values" and are ranked as $\sigma_1 > \sigma_2 > \sigma_3 \ldots \sigma_m > 0$. When the matrix $\mathbf{K}$ describes the steady state characteristic of a multivariable process, the singular values assume a precise physical meaning related to potential process control problems.[41]

The CN, defined in eq 4, is the ratio between the largest and the smallest singular values and is used to qualitatively measure the sensitivity to uncertainty. Large values of the CN may correspond to control problems. In general, configurations with a high minimum singular value and low CN are expected to have best dynamic performances under feedback control.

$$\mathrm{CN} = \frac{\sigma_{\max}}{\sigma_{\min}} \quad (4)$$

For each process design it is possible to generate a relative gain matrix in the nominal state, the correspondent CN is obtained in an open-loop control policy. The elements of each matrix are calculated considering a 0.5% positive disturbance in the nominal state of manipulated variable value (reflux ratio, reboiler heat duty, side stream flow rate and so on). The impact of the perturbations is low enough to assume a first order response. The SVD method, and consequently the singular values, depends on the scaling of the input and outputs. To remove this dependency different scaling methods have been proposed.[42,43] For the configurations reported in this study control variables such as the purity of the products there are naturally bounded between 0 and 1, but the reflux ratio and in general all the streams flow rates are unbounded.

This drawback was eliminated considering that the maximum aperture reached by the control valves is twice the steady state nominal value; therefore, in principle, the valves are opened to 50%. This implies that for the relative gain matrix, the step change is implemented in the manipulated variable divided by twice the steady state.

Optimization Procedure. The design of the different alternatives proposed was performed minimizing the multi-objective function reported in eq 5:

$$\min(\mathrm{TAC}, \mathrm{EI99}, \mathrm{CN}) = f(N_e, N, N_f, \mathrm{RR}, D, F_L, F_V, \phi, S)$$
$$\text{subject to} \quad \vec{y} \geq \vec{x} \quad (5)$$

where N_e is the number of stages for the extractor, N is number of stages for the distillation columns, N_f is the column feed stage, RR is the reflux ratio, D is the distillate flow rate, F_L is the interconnection liquid flow rate, F_V is the interconnection vapor flow rate, Φ is the column diameter, S is the solvent flow rate; y and x are the vectors of obtained and required purities, respectively. Because of the complexity of the problem, Differential Evolution with Tabu List (DETL) was used as the optimization algorithm. The differential evolution algorithm is based on four main steps: initialization, mutation, crossover, and selection, and its application with multiobjective functions was successfully proven for different engineering related problems.[44−47] To implement the optimization algorithm, Aspen Plus was linked to Microsoft Excel using the dynamic data exchange by COM technology. The design variables are sent to Microsoft Excel where these values are attributed to the process variables required by Aspen Plus. After the simulation is completed, Aspen Plus returns the results to Microsoft Excel. Microsoft Excel analyzes the values of the objective functions and proposes new values of the decision variables according to the stochastic optimization method coded as a macro in Visual Basic. The control parameters used to set the optimization code are 200 individuals, 500 numbers of generations, a tabu list of 50% of total individuals, a taboo radius of 10^{-6}, a crossover probability of 0.8, and a mutation factor of 0.6. The DETL's parameters were defined according to previous works focused on simulation and optimization of complex configurations and by tuning on preliminary simulations.[48] The selection of the final solution was obtained through a Pareto-based approach.

■ CASE STUDY

To compare the different hybrid flowsheets, a feed of 1.64 kmol h^{-1} composed, in molar basis, by 8.1% acetone, 11.3% butanol, 0.4% ethanol, and 80.2% water at 35 °C and 1 atm, was considered. The composition was defined according to Wu et al.[49] The same feed was used also by different authors for studies on hybrid flowsheets focused on the possibility of process heat integration and in the evaluation of risk analysis.[50,51] All the proposed configurations have been simulated using Aspen Plus V8.8. The NRTL−Hayden O'Connell equation of state with Henry's law was selected as thermodynamic model and hexyl-acetate was used as a mass separation agent.[52,53] The minimum purity targets were fixed

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Table 1. Design and Operative Parameters for the Configurations in Figure 1

	Figure 1a				Figure 1b			
	extractor	C_1	C_2	C_3	extractor	C_1	C_2	C_3
number of stages	5	23	16	31	5	23	47	46
feed location		12	11	25		12	31	14
reflux ratio		0.894	0.141	7.187		0.894	6.186	9.933
distillate flow rate [kg h^{-1}]		21.685	8.035	7.709		21.685	7.706	0.331
extract flow rate [kg h^{-1}]	734.586				734.586			
solvent flow rate [kg h^{-1}]	712.860				712.860			
diameter [m]	0.335	0.288	0.294	0.287	0.335	0.288	0.290	0.310
pressure [kPa]	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3
condenser duty [kW]		7.241	7.995	9.020		7.241	7.919	0.854
reboiler duty [kW]		66.222	8.368	9.015		66.222	8.256	0.883
TAC [k$ yr^{-1}]	129.42				134.79			
EI99 [kpoints yr^{-1}]	15.55				13.93			
CN	15248.60				616636.85			

Table 2. Design and Operative Parameters for the Configurations in Figure 2

	Figure 2a			Figure 2b		
	extractor	C_1	DWC	extractor	DWC	C_3
total number of stages	5	23	48	5	49	31
number of stages across the wall			18		8	
feed location		12	31		21	16
side stream location			33		20	
reflux ratio		0.894	20.314		39.053	8.284
distillate flow rate [kg h^{-1}]		21.685	7.697		8.035	7.705
Side stream flow rate [kg h^{-1}]			0.327		13.663	
Liquid split flow rate [kg h^{-1}]			2.183		39.295	
vapor split flow rate [kg h^{-1}]			9.821		481.178	
extract flow rate [kg h^{-1}]	733.873			733.873		
solvent flow rate [kg h^{-1}]	712.147			712.147		
diameter [m]	0.335	0.288	0.302	0.335	0.413	0.287
pressure [kPa]	101.3	101.3	101.3	101.3	101.3	101.3
condenser duty [kW]		7.241	23.452		47.00	10.216
reboiler duty [kW]		66.218	23.818		106.357	10.211
TAC [k$ yr^{-1}]		111.86			122.99	
EI99 [kpoints yr^{-1}]		17.50			19.50	
CN		10.35			10183.72	

on mass base to 99.5% for acetone and biobutanol, and 99.0% for ethanol. For all the columns, the pressure was optimized taking into account the availability of cooling water at 20 °C. Low, medium, and high pressure steams were considered as auxiliary fluid for the reboilers depending on the temperature of the bottom stream. DWC models are not included in Aspen Plus, for this reason their design was performed decomposing the configurations in different column sections interconnected by liquid and vapor streams. This procedure was already utilized by Torres-Ortega and Rong[29] and Errico et al.[54] for DWCs applied to the bioethanol separation.

■ LIQUID−LIQUID EXTRACTION-ASSISTED SIMPLE COLUMN DISTILLATION

A rigorous analysis includes the evaluation of all the possible liquid−liquid extraction-assisted simple column distillation alternatives, but in this case, heuristic rules can be used to reduce the computational effort. The extract stream is expected to be more concentrated in the solvent, then, following the rule to remove the most plentiful first, only the indirect and the indirect−direct configurations, reported in Figure 1, have been considered. The design and operative parameters obtained together with the values of the objective functions were reported in Table 1. From the results, it is possible to notice that the HLL-ISC configuration performs better in two of the three indexes used in the objective function. Only the EI99 is about 10% higher compared to the HLL-IDSC configuration. The Pareto front for both configurations are available as Supporting Information. Globally it is possible to select the HLL-ISC configuration as the best option among the hybrid liquid−liquid extraction assisted simple column configurations.

■ LIQUID−LIQUID EXTRACTION-ASSISTED CONVENTIONAL DWC

Considering the HLL-ISC configuration, the corresponding hybrid liquid−liquid extraction-assisted conventional DWCs are reported in Figure 2. The first case, reported in Figure 2a, was obtained by substituting the last two columns of the HLL-ISC configuration of Figure 1a with a DWC. In Figure 2b is reported the case in which the first two columns were substituted by a DWC. The correspondent design and objective functions values are reported in Table 2. An examination of the results shows that the configuration in Figure 2a, where the solvent is removed in the simple column, has the lowest values

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Table 3. Objective Function Values for the Configurations of Figure 4

objective function	Fig. 4(	Fig. 4b	Fig. 4c	Fig. 4d	Fig. 4e	Fig. 4f	Fig. 4g
TAC [k$ yr^{-1}]	108.54	105.57	115.50	101.78	100.85	100.59	97.88
EI99 [*k*-points yr^{-1}]	13.73	12.93	14.34	13.30	12.79	14.74	12.22
CN	1402	1.7	1.22×10^{17}	3.9	7.3	9888.3	18994.4

for all the objective functions. Compared to hybrid liquid–liquid-assisted simple columns arrangements, it is possible to notice an increase of the EI99 index. This is due to the highest DWC reboiler duty compared to the single simple columns. The Pareto fronts for these configurations are reported in the Supporting Information section.

LIQUID–LIQUID EXTRACTION-ASSISTED NONCONVENTIONAL DWC

The hybrid liquid–liquid configurations assisted nonconventional DWCs derived from the HLL-ISC configuration are summarized in Figure 4. Among all the hybrid configurations reported in the figure, it is possible to identify four categories:

1. Configurations for which the hybrid flowsheet is composed by a liquid–liquid extractor, a DWC and a simple column: Figure 4a and Figure 4c.
2. Configurations for which the hybrid flowsheet is composed by a liquid–liquid extractor and a DWC thermally coupled with a simple column: Figure 4b and Figure 4d.
3. Configurations for which the hybrid flowsheet is composed by a liquid–liquid extractor and a DWC thermally coupled with a single rectifying section: Figure 4e and Figure 4f.
4. Configurations for which the hybrid flowsheet is composed by a liquid–liquid extractor and a single DWC with multiple partitions and intermediate reboiler: Figure 4g.

Table 3 summarizes the objective values for all the alternatives presented in Figure 4. Taking into account the TAC and the EI99, the configuration reported in Figure 4g results the best one even if penalized by the controllability index. The design and operative parameters for this configuration are reported in Table 4.

RESULTS DISCUSSION

A comparison of the results reported in Tables 1, 2, and 3 shows that, from an economic point of view, all the liquid–liquid-assisted DWCs have a lower value of the TAC with respect to the best liquid–liquid-assisted simple column distillation reported in Figure 1a. Among the liquid–liquid-assisted conventional DWCs, the configuration of Figure 2a showed the lowest values of all the objective functions. If compared to the HLL-ISC configuration, it realized 13.6% reduction of the TAC and a better controllability, nevertheless a penalty of 12.5% in EI99 is observed. The penalty is due to the highest DWC utility consumption. When the solvent was recovered as the bottom stream in the DWC, as depicted in Figure 2b, the TAC and the EI99 was penalized compared to the reference case of Figure 1a. Similar results for were obtained for hydrocarbon mixtures by Errico et al.[55] and Lucero-Robles et al.[56] Considering the liquid–liquid extraction-assisted nonconventional DWCs, the configuration of Figure 4g has the lowest TAC and EI99 but is penalized by its controllability. The economic performance of the configuration

Table 4. Design and Operative Parameters for the Configurations in Figure 4(g)

	column section				
	extractor	1 + 2	4	3 + 5	6
number of stages	5	43	26	71	7
feed location		13			
reflux ratio					
distillate flow rate [kg h^{-1}]				7.716	
residue flow rate [kg h^{-1}]		712.159	13.681		0.317
liquid split flow rate [kg h^{-1}]		43.460	17.383		0.420
extract flow rate [kg h^{-1}]	733.873				
solvent flow rate [kg h^{-1}]	712.147				
diameter [m]	0.335	0.577	0.288	0.577	0.288
pressure [kPa]	101.3	101.3	101.3	101.3	101.3
condenser duty [kW]		0.000	0.000	11.233	0.000
reboiler duty [kW]		69.920	0.633	0.000	0.022

of Figure 4g was expected since it is the more intensified alternative in which the solvent and the ABE mixture were separated in the same column. Extending the comparison to the best liquid–liquid extraction-assisted simple column distillation, the configuration of Figure 4e realized better performance for all three objective functions. In particular it reached 22% and 18% reduction of the TAC and EI99, respectively, together with a better controllability index. Details on the configuration of Figure 4e are reported in Table 5. From the structural point of view, configurations 4e and 4g differ only for column section 6. In the configuration of Figure 4e there is a single rectifying section, whereas in Figure 4g this section is implemented inside the DWC. The differences between the two configurations regarding the TAC and the EI99 are lower than 5%, nevertheless the highest value of the CN for the configuration of Figure 4g brings to the conclusion that the alternative 4e is the most convenient. The other two configurations exhibited interesting performance; Figure 4 panels b and d have lower values of the objective functions than the reference case, and the difference with respect to the best alternative is lower than 5%. These configurations belong to the group where the DWC is thermally coupled with the simple column. The Pareto front for the configurations of Figure 4b–e are reported in the Supporting Information section.

CONCLUSIONS

Biobutanol, as a potential bioethanol competitor, is receiving industrial interest despite its optimal production process being still out of reach. Improvements in the separation of biobutanol, acetone, and ethanol by hybrid liquid–liquid-assisted distillation were considered. In particular new hybrid arrangements composed by liquid–liquid extraction and different divided wall

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Table 5. Design and Operative Parameters for the Configurations in Figure 4e

	extractor	column section 1 + 2	4	5 + 3	6
number of stages	5	43	43	71	7
feed location		13			
reflux ratio				0.644	
distillate flow rate [kg h^{-1}]				7.717	
residue flow rate [kg h^{-1}]		712.108	13.681		0.316
liquid split flow rate [kg h^{-1}]		43.463	17.383		
vapor split flow rate [kg h^{-1}]					
extract flow rate [kg h^{-1}]	733.873				
solvent flow rate [kg h^{-1}]	712.147				
diameter [m]	0.335	0.288	0.288	0.3788	0.299
pressure [kPa]	101.3	101.3	101.3	101.3	101.3
condenser duty [kW]		0.000	0.000	11.233	0.000
reboiler duty [kW]		69.920	0.633	0.000	0.023

configurations were systematically generated. All the alternatives were optimized using a triple objective function composed by the total annual cost, the eco indicator 99, and the condition number. The multiobjective function takes into account the economic, the environmental, and the controllability behavior. The alternatives were compared to the liquid–liquid extraction-assisted simple column distillation. In the best configuration selected, the extract stream is fed to a DWC equipped with two reboilers and a side rectifying stream. For this configuration a reduction of 22% of the TAC and 18% of EI99 was observed together with a better condition number. Another two configurations reached promising performance with less than 5% difference compared to the best alternative and a better controllability. The configurations proposed have been never considered for the ABE separation, and they represent a concrete possibility to improve the competitiveness of the biobutanol process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b03078.

Pareto fronts for the configurations examined (PDF)

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Notes

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