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Controllability Analysis of Process Alternatives for Biobutanol Purification

Biobutanol has characteristics similar to petroleum fuel and is considered as a superior biofuel compared to ethanol. The development of technologies for biobutanol production by fermentation has resulted in higher final biobutanol concentrations together with less energy-intensive separation and purification techniques. These new technological developments have the potential to provide a production process for biobutanol that is economically viable in comparison to the petrochemical pathway for its production. The control properties of four different possible process designs for biobutanol purification are analyzed. The results, using the singular value decomposition technique, indicated that the scheme where only biobutanol flow is purified, and both ethanol and acetone leaving the purification process mixed with water and biobutanol traces, showed the best control properties.

Keywords: Acetone-butanol-ethanol fermentation, Biobutanol, Distillation, Singular value decomposition

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1 Introduction

The increasing industrialization of the world has led to a steep rise for the demand of petroleum-based fuels. Today, fossil fuels take up 80 % of the primary energy consumed in the world, of which 58 % is only consumed by the transport sector. The sources of these fossil fuels are becoming exhausted; moreover, there has been a major contribution in greenhouse gas emissions by consumption of fossil fuels to fulfill the energy demand, which leads to many negative effects including climate change, receding of glaciers, rise in sea level, loss of biodiversity, etc. [1]. The increasing energy demand leads to a higher crude oil price, directly affecting the global economic activity.

Progressive depletion of conventional fossil fuels with increasing of energy consumption and greenhouse gas emission have led to alternative, renewable, sustainable, efficient, and cost-effective energy sources with less emissions. Butyl alcohols, such as butanol and isobutanol, are attracting attention as renewable liquid biofuels. The reasons for this interest include higher energy density, lower water sorption, and improved blending with gasoline in comparison with ethanol. Acetone-butanol-ethanol (ABE) fermentation employing solventogenic *Clostridium* species, such as *Clostridium acetobutylicum* and *Clostridium beijerinckii*, was conducted industrially during the first half of the last century. Before 1950, ABE fermentation using corn and molasses as substrates was ranked second after ethanol fermentation in importance and scale of production, but subsequently decreased owing to increasing substrate (corn and molasses) costs and the cheaper availability of petrochemically derived butanol [2].

Butanol is currently used in industries as a feedstock chemical for the manufacture of products such as butyl amines, amino resins, butyl acetates, and tires. With concerns regarding energy security and global warming, and the interest in the use of renewable raw materials for the production of fuels and chemicals, biobutanol has been touted as another source of biofuel that could advance in energy security and help mitigating global warming. The potential use of biobutanol as fuel or fuel additive represents a prospective new market for biobutanol. The fermentation process for acetone and butanol production has been studied in depth by many researchers. However, the concentration of *n*-butanol produced in the batch fermenter is quite low ($20\,g\,L^{-1}$) because of toxicity problems [3]. In addition, acetone and ethanol are also produced, which must be removed from the mixture coming from the fermenter.

Little attention has been paid to the distillation process in the production of butanol and its optimization. In the distillation process, energy consumption and separation efficiency can be greatly influenced by the water and butanol content in the overhead distillate of the butanol column. Therefore, reduction of water and butanol content in the overhead distillate of the butanol column can effectively reduce the cost of butanol fermentation.

Some studies about design and optimization of the process for the purification of butanol obtained via the ABE process

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have been reported by Van der Merwe et al. [4] and Sánchez-Ramírez et al. [5], for example. The dynamics and control of systems for purification of butanol have not been considered in depth [6]. Sánchez-Ramírez et al. [5] performed the process design, optimization, and comparison of four different possible process routes for industrial-scale biobutanol production from agricultural crops and molasses. This study is the continuation of the work of Sánchez-Ramírez et al. [5]. The dynamic behavior of the optimized study cases in the mentioned paper is analyzed.

2 Dynamic Analysis

The concept of dominant time constant with a linear first-order response for the columns, defined by Skogestad and Morari [7], was applied to generate the transfer matrix of the process. This assumption led to generate the dominant time constant from steady-state simulations, considering that the distillation columns dynamics are dominated by one large time constant. Next, by means of the frequency response, the singular value decomposition (SVD) was accomplished, Eq. (1), with a constant disturbance of –0.5 % on the control variable directly related to the product stream [8].

Transfer functions were grouped into a transfer function matrix (**G**) and were subjected to SVD:

$$\mathbf{G} = \mathbf{V}\Sigma\mathbf{W}^{\mathrm{H}} \qquad (1)$$

where $\Sigma = \mathrm{diag}\ (\sigma_1,\ldots,\sigma_n)$, σ_i is the singular value of $\mathbf{G} = \lambda_i^{1/2}(\mathbf{G}\mathbf{G}^{\mathrm{H}})$; $\mathbf{V} = (v_1,\ v_2,\ldots)$ is the matrix of left singular vectors, and $\mathbf{W} = (w_1,\ w_2,\ldots)$ is the matrix of right singular vectors. Two parameters of interest are the minimum singular value σ^* and the ratio of maximum to minimum singular values, called condition number γ:

$$\gamma = \sigma/\sigma^* \qquad (2)$$

It is possible to define γ in terms of other norms, but the induced two-norm (singular values) used in Eq. (2) is most common. A plant with a large value of γ is called ill-conditioned. Physically, this means that the gain of the plant is strongly dependent on the input direction. The singular values and condition number are scaling-dependent. For correct interpretation of these quantities, the plant should be scaled such that both the outputs and the inputs are of comparable magnitude [9].

Moreover, the condition number reflects the sensitivity of the system under uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. It is expected than the systems with higher minimum singular values and lower condition numbers would show the best dynamic performance under feedback control. Jiménez et al. [10] have demonstrated the application of the SVD technique to compare the controllability properties of complex distillation structures. It is important to highlight that the model used in each equilibrium stage includes transient total mass balance, transient component mass balances, equilibrium relationship, summation constraints, and transient energy balance. Finally, a pressure drop of 10 psi for each distillation column was assumed in accordance with the recommendation given in Seader and Henley [11].

The purity of product streams is one of the most common variables analyzed for initial control studies on distillation columns [12–14]; then, the only output variable studied for each product stream was the mass fraction. For instance, if the mass fraction of component *i* in the distillate flow was defined as output variable, the selected control variable directly related to the distillate purity is the reflux ratio. In the same way, for the mass fraction of component *j* in the bottom flow, the selected control variable directly related to the residue purity is the reboiler duty. Finally, regarding the mass fraction of the component *k* in the side stream, the flow rate was selected as control variable directly related to its purity. Tab. 1 summarizes the input and output variables and disturbances as well for all the case studies.

A typical transfer matrix of the process, suitable for the SVD analysis, is defined as:

$$\begin{bmatrix} g_{1,1}(\omega,\tau_{c,1}) & g_{1,2}(\omega,\tau_{c,2}) & g_{1,3}(\omega,\tau_{c,3}) \\ g_{2,1}(\omega,\tau_{c,1}) & g_{2,2}(\omega,\tau_{c,2}) & g_{2,3}(\omega,\tau_{c,3}) \\ g_{3,1}(\omega,\tau_{c,1}) & g_{3,2}(\omega,\tau_{c,2}) & g_{3,3}(\omega,\tau_{c,3}) \end{bmatrix} \begin{bmatrix} \mathrm{RR}_1 \\ \mathrm{RR}_2 \\ Q_2 \end{bmatrix} = \begin{bmatrix} x\mathrm{Acetone} \\ x\mathrm{Ethanol} \\ x\mathrm{Butanol} \end{bmatrix} \qquad (3)$$

where x represents the mass fraction, g the transfer function, τ_{ci} the dominant time constant for each disturbance realized, ω the frequency space, RR the reflux ratio, and Q denotes the reboiler heat duty. The subscripts 1 and 2 refer to the number of the distillation column.

Table 1. General information for controllability analysis.

Process route	Control inputs			Control outputs	Disturbance on the control inputs
A	Reflux ratio CII	Reflux ratio CIII	Reboiler duty CIV	Mass fraction of acetone, butanol, and ethanol	–0.50 %
B		Reflux ratio CIII	Reboiler duty CIV	Mass fraction of acetone and butanol	–0.50 %
C			Reboiler duty CIV	Mass fraction of butanol	–0.50 %
D	Reflux ratio CII	Reflux ratio CIII	Reboiler duty CIII	Mass fraction of acetone, butanol, and ethanol	–0.50 %

3 Study Case

Recently, Sánchez-Ramírez et al. [5] reported four optimized alternatives to purify all components from ABE fermentation (Fig. 1). These process routes employed a technology similar to previous industrial processes for biobutanol production and were fed with a fermentation broth from a batch fermentation. For this work, process route A (Fig. 1) is a scheme where all components (ABE) are purified, and for control study all streams where any component is purified are disturbed with a step change. This process design also includes a decanter in order to separate the heterogeneous azeotrope between water and biobutanol. Process route B was equally fed from a fermentation broth; however, the last distillation column does not purify ethanol, but only acetone and biobutanol. In process route C, only biobutanol flow is purified, and both ethanol and acetone leave the purification process mixed with water and biobutanol traces. Finally, process route D is different from the first three processes since the first distillation column is replaced by a liquid-liquid extractive column. According to Sanchez-Ramírez et al. [5], hexyl acetate was chosen as extracting agent in order to separate both homogeneous and heterogeneous azeotropes. After that, three distillation columns performed the separation of acetone, biobutanol, and ethanol.

For this study, five designs of each process route were selected. Those points were obtained from a previous optimization process minimizing total annual cost (TAC) as objective function [5]. The designs were generated by differential evolution with tabu list algorithm (DETL) [15]. The DETL method is a hybrid stochastic algorithm which can be readily connected to highly sophisticated simulators such as Aspen Plus. It converges towards a global optimum when computing time approaches to infinity. The evolution of the best function value for the DETL algorithm is illustrated in Fig. 2, having as stop criterion several iterations without improvement in the best objective function value.

In this case, all those five points highlighted accomplish the same constraints of purity and recovery. However, they have different TACs; point 1 is the cheapest point and the best solution found, point 5 is the most expensive point, and point 2, 3, and 4 have a cost value among the cheapest and the most expensive in increasing order (Fig. 2). In other words, each point selected of the process routes A, B, C, and D was selected trying to cover all trajectories explored by the DETL algorithm and trying to consider all TAC values (high and low values) which can accomplish all purity and recovery restrictions established before optimization. In this way, one might know whether there exists any relation between TAC and control indicator.

Thereby, all five designs are studied in order to know their control properties under an open loop dynamic test evaluated through SVD analysis considering a zero frequency. These results might clarify the relation among TAC and a control indicator, such as condition number γ or minimum singular value, in process routes designed to purify an ABE effluent from a fermentation broth. The five designs of each process route were modeled with Aspen Plus and using a feed average

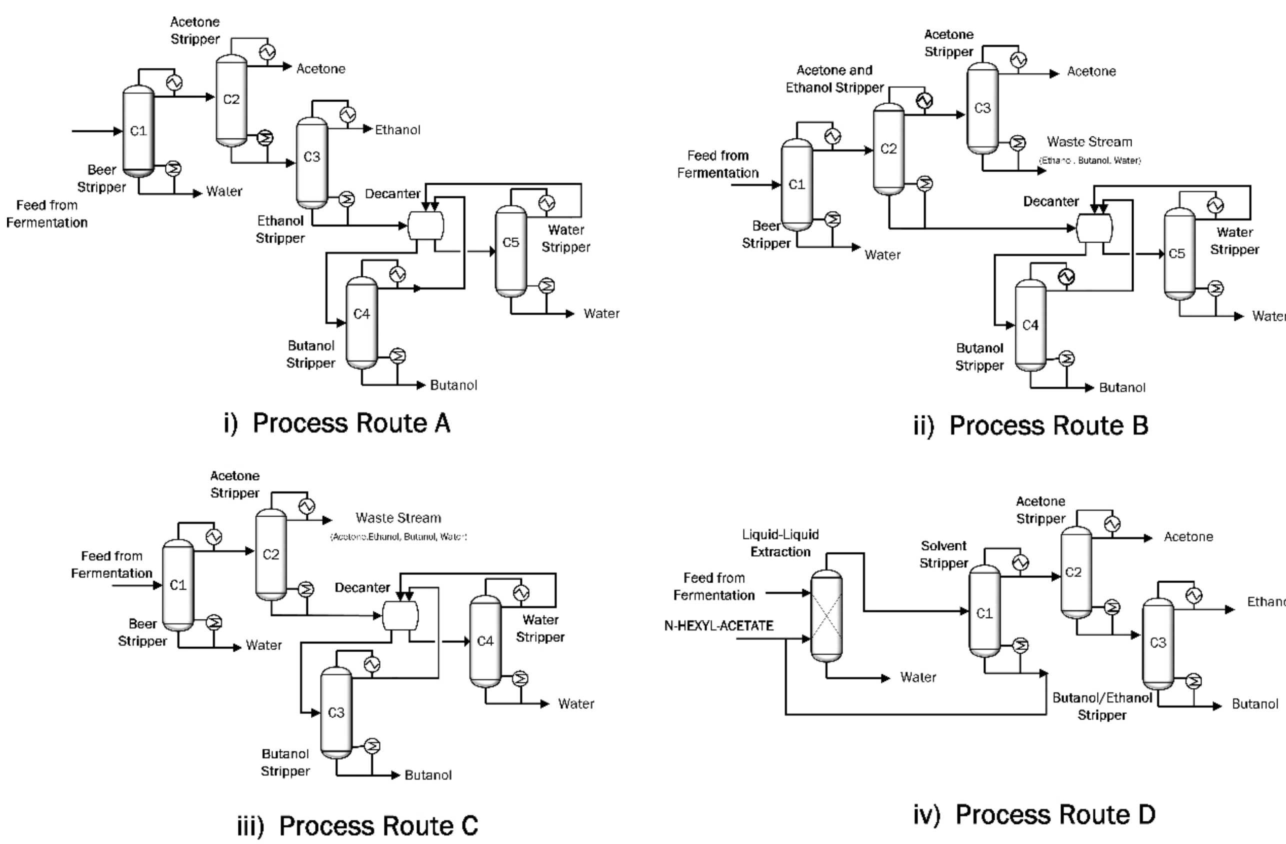

Figure 1. Processes studied in the recovery of biobutanol.

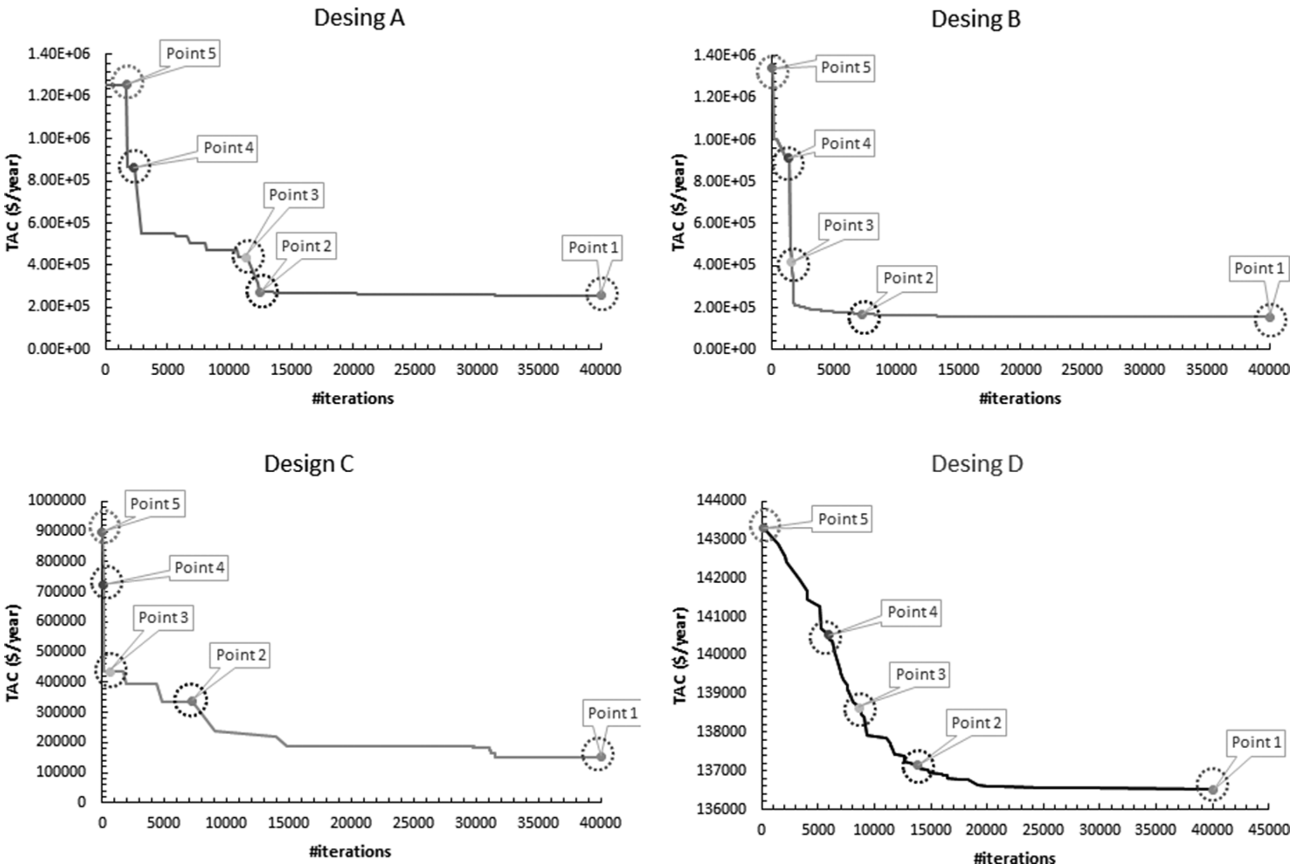

Figure 2. Optimization results of process configurations A, B , C, and D for the recovery of biobutanol.

(Tabs. S1–S4) according to Wu et al. [16]. These process models were robust and thermodynamically rigorous. According to Van der Merwe et al. [4] and Chapeaux et al. [17], NRTL-HOC was the most accurate thermodynamic model for the calculation of the physicochemical properties of the components used under the specified conditions.

4 Analysis of Results

The results for all process routes analyzed are presented. Note again that five points of each process route were considered [5] (see Tabs. S1 and S2), including the cheapest, the most expensive, and other three middle points, respectively. It is important to recall that all results presented are designs that satisfy each restriction of purity, i.e., biobutanol 99.5 wt %, acetone 98 wt %, and ethanol 95 wt % for process route A; biobutanol 99.5 wt %, acetone 98 wt % for process route B; biobutanol 99.5 wt % for process route C; biobutanol 99.5 wt %, acetone 98 wt %, and ethanol 99 wt % for process route D; and at least 95 wt % recovery of ethanol, 99 wt % recovery of acetone and biobutanol, and 99.999 wt % hexyl acetate recovery, respectively.

The application of the SVD technique might provide a measure of the controllability properties of a given dynamic system. Although the SVD technique does not allow a quantitative measure, it has the possibility to analyze qualitatively and can provide an acceptable basis in order to compare in a theoretical way the control properties among those sequences analyzed. However, before performing the SVD technique, it is necessary to disturb each product stream with a step change in the main product composition in order to obtain the corresponding dynamic response. In this work, the distillate rate and the reboiler heat duty were chosen as the manipulated variables. After that, a transfer function matrix relating the main product composition and the manipulated variables was constructed for each case, and finally the SVD was evaluated. Tabs. S1–S4 contain the basic information about every single point considered in this analysis.

The TAC, the minimum singular value, and the condition number of process route A are given in Fig. 3 and Tab. 2. It is clear that point 4 showed smaller values of γ, however, it has no small TAC value. Further, despite point 4 also showing the smallest minimum singular value σ^*, this point represents a good alternative to be considered talking about control properties. Even though its TAC is not the smallest, it is far away from point 5 which is the most expensive, both accomplishing the same purity and recovery needs. In addition, considering the heat duty in Fig. 3, point 4 showed again a value between the smallest and the highest value, however, in this case, the heat duty of point 4 is almost three times that of point 1. Besides, considering the sum of all equilibrium stages involved in all distillation columns of each point evaluated, point 4 includes almost the same equilibrium stages than point 5. This behavior would impact directly the capital cost of each point. Moreover,

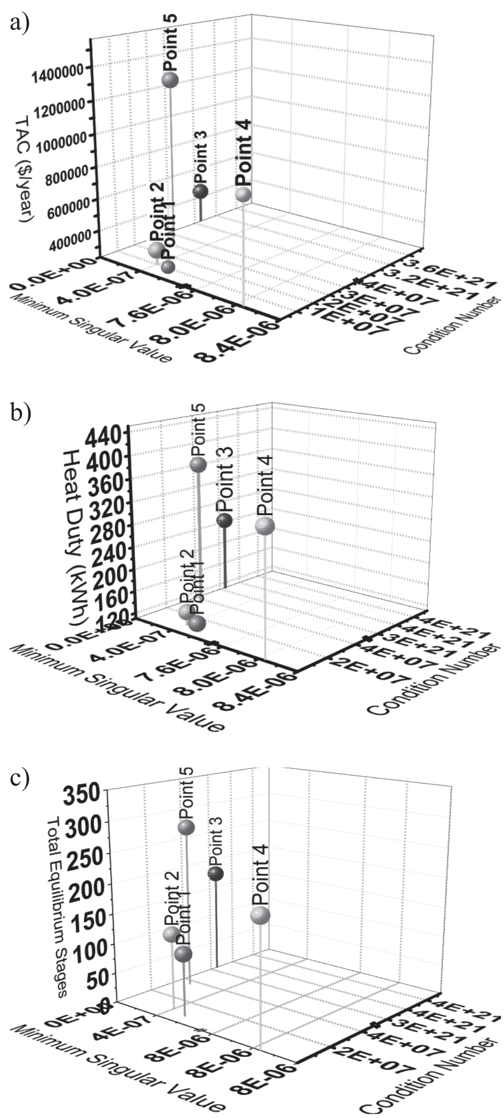

Figure 3. Relation between condition number and minimum singular value. (a) TAC, (b) heat duty, and (c) total equilibrium stages for process route A.

considering the design variables in the Tab. S1, it is clear that both reflux ratio and equilibrium stages increase from point 1 to point 5, almost in the same way than the control properties.

Considering process route B in Fig. 4, it is clear again that point 4 near the most expensive point showed better control properties. However, this point is almost seven times in TAC than the cheapest point. Moreover, regarding the heat duty, point 4 spends more than five times compared with the cheapest point. Finally, with respect to the total amount of equilibrium stages, point 4 is far away of the cheapest point, i.e., obviously those values influence directly the TAC calculation. Also, point 4 is designed with higher reflux ratios compared with the other points and almost four times in the amount of total stages. In this manner, point 4 probably is not a good option despite having good control properties.

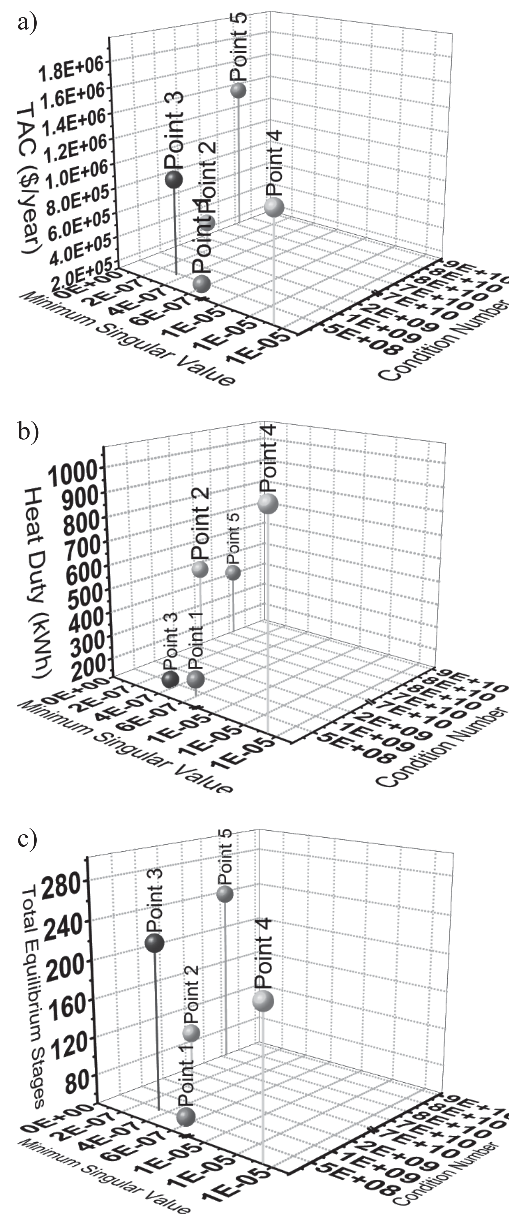

Figure 4. Relation between condition number and minimum singular value. (a) TAC, (b) heat duty, and (c) total equilibrium stages for process route B.

Despite process route C showing a similar behavior in Fig. 5, point 4 has better control properties. Alike, in process route B, there are several points that accomplish the same purity constraints, however, they did not exhibit a good control behavior compared with point 4. In this case, the difference in control properties among point 4 and the cheapest point, named point 1, would appear not as high, nevertheless a rigorous analysis including a higher frequency would clarify these differences. On the other hand, considering the most expensive point, Tab. 2 indicates that point 5 has the smallest heat duty, but despite this value, it has the biggest TAC. This value is because the capital cost of each column is higher than the other points.

Table 2. Condition number, minimum singular value, TAC, heat duty and total equilibrium stages for all processes evaluated.

	Minimum singular value	Condition number	TAC [$ per year]	Heat duty [kWh]	Total equilib. stages
Process Route A					
Point 1	5.52×10^{-7}	7.57×10^{6}	256 696	122.806	103
Point 2	3.94×10^{-7}	1.06×10^{7}	315 562	132.121	125
Point 3	1.27×10^{-21}	3.31×10^{21}	438 685	242.613	174
Point 4	8.07×10^{-6}	5.09×10^{5}	865 925	330.284	205
Point 5	1.15×10^{-7}	3.65×10^{7}	1 256 819	367.013	274
Process Route B					
Point 1	5.86×10^{-7}	3.64×10^{8}	155 020	184.643	55
Point 2	1.63×10^{-7}	1.75×10^{9}	350 002	512.277	103
Point 3	3.39×10^{-7}	4.58×10^{8}	910 734	132.858	222
Point 4	1.35×10^{-5}	9.89×10^{6}	1 001 983	976.383	202
Point 5	3.65×10^{-9}	7.62×10^{1}	1 342 443	404.184	237
Process Route C					
Point 1	1.20×10^{-5}	2.92×10^{5}	149 020	133.738	80
Point 2	9.00×10^{-8}	2.01×10^{7}	383 205	157.239	145
Point 3	3.22×10^{-5}	1.54×10^{5}	541 259	108.718	153
Point 4	4.48×10^{-5}	5.06×10^{4}	723 552	141.267	216
Point 5	2.43×10^{-8}	8.03×10^{7}	900 549	58.084	251
Process Route D					
Point 1	5.83×10^{-22}	5.80×10^{19}	136 827	92.9552	122
Point 2	7.53×10^{-23}	3.77×10^{19}	137 264	92.576	105
Point 3	1.54×10^{-23}	1.85×10^{20}	139 548	92.5808	117
Point 4	4.24×10^{-24}	6.64×10^{20}	142 876	92.6558	112
Point 5	1.97×10^{-22}	1.42×10^{19}	1 436 854	92.7349	110

Fig. 6 illustrates the variation of γ, σ^*, and its respective TAC on process route D. In this case, the variation in TAC among all points is not as big as for the other process routes. Also, condition number and minimum singular value are relatively close to each other. In general, the most expensive point showed better control properties, however, point 1 and 2 indicated similar magnitude orders in γ and σ^*. Furthermore, considering the heat duty, all points evaluated from process route D are designed with almost the same value of this design variable. Besides, according to Tab. 2, all five points have almost the same amount of stages, which is totally consistent with TAC and heat duty values. In this manner, it could be difficult to select one or the other point in this analysis. However, it is clear that all points in process route C overcome process route A, B, and D regarding the control properties. This behavior is probably due to the fact that only biobutanol is purified.

In conclusion, it is clear that the best points of each process, i.e., the cheapest, provided by previous optimization did not show a good control behavior. Moreover, in process routes A, B, and C, point 4, being nearly the most expensive, provided better control properties. In process route D, point 5 which is the most expensive, indicated the best control properties. Consequently, it is expected that those points with higher minimum singular values and lower condition numbers show a good dynamic performance under feedback control. Furthermore, these values imply that these process routes are better conditioned to the effect of disturbances and require lower control efforts in feedback operations than the other point evaluated of each process route. These results are totally consistent with some published results, i.e., Serra et al. [18] who explained that working out of the optimal operating conditions, the controllability of conventional and complex columns may improve. Thus, it is interesting to compare the controllability of several designs under non-optimal conditions.

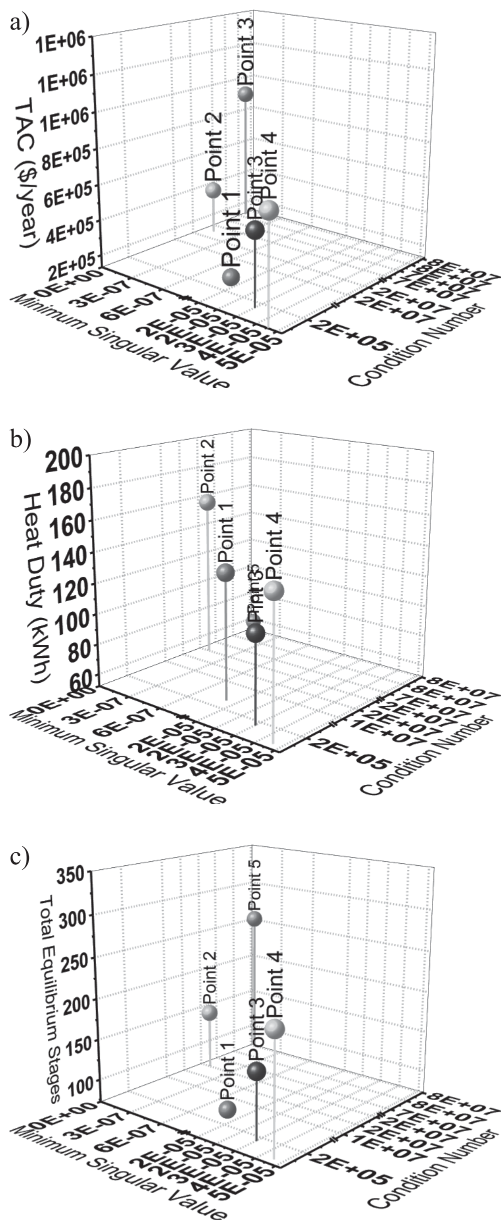

Figure 5. Relation between condition number and minimum singular value. (a) TAC, (b) heat duty, and (c) total equilibrium stages for process route C.

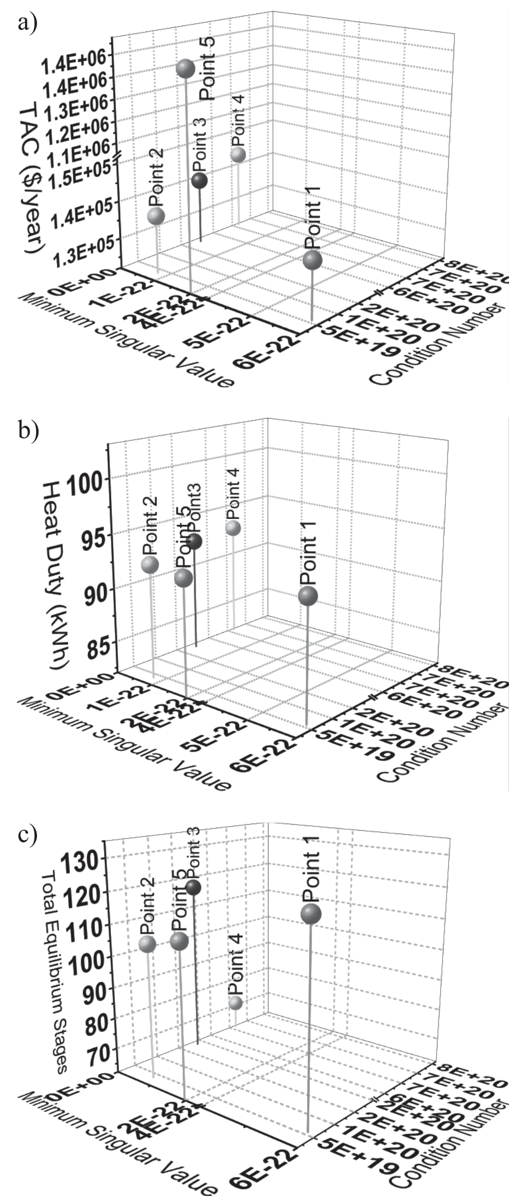

Figure 6. Relation between condition number and minimum singular value. (a) TAC, (b) heat duty, and (c) total equilibrium stages for process route D.

5 Conclusions

Even though this preliminary control analysis was performed considering zero frequency, it is a good starting point to choose an alternative among the described four process routes. It was clear that process route C is superior in all five points evaluated compared to the complete set of points assessed from process routes A, B, and D. Nonetheless, considering the TAC of all sequences, it is clear that process route D is a better option. All process routes showed the same pattern, but the point that showed the better control properties was point 4, which is nearly the most expensive, in process route A, B, and C. In process route D, the most expensive point, i.e., point 5, exhibited again the best control properties. In this way, a retrofit of this process route and a rigorous control analysis could be performed expecting better control properties.

Beyond this preliminary analysis and regarding control properties and economic indicators, the process routes C and D must be considered as a good basis design in order to propose several thermally coupled or intensified designs that could improve their TAC or any economic indicator.

Furthermore, these economic and control results open several possibilities to be considered as a third indicator, i.e., process routes C and D might be taken into account in some environmental indicators such as eco indicator 99 or greenhouse gas emission. It could even be regarded as a social impact as well.

However, there are some limitations when frequency zero is considered since a possible behavior of these process routes under bigger disturbances is not known. This scenario would be accessible only under a rigorous analysis such as open and closed-loop analysis.

The authors have declared no conflict of interest.

Symbols used

G	[–]	transfer function matrix
V	[–]	matrix of left singular vectors
W	[–]	matrix of right singular vectors

Greek letters

σ	[–]	maximum singular value
σ^*	[–]	minimum singular value
γ	[–]	condition number

Abbreviations

ABE	acetone-butanol-ethanol
DETL	differential evolution with tabu list algorithm
LLE	liquid-liquid extraction
SVD	singular value decomposition
TAC	total annual cost

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