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Control properties of sustainable alternatives to produce 2,3-butanediol

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A B S T R A C T

Current social needs, as well as political and environmental restrictions, have led to the generation of products within a framework of sustainability, and favoring production processes based on renewable raw materials. During the process design work, the role of the dynamic properties of a process, together with some other metrics, is not always considered. However, several studies have shown that there is a certain relationship between the dynamics and controllability of the process and its sustainability. In this work, the dynamic properties of different separation schemes for the purification of 2,3-BD from biomass fermentation are evaluated. The study allowed determining the best alternatives for the eventual implementation of these schemes, as well as the role of controllability concerning other sustainability indicators. As result, it was found that schemes that include a thermal coupling in their topological design allow a general improvement of all sustainability indicators. In addition, it was observed in this case study that process intensification contributes significantly to the fulfillment of various sustainability indicators.

1. Introduction

Regarding sustainability assessment, Paul Anastas and John Warner were among the first to compile a set of principles out of a variety of views on how this may be accomplished. In 1998, the 12 principles of green chemistry were published (Anastas and Zimmerman, 1998). The notions were then expanded upon by Anastas and Zimmerman (2003), who were the first to publish a set of green engineering principles, which were followed by the San Destin Principles of Green Engineering (Abraham and Nguyen, 2003). Incorporating Sustainability concepts into process design necessitates a considerable behavioral change among workers in industry and academia, and the effectiveness of this behavioral change may be measured by progress in building "greener" processes. This urge to track progress has generated new ideas for determining a process's greenness from a chemical and engineering standpoint (Constable et al., 2001; Jiménez-González and Constable, 2011). In other words, sustainability metrics must be considered in conjunction with economic and technical metrics.

A considerable number of publications have been written about the use of metrics to drive business, government, and communities towards more sustainable practices. There has also been much written about the characteristics of metrics, or what constitutes a good metric. It is generally agreed that metrics must be clearly defined, simple, measurable, objective rather than subjective, and must ultimately drive the desired behavior.

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For example, Gonzalez and Smith (2003) proposed a methodology to evaluate process sustainability called GREENSCOPE (Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluator). Other research published to define indicators and metrics for process sustainability includes analyzing environmental, economic, and social areas("GRI - Standards,").

The United Nations (United Nations. Department of Economic and Social Affairs., 2007) uses global indicators in environmental, economic, and social areas that could be applicable to an entire country. The Dow Jones corporate sustainability indexes ("Dow Jones Sustainability World Index, S&P Dow Jones Indices (n.d.)) track the performance of companies in terms of corporate sustainability. An interesting work that includes 79 indicators to evaluate sustainability performance in environmental, economic, and social areas is the Global Reporting Initiative("GRI - Standards,"). One early work proposing indicators of sustainable development for industry is that of Azapagic and Perdan (2000). This work provides 35 indicators categorized over the environmental, economic, and social areas in an attempt to contribute toward standardization of indicators for sustainable development within the industry. Veleva et al. (2001); Veleva and Ellenbecker (2001) proposed a set of 22 indicators categorized in environmental, social, and economic areas and subdivided them through five levels relative to the basic principles of sustainability.

The most extensive recompilation of sustainability indicators in the literature was proposed by Krajnc and Glavič (2003). The inventory consists of 89 indicators classified according to environmental, economic, and social areas. As described above, there are several indicators for sustainability assessment of chemical processes, which can be applied at different process or business scales. So, the sustainability framework can be approached by the identification and selection of two reference states representing the best target and worst-case for each sustainability indicator (Ruiz-Mercado et al., 2012).

Several studies have highlighted various metrics that can be used to evaluate the degree of sustainability of a process. Jiménez-González et al. (2012) have published a detailed assessment of the key parameters for evaluating and comparing process 'greenness.' Jiménez-González et al. (2012) emphasize a variety of measures in their assessment, including the E-factor, mass intensity, greenhouse gas emissions, process cost, real-time analysis (controllability), and measurement of intrinsic security or lack thereof. These green metrics can be used to gauge progress toward the overarching aim of environmental sustainability. These sustainability metrics have been applied to some work in the field of chemical engineering. For example, it has been applied to evaluate the sustainability of a process for the recovery of effluents from a nylon industry (Bravo-García et al., 2021a), the recovery process involved mainly conventional, thermally coupled, and intensified distillation equipment. Similarly, several metrics have been evaluated and analyzed in the butanol purification process (Segovia-Hernández et al., 2020). In such a work, the sustainability of highly intensified separation schemes such as dividing wall columns was evaluated. In the same way, sustainability has been evaluated in the production of fuels from biomass gasification (Ibarra-Gonzalez et al., 2021), considering various major equipment such as reactors, distillation columns, flash distillation units, etc. In the vast majority of case studies analyzed in a sustainability framework, the use of economic, environmental, and even safety metrics has been highlighted. However, process controllability is somewhat neglected and the impact of process dynamics on process sustainability is not analyzed. Thus, the question arises as to what role does process controllability play in sustainability assessment?.

Green Chemistry Principle #11 (Real-time Process Analysis and Monitoring for Pollution Prevention) indicates a need for real-time process analysis and monitoring (Jiménez-González et al., 2012). The goal of this approach is straightforward: to avoid waste by detecting process deviations as they occur. By doing so, there may be enough time to change process settings to reverse the excursion while ensuring that the final product quality is unaffected. With the installation of Distributed Control Systems (DCS), real-time analysis and control are becoming more available in pilot and full-scale facilities. Such systems allow for the monitoring of a wide range of process parameters, including inputs like pump settings, heater power settings, valve settings, and reflux ratio settings, as well as outputs like the temperature at various locations in the reactor system, liquid levels, and liquid flow rates. The impact of making a change may be foreseen and observed throughout the process thanks to real-time monitoring, which enables for modeling and trending of these parameters. When monitoring data is paired with chemical data from process samples, it's easier to figure out where the best processing window is. Even more important, tracking trends allows for quicker identification of causes in the event of a deviation that may have harmed the quality of the final product. In addition, after an unexpected event, it is possible to collect information about it and thus prevent such events in the future. Simple feedback control systems have been available in the laboratory for years, and the ubiquitous availability of low-cost computing power makes monitoring operations easier to automate. Processes that aren't tightly controlled produce more waste, require more resources and energy per unit of the final product, and result in slower throughput and cycle times. In some situations, failing to keep the process under control will fail to fulfill product criteria, necessitating the need to either reprocess the off-spec product or discard it entirely. An out-of-control process is a concern, either of the excess waste produced or the materials consumed (Jiménez-González et al., 2012; Tabone et al., 2010).

The intention of analyzing controllability in the light of other sustainability indicators is not entirely new; several efforts have been made to evaluate and determine the importance of the controllability of a process and its relationship with other sustainability indicators. There are pioneering works where hints and minimal sketches of the relationship between controllability and sustainability are generated (Contreras-Zarazúa et al., 2017; Vázquez-Castillo et al., 2015), however, a real relationship between controllability and sustainability was not generated. More recently, efforts have been presented to know the relationship between controllability with environmental impact (Sánchez-Ramírez et al., 2017). Finally, in the work presented by Sánchez-Ramírez et al., (2021), as well as the work presented by Bravo-García et al., (2021) controllability was evaluated in the light of other indicators such as economic, environmental impact, or inherent safety. However, controllability was evaluated in a simplified manner and without

Table 1 – Objective function values for all configurations developed.

Objective function	Direct Fig. 1a)	Indirect Fig. 1b)	Thermally Coupled Fig. 2a)	Thermodynamic Equivalent Fig. 3a)	Intensified Fig. 4a)
TAC [$ yr^{-1}]	35032419	51155609	31360313	313055124	30536031
EI99 [Points y^{-1}]	14328558	22627903	12559191	12557857	12407199
IR [Probability Y^{-1}]	0.0006686	0.0006663	0.0006795	0.0006684	0.00033411

considering the complete dynamics of the processes studied. That is, the controllability analysis was performed at zero frequency and not the entire frequency range. This limitation in the controllability analysis considers that the perturbations are small enough to consider first-order behavior. These considerations can generate an interesting sketch, but also a limited approach to process controllability.

Recently, Sánchez-Ramirez et al. (2019) presented several alternatives to purify an effluent from biomass fermentation for the production of 2,3-Butanediol. The importance of the case study considered by Sánchez-Ramirez et al. (2019), lies in the production of a high value-added product, starting from agro-industrial waste. In other words, the production of 2,3-Butanediol (2,3-BD) is a clear example of a chemical compound in great demand in the industrial sector that can be produced in biorefineries through the transformation of biomass (Celińska and Grajek, 2009; Wu et al., 2008). 2,3-BD has potential applications in the manufacture of a wide variety of products including printing inks, perfumes, pesticides, wetting and softening agents, explosives, plasticizers, fuels, foods, pharmaceuticals, among others (Garg and Jain, 1995; Syu, 2001). One of the main applications of 2,3-BD is its conversion into 1,3-Butadiene, which is mainly used in the production of synthetic rubber, polyester, and polyurethane. The global demand for butanediols (1,4-Butanediol, 1,3-Butanediol, and 2,3-BD) has increased considerably in recent years, specifically in 2010 the global demand for butanediols was 58,000 tons, by 2018 it reached 74,400 tons and by 2024 the demand for butanediol is estimated to reach 4200 kilotons, of which most of it will correspond to 1,4-Butanediol.

The work presented by Sánchez-Ramirez et al. (2019), framed the synthesis and design of separation alternatives in a sustainability framework. The study considered sustainability indicators (total annual cost, environmental impact, and safety). However, once again, the controllability study was left out of the analysis. Incomplete analysis of the dynamic of the processes may violate dynamic limitations, over-design, and perform poorly in terms of control qualities, hence the overall performance of any given design cannot be guaranteed (Zhou et al., 2015). In addition, there are clear implications for the inherent safety analysis of the process. In other words, separation alternatives with little flexibility may have additional dynamic repercussions on operating performance and intrinsic safety, resulting in separation schemes with high risk because of the use of high energy requirements, explosive substances, and column size.

Thus, considering all the information mentioned up to this point, the objective of this work is to analyze and evaluate the dynamic and controllability of a process for the purification of 2,3-BD. The intention, besides knowing the controllability of the process, is to visualize the existing connection between the controllability of this separation process and its sustainability. In other words, once the dynamic behavior of the process is known, the results obtained will be evaluated in the light of other indicators previously calculated in another work. In this way, a relationship between various sustainability metrics (total annual cost, environmental impact, and safety) and the controllability of the process can be determined for this case study.

The evaluation of the dynamic behavior of the case study will be performed by means of an open-loop analysis and a closed-loop analysis. The open-loop analysis will be performed using a singular value decomposition (SVD) of the transfer matrix obtained from the separation process. On the other hand, the closed-loop analysis will be performed considering the action of a PI controller in case of a disturbance in the system studied.

2. Case of study

Because of its numerous applications, 2, 3-butanediol is a particularly promising chemical. 2, 3-Butanediol is now made by a chemical technique. However, microbial production also produces it. Several metabolic techniques are being tested to increase the generation of 2,3-Butanediol; nevertheless, due to its low concentration, recovering 2,3-Butanediol from the fermentation broth remains a difficulty. According to the work published by (Ma et al., 2009), the average concentrations resulting from a fermentation process can be represented as a mixture of water, acetoin, and 2,3-BD with a mass fraction of 0.841, 0.009, and 0.149 respectively. by the information shown in Table 1.

The thermodynamic interactions between the components of the mixture in Table 1 do not present azeotropic interactions between them, so the separation and purification of the components are relatively simple. In that sense, Sánchez-Ramírez et al. (2019) presented several alternatives to purify the mixture in Table 1. All options in Fig. 1 were modeled using the Aspen Plus modeler and the NRTL thermodynamic model, which Penner et al., 2017) claim better reflects the interactions between all components. On a mass basis, the minimum purities were set at 99.5 % for 2,3-BD and water, and 99.0 % for acetoin. The pressure in each column was adjusted to account for the availability of cooling water. The alternatives generated had as a starting point a separation scheme based on two conventional distillation columns. Further, using a systematic methodology to synthesize all alternatives to separate 2,3-BD a thermally coupled, thermodynamic equivalent, and intensified alternatives were developed. In general terms, the methodology to predict new alternative schemes is based on the introduction of thermal couplings, transposition of column sections, and column section removal.

The design strategy is based on a retrofit scheme, which involves that the topological structure of the separation process is maintained. That is, there may be movement of the stripping and rectification sections, but no increase in the equilibrium stages. All the alternatives presented were designed and optimized using a hybrid stochastic optimization method, Differential Evolution with Tabu List. The optimization strategy considered several objectives such as objective functions, total annual cost (TAC), environmental impact

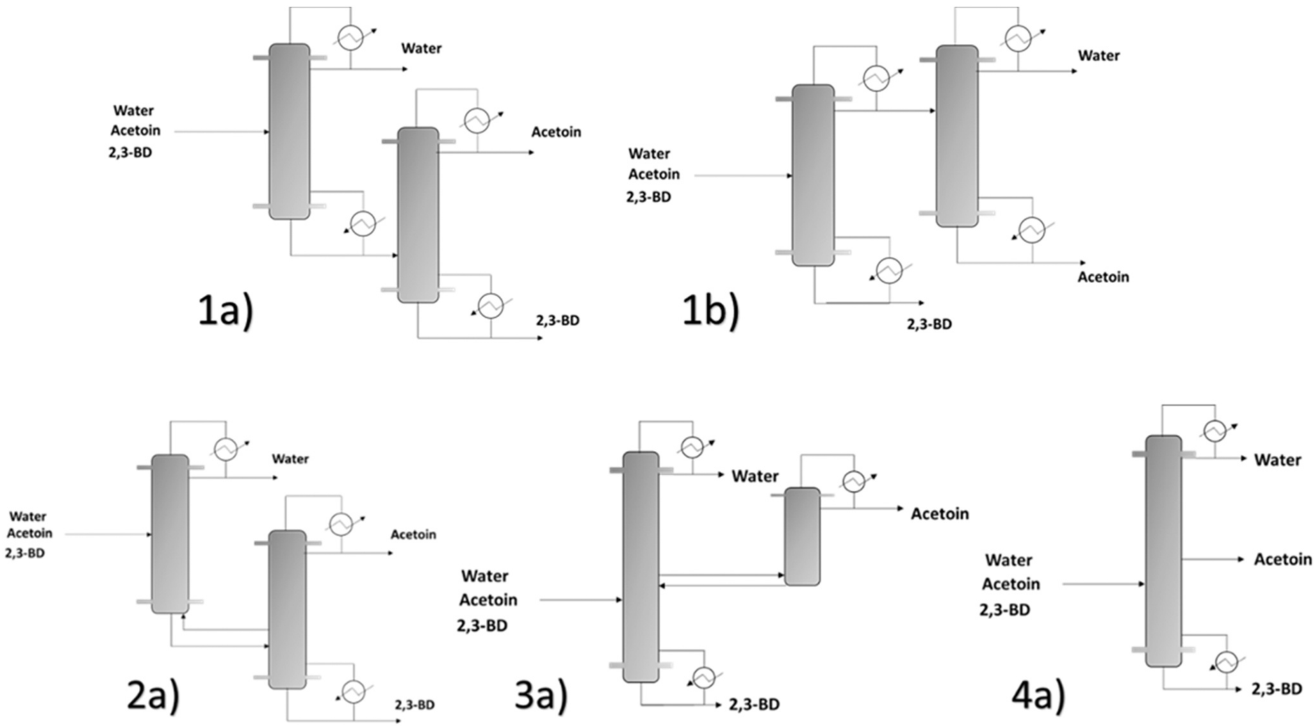

Fig. 1 – Purification alternatives to obtain 2,3-BD: Direct Sequence (1a), Indirect Sequence (1b), Thermally Coupled Sequence (2a), Thermodynamic Equivalent Sequence (3a), and Intensified Column (4a).

(Eco indicator 99), and inherent process safety (IR). Further details of the synthesis, design, and optimization process can be found in the work presented by Sánchez-Ramírez et al. (2019). Once the optimization work was performed, the results shown in Table 1 were obtained.

According to Sánchez-Ramírez et al. (2019), the results showed that the direct sequence is superior to the indirect scheme when the optimization test was applied to the provided alternatives via a synthesis technique. In comparison to all other options, the intensified alternatives, which separate and purify the input stream in a single column, had the best performance index (economic, environmental, and safety). Fig. 2 shows the composition profile of the intensified scheme.

3. Methodology

The control study was split into two components to compare the controllability of all designs. To begin, a singular value decomposition (SVD) technique was used to create a comparative framework for those schemes' control features. Following that, a composition disturbance scenario was used to test the closed-loop control policy. This type of analysis is extremely effective for determining theoretical attributes and dynamic behavior under feedback control, as demonstrated by various authors (Gómez-Castro et al., 2008; Segovia-Hernández et al., 2007a). Control analysis also reveals the optimum structures from a dynamic standpoint, as

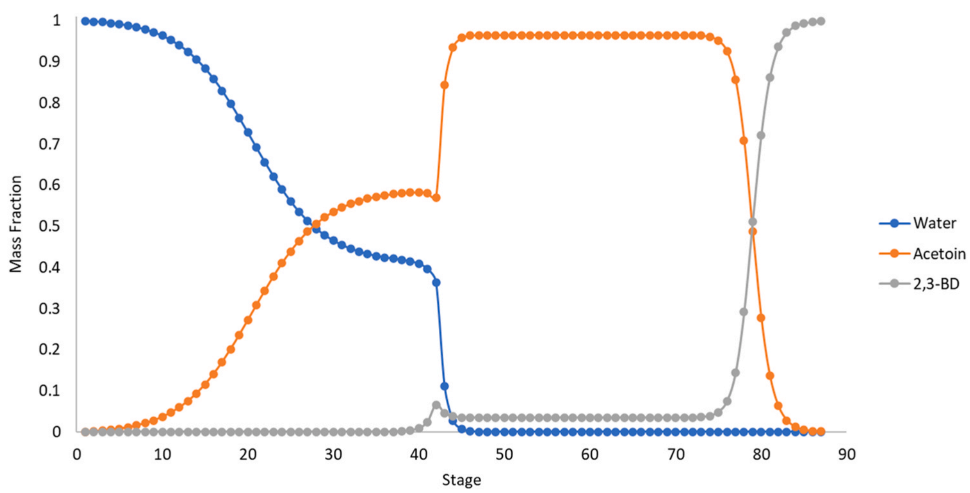

Fig. 2 – Composition profile (mass fraction) of the intensified alternative (4a).

well as which of the separation and purification techniques has the best dynamic behavior.

3.1. Singular value decomposition

Aspen Dynamics simulation was used to obtain the dynamic responses. Once all dynamic responses were obtained, the transfer function matrices (G) were elaborated and subjected to the singular value decomposition (SVD), which was calculated as follows:

$$G = V\Sigma W^H \quad (1)$$

Where Σ = diag ($\sigma_1, \sigma_2, ..., \sigma_n$), σ_1 = singular value of $G = \lambda^{\frac{1}{2}}(GG^H)$, $V = (v_1, v_2, ..., v_n)$ matrix of left singular vector and $W = (w_1, w_2, ..., w_n)$ is the matrix of right singular vectors.

The minimal singular value σ_* and the ratio of maximum to minimum singular values, always called condition number, are the two parameters that we are interested in while calculating G:

$$\gamma^* = \sigma^*/\sigma_* \quad (2)$$

A small adjustment around the operational point was made to acquire the open-loop dynamic responses. The magnitude of the step change was 0.5 % negative of the manipulated variable, and each manipulated variable was chosen according to each product stream, for example, when a component is purified at the top of a distillation column, the manipulated variable was reflux ratio, but when the component was purified at the bottom, the manipulated variable was reboiler heat duty, and so on.

In practice, the minimum singular value assesses the invertibility of the schemes under consideration, as well as the system's potential difficulties under feedback control. In addition, condition number can be regarded as the system's sensitivity to uncertainty and modeling errors. Condition numbers, on the other hand, only provide a qualitative assessment of the theoretical control properties of the schemes under consideration. In general, process design with lower condition number values under feedback control are likely to perform better dynamic behavior (Gabor and Mizsey, 2008). On the other hand, several authors used the SVD technique to determine the dynamic features of various complex designs (Gómez-Castro et al., 2008; Segovia-Hernández et al., 2007a).

One of the drawbacks of SVD is that the singular values depend on the unit system used. The application of the SVD to transfer functions with units lacks validity since the matrix transformations will include the effect of the units. This has given rise to the need to find a scaling method that eliminates this dependence and provides reliability and physical meaning to the results.

Johnston and Barton (1987) presented a physically based method considering the operation of the system, in which the manipulated variables and measurements are scaled differently. They proposed that the outputs are scaled in such a way that a change in magnitude has the same meaning for all outputs from the point of view of controllability. That is since each variable has a different influence on the process, the same scaling factor cannot be used for all variables. Accordingly, the variables should be scaled in such a way that a change in magnitude represents an equivalent amount of control action for all variables. This method includes information relating to the importance of each output and the size of the disturbances that a control system would have to dampen.

For the separation sequences to be studied, there are three important variables to be controlled (fractions of each component of the ternary mixture) which are naturally bounded between 0 and 1. Three manipulable variables are used, reflux ratio, reboiler duty, or side stream flow. These variables have units and are not naturally bounded. To eliminate this drawback, it is proposed to bound the manipulated variables considering that the maximum opening that the control valves can reach is twice the steady state nominal value; therefore, in principle, the valves are 50 % open. This implies that to obtain the gain matrix, the step change implemented in the manipulated variable must be divided by twice the steady state in order to have the same range of variation in both the closing and opening operation of the control valves. This allows us to give a physical interpretation of the scaling of the manipulated variables. That is, by linking the magnitude of change of the manipulated variables with the magnitude of change of the valve stem position, it can only vary between 0 % and 100 % opening (0 and 1). With this form of scaling, normalization and dimensionlessness of the manipulated variables are achieved simultaneously.

3.2. Closed-loop analysis

For the closed-loop control policy, the analysis was using a proportional-integral (PI) controllers. This kind of controller was chosen because of the wide use that the PI controller has in industrial practice. When a control strategy is applied, the main issue is to tuning up the controller parameters. In this study, a common strategy was considered to compare and optimize the controller parameters (please see Fig. 3). Since we consider PI controllers, proportional gain (Kc) and reset times (τ_i) was tuned up for each scheme, also we followed the integral of the absolute error (IAE) criterion (Häggblom, 1992). The IAE value (Eq. 3) allows for globally integrating the dynamic response between an initial point and the new set-point, including the known kinds of dynamics (overshoot, damping ratio, characteristic times). Thus, it is possible to evaluate the responses with an indicator without considering globally the type of dynamic response obtained (Corripio and Smith, 2006).

$$IAE = \int_0^\infty |\varepsilon(t)|\, dt \quad (3)$$

As equals, a key part of this dynamic analysis of each loop is the selection of control outputs and their respective manipulate variables. To control the distillate and bottoms output composition a structure based on energy balance considerations is used. That is, it is used a LV control structure, which uses the reflux flowrate L and the vapor boil-up rate to control distillate and bottoms composition, respectively (Häggblom, 1992). In other words, we chose as manipulated variables, the corresponding reflux flowrate for the top of the column, reboiler heat duty at bottom of the column, and side stream flowrate for side streams. This kind of control loop has been applied with satisfying results and also studying thermally coupled schemes (Jiménez et al., 2001; Segovia-Hernández et al., 2007b). Fig. 3 shows a simple schematic of the closed-loop controllers, as well as the control strategy used to tune the Kc and τ_i values.

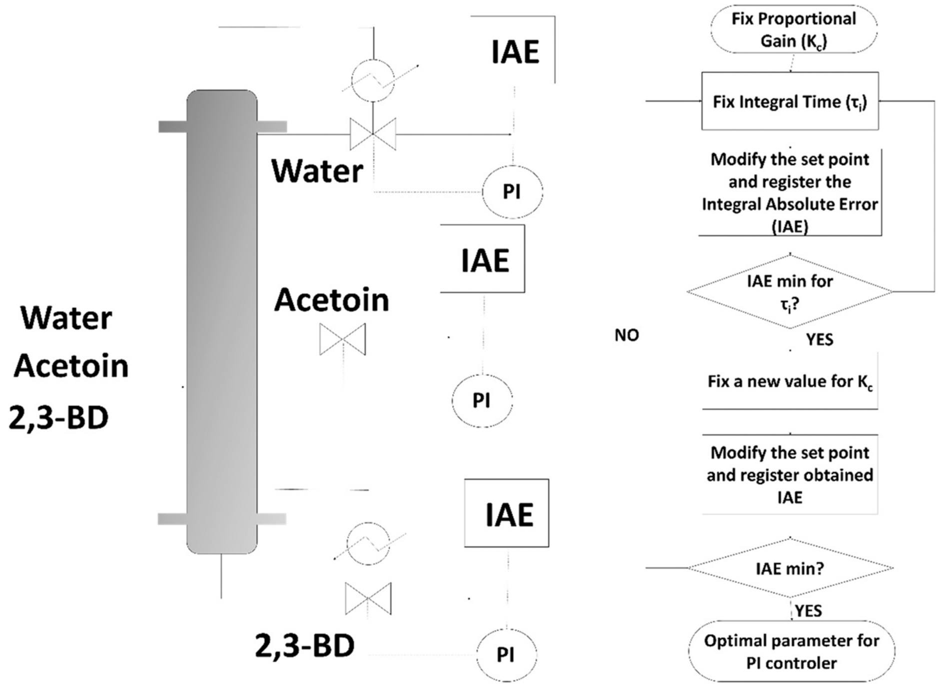

Fig. 3 – Methodology for the minimization of IAE.

This methodology was repeated with other proportional gain values until a global minimum IAE value was obtained. Note that this procedure was conducted considering one control loop at a time until all loops were considered. For dynamic analysis, individual setpoint changes of 0.5 % negative for product composition were implemented in the product streams of acetoin, water, and 2,3-BD (99.5 % for 2,3-BD and water, and 99.0% for acetoin). In dynamic control, a disturbance is inevitable and often exists. Luyben (2013, 1992) tested the control performance of the control structure by disturbances in several systems with representative disturbances. This approach is usually to increase or decrease the content of a certain component in a product stream. This is a common method for testing the performance of the control structure (Gómez-Castro et al., 2008; Lucero-Robles et al., 2016; Segovia-Hernández et al., 2006, 2007a; Segovia-Hrernández et al., 2005). The magnitude of the disturbance usually includes 5 %, 10 % and 20 % in references. The system that can resist 20% disturbance usually has better robustness for 5 % and 10 % disturbances.

4. Results

In this section, the results concerning the control analysis in both open and closed loops will be shown. Initially, we will start with the open-loop dynamic analysis that was explored through the SVD analysis.

4.1. *Open-loop dynamic analysis*

The theoretical properties obtained using the SVD approach are initially examined. The condition number and the minimum singular value are the main parameters in open-loop analysis, as previously stated. As a result of applying the methodology described in Section 3.1, once the dynamic behavior of the separation schemes was adjusted to a transfer function, it was possible to generate the matrix transfer functions of the process. Table 2 shows the transfer functions of the intensified scheme and the thermodynamically equivalent scheme.

Table 2 – Matrix of transfer functions for thermodynamic equivalent and intensified schemes.

	X_{water}	$x_{acetoin}$	$x_{2,3\text{-}BD}$
RR_{water} 1	$\frac{0.04}{1+5.4816s}$	$\frac{-34.0668}{1+18.7066s}$	$\frac{0.0011}{1+5.4816s}$
$RR_{acetoin}$ 1	$\frac{-396.057}{17.1139s^2+8.2738s+1}$	$\frac{-396.0303}{29.161s^2+10.8002s+1}$	$\frac{-0.1316}{1+10.1167s}$
Q 1	$\frac{-85.5556}{1+6.735s}+\frac{49.77}{1+14.6791s}$	$\frac{3.9344}{1+0.4515s}$	$\frac{-0.8448}{1+33.7199s}$

	X_{water}	$x_{acetoin}$	$x_{2,3\text{-}BD}$
RR_{water} 1	$\frac{0.1764}{1+3.2359s}$	$\frac{-0.0012}{1379.4539s^2+74.282s+1}$	$\frac{-130.2388}{39.0488s^2+12.4978s+1}$
Side 1	$\frac{-340.4644}{1+2.8094x10^{18}s}$	$\frac{0.0014}{1+0.6254s}$	$\frac{-396.054}{2.1565s^2+2.937s+1}$
Q 1	$\frac{-38.5688}{14.542s^2+7.6268s+1}$	$\frac{0.0124}{996.324s^2+63.1292s+1}$	$\frac{3.8732}{1+0.3242s}$
	$14.542s^2+7.6268s+1$	$996.324s^2+63.1292s+1$	$39.0488s^2+12.4978s+1$
	R_1	F_L	Q_1

Fig. 4 shows the minimum singular value obtained over a wide frequency range.

As a complement, Fig. 5 shows the different values obtained for the condition number over a wide frequency range.

The direct analysis for Figs. 4 and 5 is, in the first instance, relatively simple. Considering that the objective of this control analysis is to obtain the minimum condition number as well as the largest minimum singular value, the first instance reading is simplified. In Fig. 4, the scheme that presents the largest minimum singular value is the indirect scheme. On the other hand, Fig. 4 adequately complements what is observed in Fig. 5, i.e., the indirect scheme presents the minimum number of condition. However, it should be noted that this behavior is presented at low frequencies, i.e., the indirect scheme presents the best dynamic properties at low frequencies. When the intensified scheme suffers a relatively small perturbation, it will be the best-conditioned scheme for that perturbation.

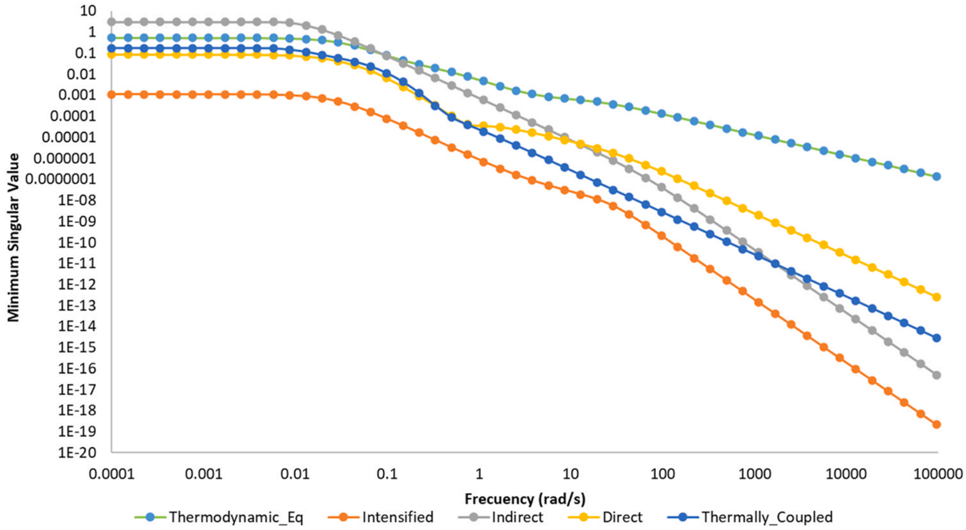

Fig. 4 – Minimum singular value for the studied schemes.

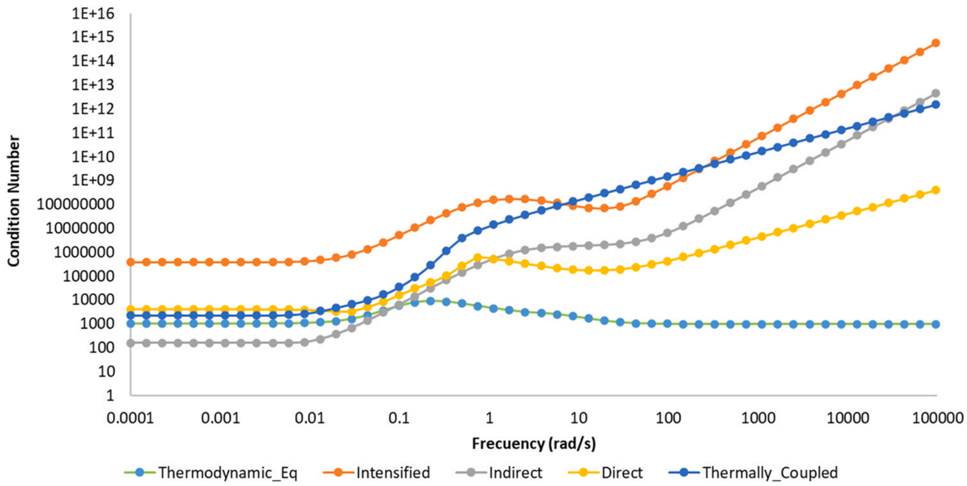

Fig. 5 – Condition number for the schemes studied.

On the other hand, as the frequency values increase, it is observed that the thermodynamically equivalent system presents the best values in terms of condition number and minimum singular value. This means that, as long as the separation scheme undergoes slightly larger perturbations, the STEQ scheme would be better conditioned to such perturbations.

Keeping in mind that the objective is to obtain the minimum number of condition, and the highest minimum singular value, allowing to differentiate the studied models. In this sense, a studied scheme/model can have at frequencies close to 0 the minimum number of condition, and while advancing in the value of the frequency, it can increase this value above some other analyzed scheme. This type of behavior described may be an indicator that the system will respond better than the other systems evaluated under small disturbances. That is, perturbations that do not generate a set point change far away from the initial steady state. On the contrary, when the system suffers a larger perturbation that moves it further away from the steady state, the behavior would be the opposite. Due to the qualitative nature of the open-loop study, a closed-loop study is carried out to quantitatively establish the differences in controllability between one studied system and another (Klema and Laub, 1980; Moore, 1986).

Therefore, as a preliminary conclusion, we can express some ideas. The indirect scheme (SI) and the thermodynamically equivalent scheme (STEQ) presented the best control properties at low frequencies and relatively high frequencies, respectively. Additionally, considering this statement, it is expected that under a closed-loop control analysis, both schemes present a better dynamic behavior compared to the other schemes.

4.2. *Closed-loop dynamic analysis*

The ability to forecast a process's transitory reaction is critical since the process's effective control must be known. As previously stated, closed-loop simulations were carried out using a single-input/single-output feedback control to introduce a step-change in the set point for the product composition of 2,3-BD, acetoin and water. All simulations were run in Aspen Dynamics, with PI controllers taken into account. The parameters of those controllers were fine-tuned with the integral of absolute error minimization as a criterion (IAE). Fig. 6 shows the results of the individual servo tests performed on all cases study.

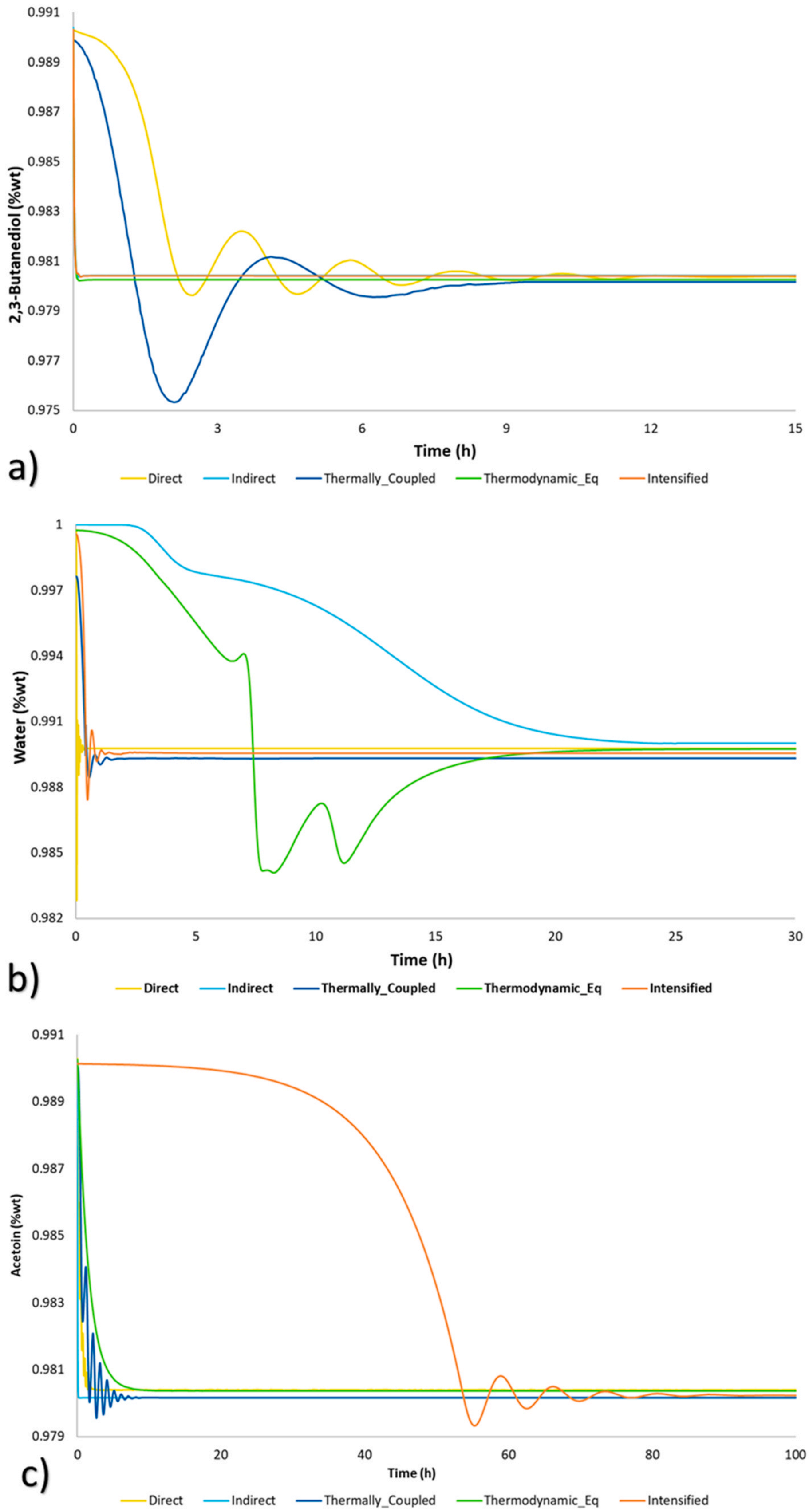

Fig. 6 – Dynamic behavior under a setpoint change for: a) 2,3-BD with reboiler duty as manipulated variable; b) Water with reflux ratio as manipulated variable; c) Acetoin with reflux ratio as manipulated variable for direct, thermally coupled and thermodynamic equivalent schemes, reboiler duty for the indirect scheme, and side stream flow for the intensified scheme.

Table 3 – k_C, τ_i and IAE values for the tuning process.

Secuencia	Water			Acetoin			2,3-BD		
	k_C (%/%)	τ_i (min)	IAE	k_C (%/%)	τ_i (min)	IAE	k_C (%/%)	τ_i (min)	IAE
Direct	250	1	3.97E-04	200	11	1.83E-03	4	67	1.84E-02
Indirect	250	1	1.13E-01	250	1	1.61E-04	250	1	1.72E-04
Thermally_Coupled	250	8	3.22E-03	55	25	4.58E-03	5	5	5.07E-03
Thermodynamic_Eq	50	150	8.15E-02	50	45	7.43E-03	250	1	1.71E-04
Intensified	250	5	3.57E-03	250	30	4.48E-01	250	1	1.66E-04

The closed-loop control analysis will serve to complement the open-loop study. Additionally, a quantitative comparison can be generated using a performance metric through the IAE.

Using the PI controller tuning process, the best values of $k_C$and τ_i were obtained for each control loop associated with the product streams. Next, the stabilized responses by the action of the PI controller in each product stream are obtained. The k_C values comprise a range of values from 1 to 250 while the τ_i values range from 1 to 150. The parameter k_C is related to the valve opening of the physical control element in a feedback control loop and the parameter τ_i to the time in which the opening of this valve will be manipulated. The higher the value of k_C, the greater the opening of the valve associated with the control loop. This effect is related to the maximum proportional gain allowed and the impact that generates on the system. On the other hand, the higher the value of τ_i the opening assigned to the valve will be manipulated faster, in some cases, this can lead to significant overruns in the process due to the violent control action exerted.

Fig. 5 shows the closed-loop responses obtained for the 3 components of interest evaluated in the separation schemes.

Fig. 6 shows the closed-loop responses for the three components of interest in the separation scheme. According to what was observed in the open-loop analysis, it is expected that the indirect scheme and the thermodynamically equivalent scheme show good behavior under a closed-loop study. For the 2,3-BD loops (product of major interest), the intensified and thermodynamic equivalent were able to reach a new setpoint relatively in a short time. The other alternatives reach a new set point in a bigger time near 8 h. As far as water is concerned, only the indirect and thermodynamically equivalent schemes showed longer settling times compared to the other schemes, however, the response obtained was relatively smooth compared to the other responses. Finally, in the acetoin loop, all responses succeeded in adjusting the composition upon step change in a relative short time in comparison with the intensified alternative.

In summary, there was no scheme under this control strategy that reached the new set point in a short time for all components. In this sense, the most balanced scheme can be considered as the one that reaches the new set point for the most components, or for the component of greatest interest. Thus, considering the results obtained in this analysis, the thermodynamically equivalent scheme, or the coupled system could be the most balanced alternatives in the closed loop study. Quantitatively, the performance criterion for the closed-loop is the IAE. In that sense, Table 3 shows the IAE values, as well as the values of k_C, and $\tau_i$for each case studied.

According to Table 3, the results obtained under the closed-loop control analysis are congruent with those obtained under the open-loop analysis. That is, it was expected that the indirect and thermodynamically equivalent separation schemes will perform well under a feedback control system. Thus then, the numerical data of the IAE show that both loops 2,3-BD and acetoin, showed the smallest IAE values. While the water loop does not favor both schemes, the higher value-added compounds do. It should be noted that the intensified system did not exhibit good performance in the open-loop analysis. However, in the closed-loop analysis it showed the best IAE values for the compound of interest.

In light of these open and closed-loop results, some conclusions can be drawn. For the purification of this mixture, from a controllability point of view, an indirect separation scheme is preferred. Although the synthesis work was performed as a retrofit, it was possible to observe changes in the dynamic properties of the separation schemes. For example, it was observed that the application of a thermal coupling in a 'non-product' stream does not improve the control properties. However, considering a thermal coupling, accompanied by the movement of a column section, does substantially improve the control properties. Finally, while eliminating column sections in the equipment design part of the design to generate intensified schemes with less than N-1 columns can generate a decrease in equipment cost, however, for this case study the control properties worsen compared to conventional schemes. Table S1 in Supplementary Material shows the main design parameters of the schemes with the best control properties.

An interesting issue is to look at all the performance criteria evaluated together. That is, considering the previous work of Sánchez-Ramírez et al. (2019), it is possible to evaluate the values of economic impact, environmental impact, safety, as well as process controllability. Simplifying the controllability of the process to the sum of IAE value, it is possible to generate Fig. 7, in which the indicators are shown globally.

An interesting aspect of Fig. 7, is the direct difference between the direct and indirect separation scheme. In the previous work of Sánchez-Ramírez et al. 2019, a substantial improvement between one separation scheme and the other was observed, considering up to that point the direct scheme was the most balanced system, and thermally coupled and intensified sequences as promissory alternatives. However, considering the controllability results obtained in this study, it is possible to observe that the scheme with the best control

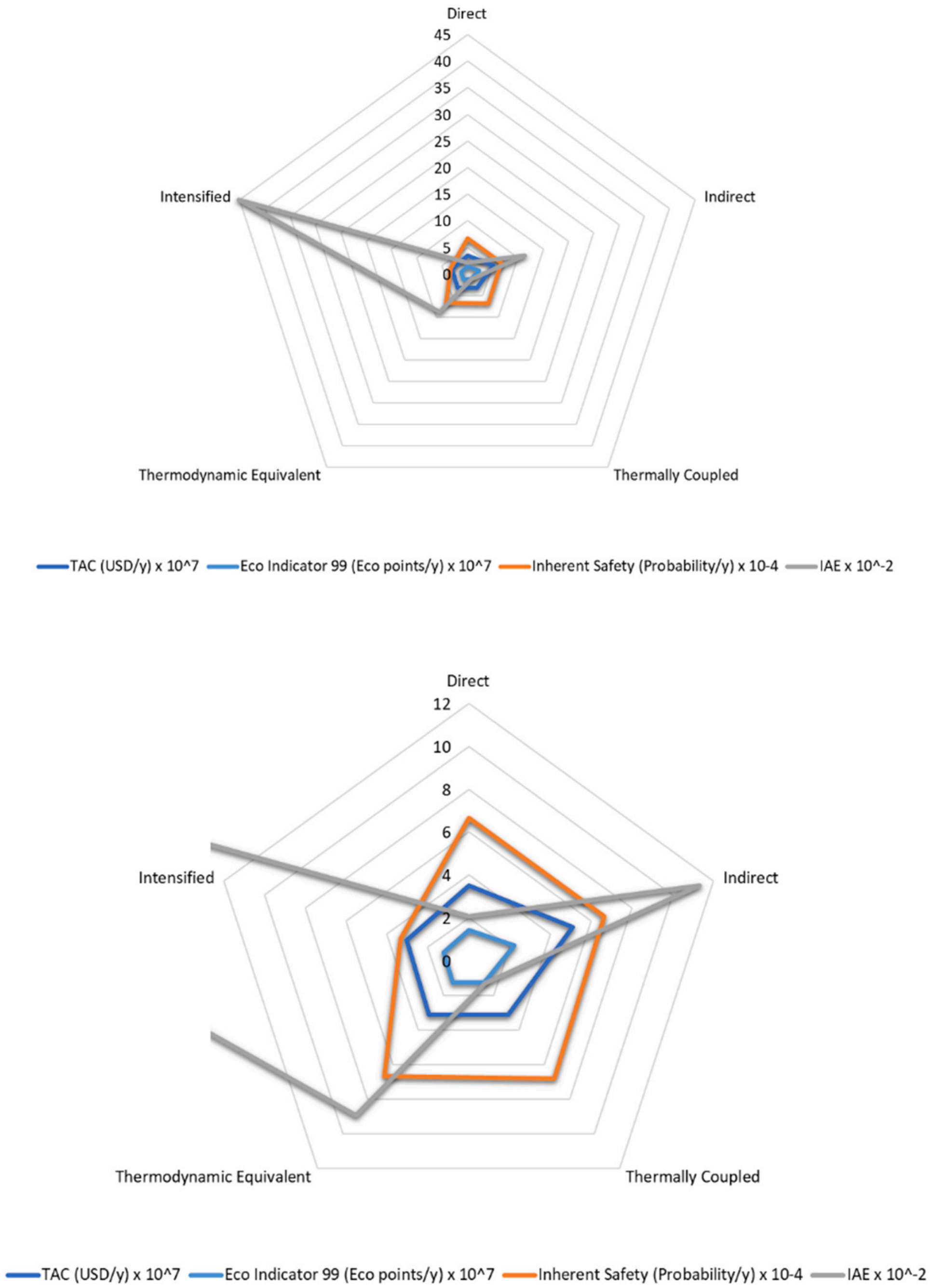

Fig. 7 – Sustainable indicators for all separation alternatives.

properties is indeed the one previously considered as the one with the best balance as far as sustainability indicators are concerned.

Considering all the schemes generated, as well as all the indicators evaluated, the importance of thermal coupling can be observed. That is, the thermal coupling considered in the coupled and thermodynamically equivalent systems generated the most balanced separation schemes in terms of sustainability. On the other hand, it could be corroborated that for 2,3-BD separation, the movement of column sections does not globally improve the process indicators. The simple inclusion of a thermal coupling in streams where no product is obtained is a good detonator to considerably improve the cost, environmental impact, safety and controllability of the process.

Additionally, with regard to the design variables, it can be noted that the immediate difference between the thermally coupled and thermodynamically equivalent scheme is the volume associated with the interconnecting flows. The thermally coupled scheme is designed with larger flows, which could be translated into improved control properties.

Up to this point, it would seem that as the degree of process intensification increases, sustainability indicators would improve. However, the intensified scheme considering a distillation column with a side stream did not confirm the above. That is, the elimination of column sections only allowed an improvement in the inherent safety of the process. On the contrary, it generated that the column sections that performed the separation task did so under operating conditions that demanded higher energy requirements, generating a direct impact on service costs and environmental impact. Finally, through the controllability study applied to the intensified scheme, it was observed that the dynamic behavior worsened. Thus, for this case study, it was observed that the higher the degree of intensification, does not produce the global better separation alternative.

A previous work presented by Bravo-García et al. (2021) concluded in the same way. In that work, a relatively similar strategy of alternative design to purify effluent from a Nylon industry was analyzed. In the work developed by Bravo-García et al. (2021b) a similar conclusion was reached in terms of economic, sustainability, and controllability indicators. However, note that in that work the evaluation of controllability was performed in an analysis at zero frequency, leaving as unknown what would happen in the range of all frequencies.

5. Conclusions

The present work evaluated the dynamic properties of various purification alternatives to obtain 2,3-BD from a fermentation broth. The importance of controllability in a sustainability scheme was discussed because controllability can be associated with various sustainability metrics. Once the dynamic properties were evaluated, it was possible to generate several relationships between process controllability, process sustainability, and the design variables of the schemes. It was observed that in general, the indirect separation system and the thermodynamically equivalent design presented the best control properties. However, weighing controllability in light of the other sustainability metrics, the indirect separation scheme is not a viable alternative.

Additionally, it was possible to find a direct relationship between the synthesis and design of intensified schemes and the sustainability of the separation alternatives. Additionally, it was possible to demonstrate that for this case study, the intensified schemes can adequately cover most of the sustainability indicators. Regarding intensification strategies, the schemes with a thermal coupling allow for improving all the sustainability indicators of this case study, including controllability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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