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Purification of Butanol from the ABE Mixture: Effect of Intensification on the Dynamic Behavior

Ernesto Flores-Cordero, Eduardo Sánchez-Ramírez, Gabriel Contreras-Zarazúa, César Ramírez-Márquez, and Juan Gabriel Segovia-Hernández*

Cite This: https://doi.org/10.1021/acs.iecr.2c02417

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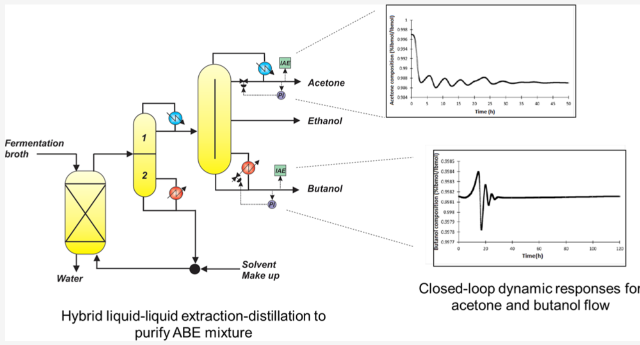
ABSTRACT: Process intensification is a strategy that has reduced costs and equipment while improving on the energy efficiency, safety, and environmental impact of processes. There is a widespread belief in the community that a more intensified process is better; however, the higher the level of process intensification, the more complex its operation becomes. In this paper, we will evaluate how the degree of intensification and the position of the intensification equipment affect the control dynamics. As a case study, the separation of butanol from the acetone−butanol−ethanol (ABE) mixture has been considered due to the thermodynamic complexity of the mixture and the several intensification alternatives that the process can have. On the one hand, the results indicate that the most intensified equipment is not necessarily the best alternative from the operation and control point of view. On the other hand, a strong impact of the location of the intensified equipment on controllability is observed. The configurations with the intensified equipment at the end of the separation were the alternatives with the best dynamic responses.



1. INTRODUCTION

Nowadays, the process industry is facing several challenges to reduce novice toxic emissions, water utilization, and resource depletion; therefore, the manufacturing sector is undergoing several changes and developments with the intent to obtain processes with greater energy efficiency, better raw material utilization, and a lower environmental impact. To obtain these improved processes, the processing sector is basing its new advances and developments on process intensification (PI). PI is a development that leads to a reduced, cleaner, and more efficient technology which combines multiple operations into more compact equipment.[1,2] The concept of PI was introduced in the 1970s, a period characterized by scarce and expensive energy resources.[3] Since then, PI has been successfully applied in different processes. Some remarkable examples implemented by the industry are the methyl acetate process of Eastman Chemical Co., which reduces the process into a single piece of equipment, also called the single-unit hydrogen-peroxide distillation plant.[4] Traditionally, PI has been associated with the petrochemical and chemical industry, and it has recently started to be associated with new sectors such as bioprocesses, fine chemistry, and the pharmaceutical industry.[5−7]

As previously mentioned, in recent years, the bioprocess industry, especially that which is focused on producing biofuels, has tried to apply PI to reduce energy consumption and improve the economic feasibility of processes. Biodiesel production is a good example, as the esterification reactions involved are strongly constrained by chemical equilibrium. These limitations can be addressed using reactive distillation, which drastically saves on energy and costs.[8,9] On the other hand, Contreras-Zarazúa et al.,[1011] have proposed several intensified azeotropic and extractive distillation schemes to produce furfural. Their results indicate that the intensified alternatives have energy reduction and important improvements on safety issues that contrast with the conventional distillation processes. Errico et al.,[12] proposed different intensified hybrid extractive distillation alternatives to reduce energy consumption. These alternatives are the reduction of the environmental impact and improvement of the control properties in an open loop. Their results indicate that energy savings of up to 22% can be obtained using dividing-wall columns with acceptable control properties.[12] Kumakiri et al.,[13] have investigated the implementation of membrane separation to purify bioethanol-grade fuel. Their results showed that the energy consumption can be reduced by up

Received: July 8, 2022
Revised: October 24, 2022
Accepted: November 10, 2022

to 30% using this intensified alternative. Last but not least, Romero-Izquierdo et al.,[14] proposed several intensified schemes based on thermally coupled schemes to purify jet fuel produced by the alcohol-to-jet (ATJ) process. Their results indicate that notably energy and CO_2 saving can be achieved using these intensified alternatives.

It is indisputable that PI is a useful and powerful strategy to obtain processes that are more efficient, cheaper, safer, and eco-friendly. Despite these benefits, it is important to highlight that the intensified processes are characterized by their notably greater complexity (important challenges to overcome). Another one of these challenges is the development of a specific intensified process during its industrial operability, which is determined by the controllability of the process. The increased complexity of an intensified process could generate a process that is difficult to control or one that requires a more sophisticated or novel control structure.[15,16] For the most part, a multifunctional unit that integrates different tasks into a single piece of equipment has fewer degrees of freedom than a traditional process which restricts the control options.[16] An example of this degradation of controllability is presented by Hendershot,[17] who discusses an intensified process that becomes alarmingly unstable when one of the reactants is overfed; in this case, the conventional semibatch reactor process is noticeably safer to control. Based on the previous information, several authors have established and emphasized the importance of considering control and operability studies for the intensified processes. Tian and Pistikopoulos[18] remarked on challenges and opportunities in the operability and control of intensified and modular processes. In their review, the authors established the need to generate a fundamental understanding of intensified process that includes advances in the modeling of processes.

Regarding controllability studies on dividing-wall columns (DWCs), Ling and Luyben[19] proposed a control framework for disturbances in the composition of the hydrocarbon feed to manage the compositions of the heaviest components in the prefractionator. As a result, they demonstrated that a DWC-type method outperforms a standard distillation train with the same separation goal in terms of control features. The dynamic models of the DWC have also been studied by Joglekar et al.,[20] presenting a dynamic model to separate benzene, toluene, and o-xylene using a DWC. They employed genetic algorithms modeled in MATLAB to identify the best operation of the column.

Wojsznis et al.,[21] on the other hand, used model predictive control approaches. When measurements or samples taken in a laboratory column fail, control parameters can be estimated using the model predictive control approach. The operation of the controller and the challenges of using this sort of controller in pilot plant-level columns are described in greater detail in their work. An experimental study of a DWC to control the presence of trace components in feed streams was described by Donahue et al.[22] Traditional controller design approaches are employed in their research to create multiloop control structures that govern the concentration of a trace feed contaminant in product streams. It has been demonstrated that contaminants can be managed relatively successfully using temperature controllers.

Lukac et al.,[23] demonstrate that a temperature-based control structure, in combination with strict temperature control in the prefractionation portion of a DWC as well as in the product draw sections of the column may restore the operation from common feed quality and quantity problems. When temperature-based control is combined with two composition controllers, the column can be operated with narrower margins, resulting in less over-purification and overall energy consumption. Rewagad and Kiss[24] show how to accomplish dynamic optimization using an advanced control technique based on model predictive control (MPC). The dynamic model of the DWC employed in this study is a full-size nonlinear model that is indicative of industrial applications. It is not a simplified version. The nonlinear model is used to determine the quality of the linearized model utilized for predictions inside MPC. The variables are chosen to fulfill the goal of regulatory and inventory management in the column while lowering energy consumption in a practical way. The optimal energy control is based on a simple method that adjusts the liquid split to regulate the heavy component composition at the top of the prefractionator side of the DWC. The performance of the MPC is evaluated against a conventional proportional−integral−derivative (PID) control structure, which was previously reported to be the best-performing structure to operate a DWC.

Azeotropic mixes have been studied using a DWC. The butanol−water mixture, for instance, produces a heterogeneous azeotrope. Yu et al.,[25] used cyclohexane as an entrainer to model an azeotropic DWC for the separation of butanol. Their findings demonstrated 23.8% energy savings and a 19.93% reduction in total annual cost. In addition, a control framework was placed to mitigate the effects of the disturbances.

In 2001, Jimenez et al.,[26] used the singular value decomposition approach and closed-loop responses under feedback control to offer a controllability analysis of seven distillation sequences for the separation of ternary mixtures. Nontraditional distillation sequences, such as the Petlyuk column, had higher control qualities than nonintegrated systems, according to the findings. This is significant because the presence of recycling streams was predicted to cause control issues. Segovia-Hernandez et al.,[27] conducted a similar investigation on ternary mixtures, comparing the controllability properties of thermally connected distillation sequences (including the Petlyuk column) to those of standard direct and indirect sequences. Closed-loop responses to setpoint changes were tested, and controllers were fine-tuned to have the lowest square-error criterion (ISE) values possible. The results show that integrated systems have greater control qualities than standard distillation column sequences. Segovia-Hernandez et al.,[28] investigated the control properties of six alternative thermally coupled distillation schemes of the Petlyuk system as part of a series of studies that assess the control properties of dividing-wall columns in the context of traditional separation schemes. The singular value decomposition approach is used to investigate the theoretical control properties. To supplement the theoretical approach, rigorous closed-loop simulations are used. The findings show that reducing the number of interconnections in the Petlyuk architecture does not always result in improved controllability properties. Segovia-Hernández et al.,[29] also claimed that in the control of the Petlyuk column, a PI controller with a dynamic estimation of uncertainties must be used. To evaluate the performance of the suggested controller in the face of unknown load disruptions in feed composition and setpoint changes, it was compared to the classical PI control law. The results reveal that implementing the controller with a dynamic

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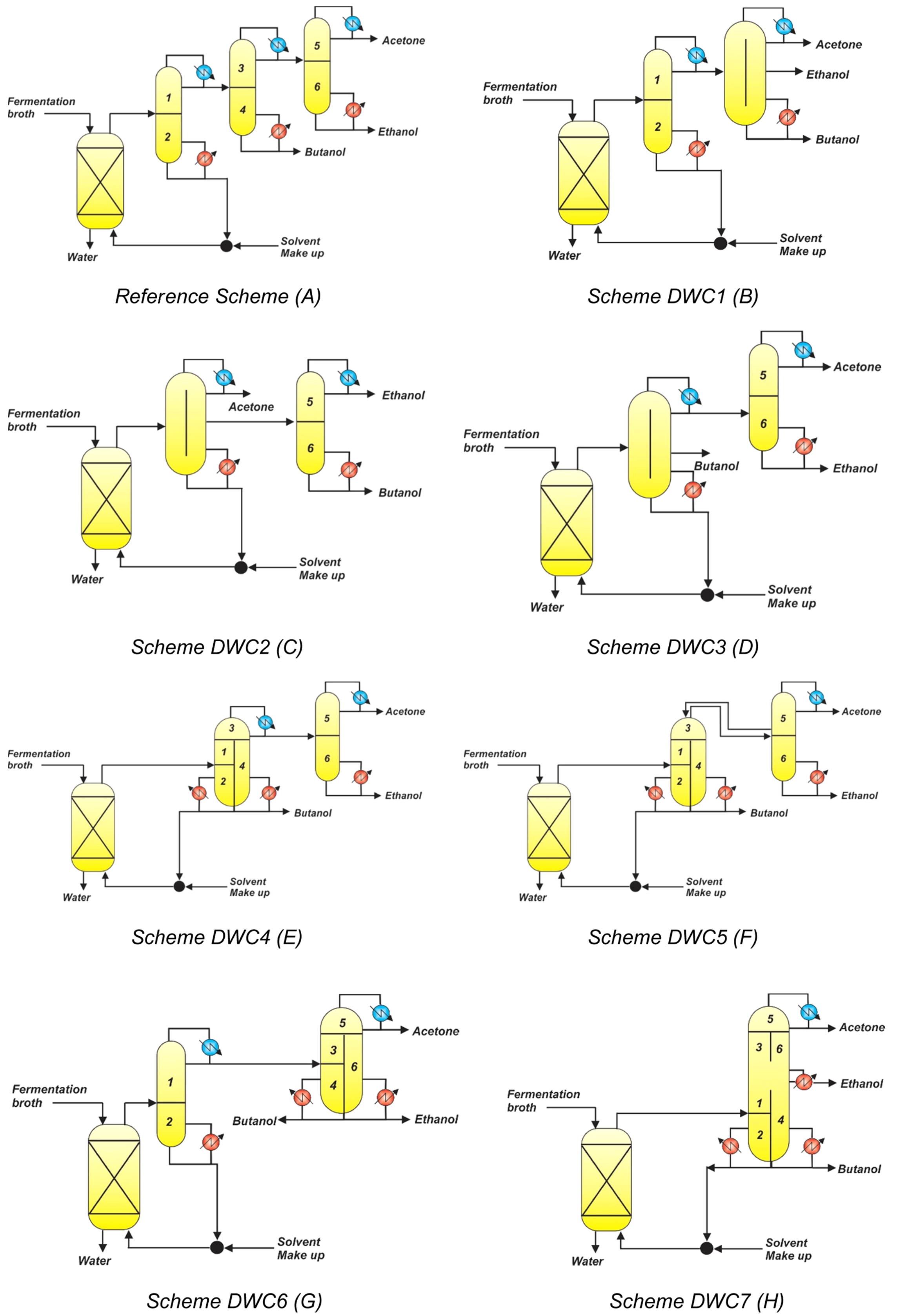

Figure 1. Hybrid liquid−liquid extraction−distillation to purify the ABE mixture.

estimation of uncertainty significantly enhanced the PI controller's closed-loop responses.

Zavala-Guzmán et al.,[30] devised a systematic method for tuning PI controllers for a class of DWCs with periodic discrete measurements. This technique generates effective

https://doi.org/10.1021/acs.iecr.2c02417
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gains for each DWC controller straightforwardly and simultaneously, using classical characteristics of the process dynamics (static gains and time constant of open-loop response) and the sampling-delay time of measurements. Lucero-Robles et al.,[31] proposed separating a multicomponent hydrocarbon mixture in a sequence including one or more DWCs in terms of overall energy usage, environmental impact, and controllability in a simulated environment. The location of the DWC in the separation train is determined by the parameters of the purified mixture and has an impact on control and energy consumption. Tututi-Avila et al.,[32] investigated the design, dynamics, and control of a satellite column, also known as an extended dividing-wall distillation column, and compared its performance to that of a DWC and a direct distillation sequence for the separation of benzene, toluene, and the three xylene isomers (BTX) mixtures. The satellite column is the most energy-efficient form in terms of dynamics, according to the results of the optimum designs for these distillation structures.

Following the assessment of the literature, it is obvious that while a variety of controllers are employed for binary distillation columns, only a few control structures for dividing-wall columns have been investigated. PID loops inside a multiloop architecture controller were used to steer the system to the desired steady state in most cases.

Many works emphasize the importance of control and controllability analyses for intensified processes since the results of these analyses determine the feasibility of industrial operation of an intensified process. This point is important because whenever a system is more intensified, the energy consumption and operating costs are lower, even though few studies have been reported on the degree of enhancement control properties. This point has already been identified by Ponce-Ortega et al.,[33] as a challenge in studies on process intensification. They identified that there are no studies that evaluate the degree of intensification with the controllability in the case of purification of azeotropic mixtures. Similar studies have only been reported in the case of hydrocarbon purification, such as the one reported by Lucero-Robles et al.[31]

The novelty of the work is to evaluate the control properties of different intensified distillation schemes in the separation of butanol from the acetone−butanol−ethanol (ABE) mixture. The operational study of a complex mixture such as ABE, the operational analysis of different intensified schemes, and the evaluation of the effect of the location of the intensified unit on the overall control behavior of the process are among the important contributions obtained from this work. Likewise, with the evaluation of controllability in the design of industrial processes, as is the case in the separation and purification of the ABE mixture, the concept of green chemistry and sustainability, as mentioned by Jimenez-Gonzalez and Constable,[34] is guaranteed. Control properties for all of the studied sequences are obtained to establish which structure demands the lowest energy requirements and better control properties in the separation of the analyzed mixtures. The analysis will allow us to establish which is the best DWC location and the degree of the intensification train in the separation of a multicomponent mixture. The control study for this work was carried out using different control loops and generating disturbances to observe the capacity of the processes to respond to these disturbances. The integral of absolute error (IAE) was used to evaluate the control performance.

2. CASES OF STUDY

The base cases for this study are the purification processes previously reported by Errico et al.[12] In this work, different hybrid processes to purify the ABE mixture are proposed and optimized. These processes are considered hybrid because they combine and link two common process separations: a set of distillation columns and a liquid−liquid extraction column. To reduce the energy consumption, the number of process equipment, and plant size, different intensified options were proposed and designed by Errico et al.[12]Figure 1 shows the complete set of alternatives studied. According to the information provided by Errico et al.,[12] these alternatives are allocated after the fermentation reactor, which generates an output stream with a molar flow rate of 1.64 kmol/h and a composition in molar basis of 80.2% water, 11.3% butanol, 8.1% acetone, and 0.4% ethanol at 35 °C and 1 atm. This stream is fed to an extraction column that uses *n*-hexyl-acetate as a solvent to remove the water from the mixture. Once the water is removed, a stream rich in solvent, ethanol, butanol, and acetone is obtained by the top of the extraction column. This organic rich stream is fed to a distillation column where the solvent is recovered at the bottom, and the ABE mixture is obtained at the top. Butanol with high purity is recovered at the bottom of a second distillation column, whereas acetone and ethanol are recovered in a third distillation column (see Figure 1A). Figure 1A is considered the reference scheme, and it is used as a benchmark. As already stated, different intensified alternatives are considered by Errico et al.[12] These alternatives are designed due to the need to reduce energy requirements. The schemes of Figure 1B−H were generated from a reference scheme using the moving section method reported in several previous works.[18,19] It is important to highlight that these configurations were simulated in Aspen Plus using the thermodynamic model NRTL-HOC, according to the information provided by Errico et al.[12]

3. CONTROL STUDY: CLOSED-LOOP DYNAMIC POLICIES

This work considers different intensified separation options to purify the ABE mixture. Due to the intensified processes being significantly more complex than a conventional process, a control study must be performed to determine the feasibility of implementing these alternatives at an industrial scale. Furthermore, a control study allows the process to determine the influence of the intensification level and location of the intensified equipment in the control properties. Therefore, in this section, the methodology used to perform the control study is explained. It is important to highlight that this study is carried out to minimize the number of disturbances and the time required to stabilize the process.

The number of disturbances and time required to stabilize them are two important factors that must be analyzed, especially when a change in the feed composition or an outlet composition is required. The alteration of the composition requirement in a feed or outlet stream is a common situation in a chemical plant due to the quality of raw materials or products not always being equivalent. As Skogestad[35] establishes, for preliminary studies about the dynamic behavior of a distillation column, a simple regulatory control layer is sufficient. This control layer can be assumed as a setpoint change on one of the manipulable variables. Following the ideas presented in the work of Wolff and Skogestad,[36] it is suggested that the change

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Table 1. Optimal Parameters and IAE Values for PI Controllers Considering the PA1 Disturbance

sequence	acetone loop K_C(%/%)	acetone loop τ_I (min)	acetone loop IAE	butanol loop K_C(%/%)	butanol loop τ_I (min)	butanol loop IAE
reference scheme (A)	250	150	2.9111×10^{-2}	115	35	5.95615×10^{-3}
DWC1 (B)	100	140	2.3398×10^{-2}	127	27	4.51334×10^{-3}
DWC2 (C)	150	120	2.0019×10^{-2}	90	110	6.28173×10^{-2}
DWC3 (D)	250	150	3.1973×10^{-2}	250	3	1.37633×10^{-2}
DWC4 (E)	250	145	3.2307×10^{-2}	250	25	8.38381×10^{-3}
DWC5 (F)	230	100	1.7254×10^{-2}	245	30	1.76072×10^{-2}
DWC6 (G)	250	110	3.2235×10^{-2}	150	30	5.61052×10^{-3}
DWC7 (H)	245	150	2.9277×10^{-2}	250	115	8.29786×10^{-2}

Table 2. Optimal Parameters and IAE Values for PI Controllers Considering the PA2 Disturbance

sequence	acetone loop K_C(%/%)	acetone loop τ_I (min)	acetone loop IAE	butanol loop K_C(%/%)	butanol loop τ_I (min)	butanol loop IAE
reference scheme (A)	100	50	1.6079×10^{-4}	250	60	1.97919×10^{-4}
DWC1 (B)	66	150	1.8818×10^{-4}	115	10	4.6562×10^{-5}
DWC2 (C)	150	150	7.7014×10^{-5}	unstable		
DWC3 (D)	190	150	1.6680×10^{-4}	250	1	7.8273×10^{-4}
DWC4 (E)	unstable			250	150	2.6394×10^{-3}
DWC5 (F)	250	150	2.0410×10^{-4}	95	150	6.5368×10^{-3}
DWC6 (G)	230	150	1.5792×10^{-4}	250	60	2.1007×10^{-3}
DWC7 (H)	250	150	3.1598×10^{-4}	250	115	3.4852×10^{-3}

of the manipulable variables on the control variables chosen in the output flow rate compositions be analyzed. These variables are coupled as follows:

- Reflux ratio, to control the purity of the products at the top of the column.
- Reboiler duty, to control the purity of the products at the bottom of the column.
- Side stream flow rate, to control the purity of the products at the side stream.

These typical structures consist of an *LV* control arrangement that uses the liquid stream of reflux rate (L) and the vapor boil-up rate (V) to control the purities of tops and bottoms, respectively (see Figure S1). Based on the mass and energy balance, the reflux rate and the vapor boil-up rate can be adjusted using the reflux ratio and reboiler duty, respectively; thus, these last two rates are considered the manipulated variables.[37]

In the Aspen Plus Dynamics simulator, the composition control test was performed as follows. Once the controllers are set, initial values are supposed for the proportional gain (K_c) and the integral time constant (τ_i). The composition to be analyzed is then modified by 5%[37] of its nominal value, and the simulation is performed until the setpoint is achieved. To compare the different responses, the integral of the absolute error (IAE) criteria is used.

$$\mathrm{IAE} = \int_0^{\infty} |\varepsilon(t)| \mathrm{d}t \tag{1}$$

where ε(t) is the function of the integral time, which is given by

$$\varepsilon(t) = y_{\mathrm{d}} - y \tag{2}$$

The best configurations are those with the lowest IAE. Nevertheless, it is important to obtain the values of K_c and τ_i that minimize the IAE for each sequence; thus, those values are optimized for each sequence through a parametric analysis approach, following the methodology shown in Figure S2 (Supporting Information). The objective function to be minimized is, as aforementioned, the IAE, which penalizes the control error and overshoot.[38] According to Hussain et al.,[39] the IAE increases for either a positive or a negative error, resulting in a fairly good underdamped system. This criterion has been widely used for control studies of nonconventional distillation sequences.[40,41]

4. RESULTS

4.1. Results of the Tuning Procedure. This section provides the results obtained during the control study. The simulations were performed using a Dell Inspiron 15 7000 computer with Intel Core i7-7700HQ @2.8GHz and 8GB of RAM; regarding that, this study is applied to output streams for the compounds of interest, which are acetone and butanol. On the other hand, the output stream for ethanol was not considered because of its low molar flow rate (0.4% of the total molar flow rate) in contrast to other products. Previous studies have demonstrated the low feasibility and high cost in terms of controllability that would be involved in considering ethanol as a product of interest.[42] While conventional distillation sequences have reported on the success in controlling ethanol composition, other works[43] have had to carry out design strategies to avoid facing the same control problem regarding ethanol. Patrascu et al.,[44] reported modifications in the column separating ethanol. This is part of the recycle loop of butanol—water separation done to prevent ethanol accumulation. However, the ethanol obtained in this process is of low purity. On the other hand, Patrascu et al.,[45] implemented a dynamic study of a DWC to separate the ABE effluent. In their study, to avoid the conflict generated in the purification and controllability of ethanol, the ethanol efflux is obtained when mixed with water. In that regard, the ethanol loop will not be considered in this work for the dynamic analysis performed.

Considering the eight study cases and the two types of disturbances carried out during this study, the total number of

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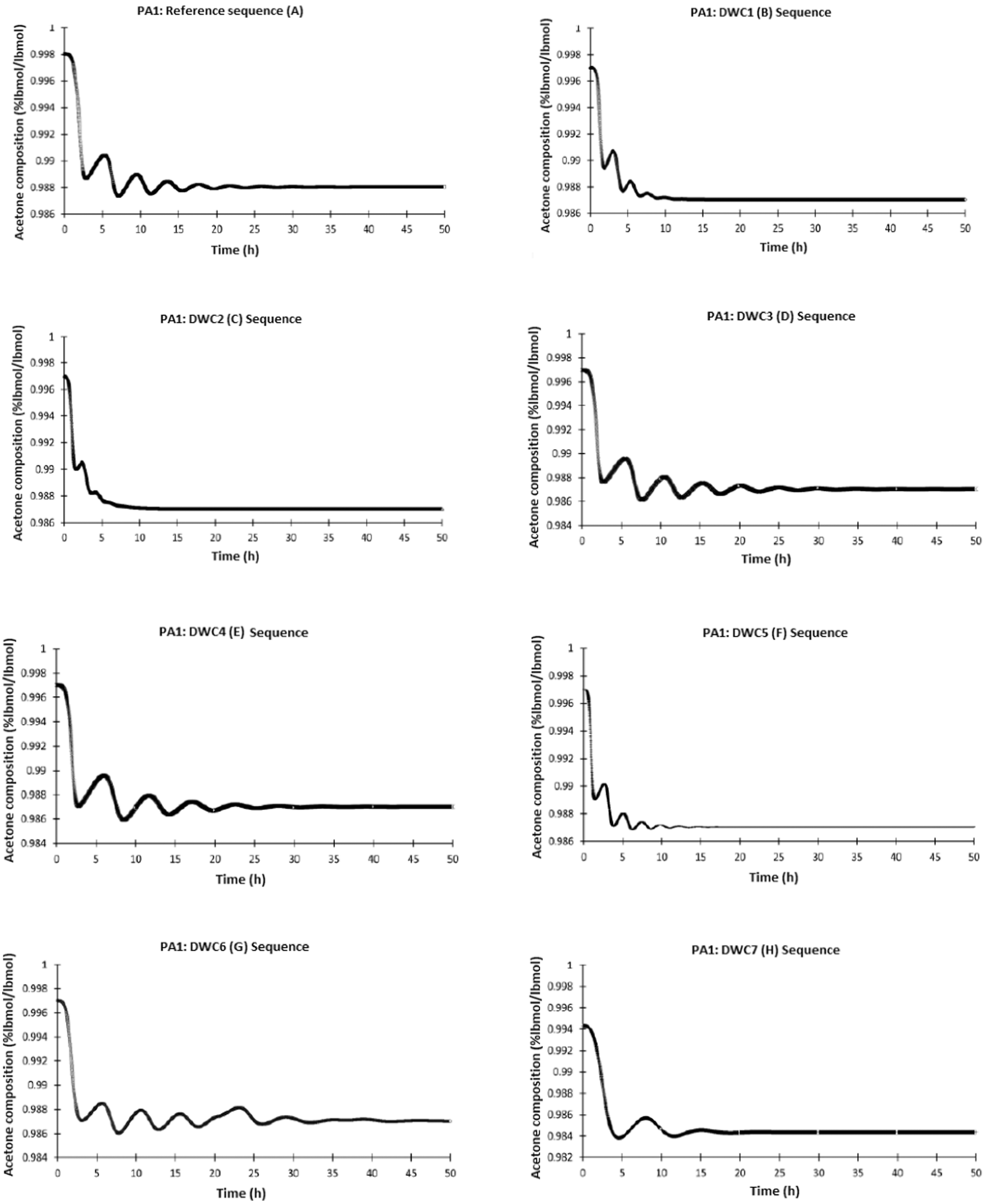

Figure 2. Closed-loop dynamic responses for acetone flow, performing the PA1 disturbance.

control loops implemented was 32. The PA1 disturbance has 16 control loops. Eight of these control loops correspond to the butanol stream, while the other eight control loops correspond to acetone. On the other hand, the disturbance PA2 contains the other 16 control loops, with eight loops being for butanol and the other eight loops for acetone. It is important to highlight that all of the sequences showed good

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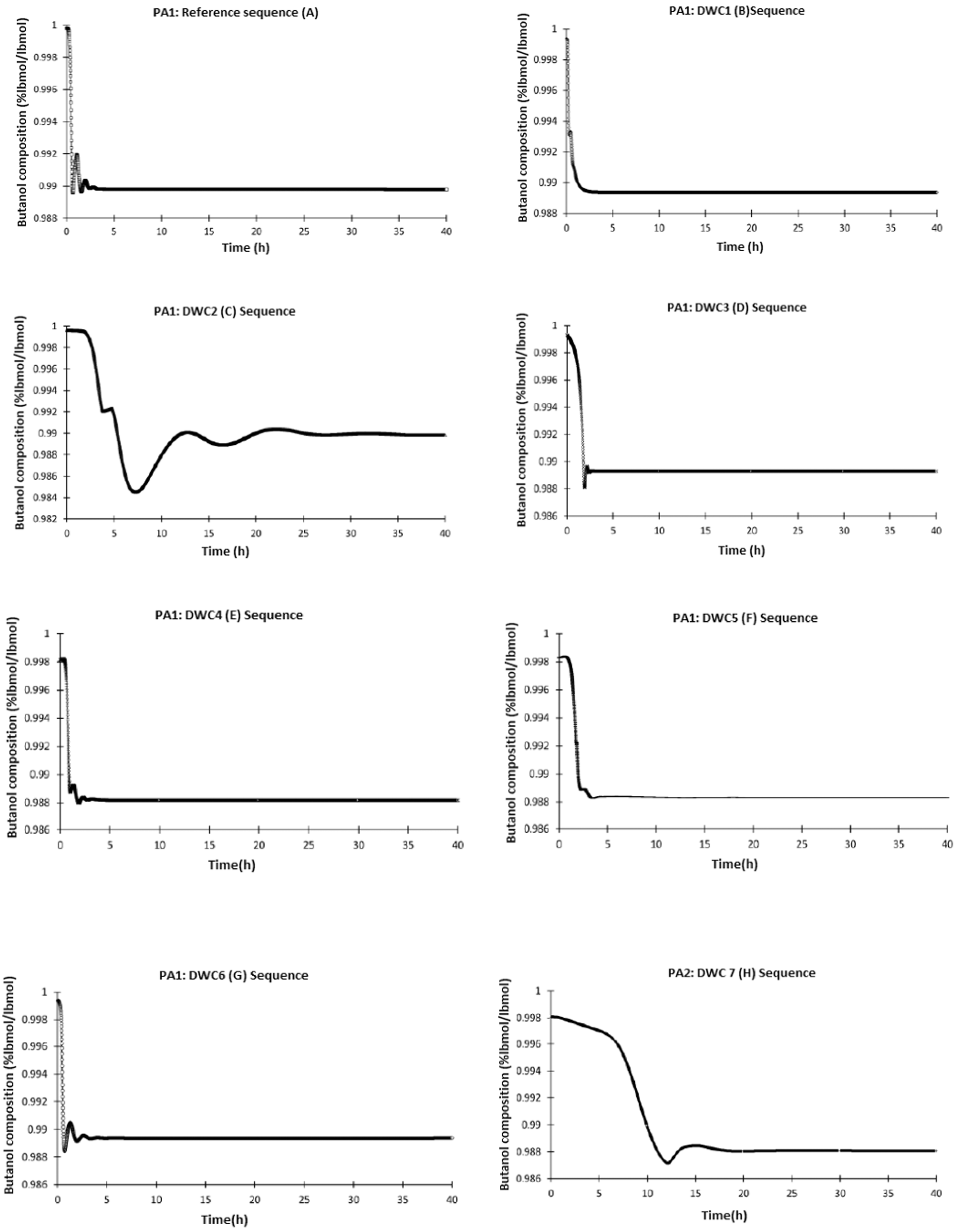

Figure 3. Closed-loop dynamic responses for butanol flow, performing the PA1 disturbance.

dynamic responses for the optimal control parameters obtained during the tuning procedure.

Table 1 shows the optimal parameters of the PI controllers for the PA1 disturbance. These parameters were obtained during the tuning procedure. The IAE values for these optimal parameters are presented in Table 1. Table 2 shows the results obtained for the disturbance PA1. Similarly to Table 1, the optimal PI controller parameters are presented together with

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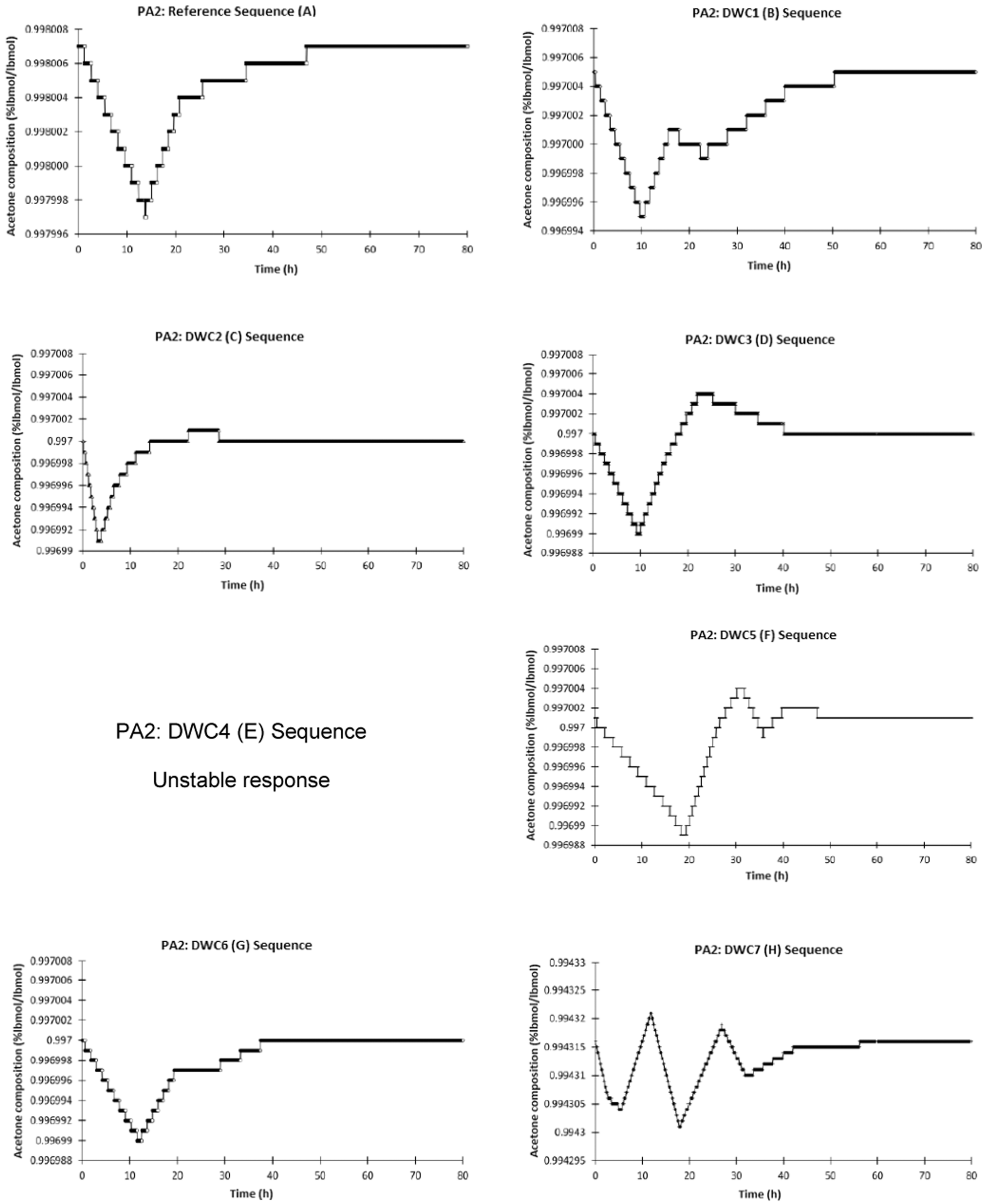

Figure 4. Closed-loop dynamic responses for acetone flow, performing the PA2 disturbance.

their respective IAE value. Figures 2−5 present the dynamic responses for each sequence, control loop, and disturbance. These dynamic responses were obtained using the optimal controller parameters.

4.2. Analysis of Dynamic Responses.

To analyze and study the dynamic responses, the results are divided according to each disturbance. First of all, the PA1 disturbance is analyzed. Please note that in Table 1, sequence F (DWC5) has

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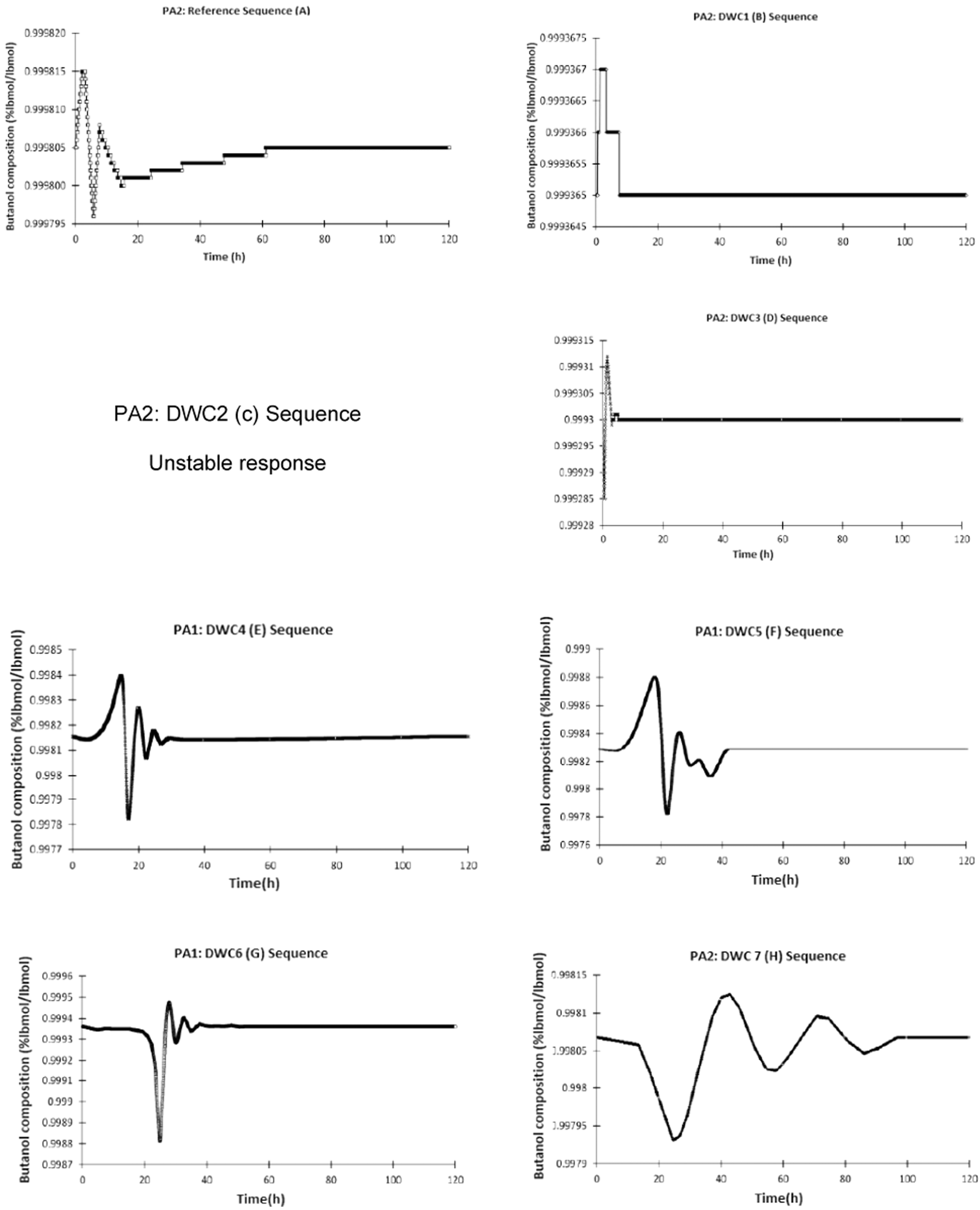

Figure 5. Closed-loop dynamic responses for butanol flow, performing the PA2 disturbance.

the lowest IAE value for the acetone loop. In contrast to sequence F, sequence E (DWC4) shows the highest IAE value, which indicates a more oscillatory response (see Figure 2). In the case of the butanol loop, sequence B (DWC1) has the best (the lowest) IAE value (4.51334E-3). According to Figure 2-F5, the dynamic response of this sequence shows almost no oscillation, and it quickly stabilizes compared to the other alternatives, confirming its lowest IAE value. On the other

https://doi.org/10.1021/acs.iecr.2c02417
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Table 3. Total Annual Cost (TAC), Eco-Indicator 99 (EI99), Condition Number (CN), and Integral of the Absolute Error (IAE) of Each Sequence Studied

				PA1		PA2	
	TAC [k$/y]	EI99 [kpoints/]	CN	IAE (acetone)	IAE (butanol)	IAE (acetone)	IAE (butanol)
Scheme (A)	129.42	15.55	15248.6	2.91×10^{-2}	5.96×10^{-3}	1.61×10^{-4}	1.98×10^{-4}
DWC1 (B)	111.86	17.5	10.35	2.34×10^{-2}	4.51×10^{-3}	1.88×10^{-4}	4.66×10^{-5}
DWC2 (C)	128.45	16.74	2982	2.00×10^{-2}	6.28×10^{-2}	7.70×10^{-5}	unstable
DWC3 (D)	122.99	19.5	10183.72	3.20×10^{-2}	1.38×10^{-2}	1.67×10^{-4}	7.83×10^{-4}
DWC4 (E)	108.54	13.73	1402	3.23×10^{-2}	8.38×10^{-3}	unstable	2.64×10^{-3}
DWC5 (F)	105.57	12.93	1.7	1.73×10^{-2}	1.76×10^{-2}	2.04×10^{-4}	6.54×10^{-3}
DWC6 (G)	115.5	14.34	1.22×10^{17}	3.22×10^{-2}	5.61×10^{-3}	1.58×10^{-4}	2.10×10^{-3}
DWC7 (H)	97.88	12.22	18994.4	2.93×10^{-2}	8.30×10^{-2}	3.16×10^{-4}	3.49×10^{-3}

hand, sequence H (DWC7) shows the worst IAE value due to its highest value.

If the time required to stabilize the process is taken as a parameter in the evaluation of the dynamic responses, then in Figure 2, we can acknowledge that sequences B (DWC1), C (DWC2), and F (DWC5) have the lowest time to stabilize. In this case, the three sequences required around 10 h to achieve a stable response. Sequence H, on the other hand, was stabilized after 20 h, and sequences A, D, E, and G were stabilized after 35 h, which confirms that this slow behavior has a direct impact on the IAE value. In the case of the butanol loop, which is shown in Figure 3, it can be noted that the time required to stabilize the composition is notably less as opposed to the acetone loop. For this loop, sequences A, B, D, E, F, and G needed the lowest time (around 5 h) to stabilize. Sequence B was the fastest scheme out of all six to stabilize. In contrast to these sequences, schemes H and C required 20 and 30 h, respectively, to stabilize.

When sequences B to H are compared to the reference sequence A, it can be noted that all of the alternatives have stable dynamic responses. However, sequences B and F are better than the reference schemes because they have less time to stabilize than A. These results can be appreciated by observing the lower IAE value of these sequences.

The results for the disturbance PA2 indicate that the best controller parameters were obtained during the tuning procedure for almost all sequences. In this case, the results of PA2 are shown in Table 2 and Figures 4 and 5. According to Table 2, sequence C (DWC2) has the lowest IAE value (7.70147E-5) for the acetone loop; contrary to this scheme, alternative H (DWC7) obtained the worst (highest) IAE value, which is 3.15984E-4. Furthermore, the results for the butanol loop indicate that sequence B is the best, with the lowest IAE value (4.65626E-5), whereas sequence F has the highest value. Please note that in this case, sequences C and E were unstable in at least one loop. It is because of this that these sequences are not considered good alternatives and are thus discarded.

In the set of sequences analyzed in Figure 4, it is evident to appreciate that in spite of perturbing the setpoint, the difference in the composition is less than 0.00001, which denotes a stable loop. In other words, acetone loops are well conditioned in comparison to butanol loops. Regarding acetone, a similar behavior is observed in the work presented by Sánchez-Ramírez et al.,[42] since IAE values and settle times were relatively good and similar among those analyzed schemes. A similar behavior is shown in the case of Figure 5, although it can be said that the best dynamic responses correspond to sequences B and D since they stabilized quickly. On the other hand, sequences A, E, F, and G require more time, while scheme H achieved the longest stabilization time. When sequences B−H are compared to the reference sequence A, it is evident that sequences B and G are better than A due to their lower IAE value and the time required to stabilize each of them.

Once the dynamic responses and IAE values have been analyzed, some important points must be remarked:

1. First: It can be effortlessly appreciated that sequence B has the best dynamic behavior. This alternative showed better performance than the reference scheme and the other intensified alternatives.
2. Second: Sequences D, F, and G have shown similar control performance to that of the reference scheme A.
3. Third: Scheme H has stable dynamic responses, but its performance is worse than the reference schemes. This is because of its slow stabilizing responses.
4. Fourth: Sequences C and E do not have good control properties because they showed an unstable loop.

Almost all intensified processes have shown similar or even better control performance than the conventional process. It is important to highlight two factors that are contributing directly to the control properties of the intensified sequences. These factors are the grade of intensification and the location or position of the intensified equipment. Based on Figure 1 and the results obtained, please note that the best control behaviors were obtained in those sequences that were not completely intensified. These sequences are characterized by having a conventional column and a DWC. In this case, sequence B is the best and shows the best dynamic performance, whereas the fully intensified alternative H shows the worse dynamic behavior compared to all of the other sequences.

If Figure 1 is taken as a reference, it can be observed that those alternatives which started the separation with a conventional column and have the DWC up to the end showed better dynamic behavior and control properties. In contrast, the sequences that began the separation using a DWC showed worse dynamic behaviors. This can be extended to fully intensified alternatives, where only one intensified column is used (scheme H in this case). Sequence H has the slowest stabilization and the worst dynamic response. For these reasons, it is concluded that a conventional column contributes to stabilizing the process due to a more simple operation. In contrast, alternatives with a more complex operation (more grade of intensification) generate worse dynamic responses.

An interesting aspect to be considered from the process design point of view is the sizing of the equipment. That is to say, the size of the equipment has a relevant effect on the analysis of the process dynamics. According to what is

https://doi.org/10.1021/acs.iecr.2c02417
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observed in Tables S2–S8 (Supporting Information), the equipment with larger dimensions resulted in better dynamic behavior. The reason for this direct relationship is due to the fact that internally, larger equipment is capable of having larger internal flows. The consequence of having a greater amount of flow is the capacity to better dampen the disturbances received by the system. On the contrary, equipment with smaller dimensions has greater difficulty dampening the disturbances obtained.

Table 3 shows the results of the optimization performed by Errico et al.[12] These results were obtained by optimizing a triple objective function composed of the total annual cost (TAC), ecological indicator 99 (IE99), and condition number (CN). The results show that the best configuration in economic and environmental terms is scheme H (with a 22% reduction in TAC and an 18% reduction in EI99). Moreover, both the CN and the IAE measured in the present work show that alternative H has a good control performance. Nevertheless, scheme B results as a good option in economic (111.86 k$/y) and environmental (17.5 kpoints/y) terms and with the best control performance of all of the configurations studied. Undoubtedly, they represent a concrete possibility to improve the competitiveness of the biobutanol process.

Although only a few works have been made on the evaluation of the separation control and purification process of the ABE mixture, it is important to highlight the novelty of the present study in comparison with works that have been carried out. Kaymak[46] presents a work on the design and control of biobutanol purification of the ABE blend. He exhibits butanol purification schemes by conventional distillation, which differ from the intensified schemes presented in this work. Kaymak[46] studies the controllability and dynamic behavior by means of SISO multiloop control structures, which indicate robust control schemes against feed and composition perturbations. The novelty of the results presented in this work in comparison to the work of Kaymak[46] is the verification that intensified schemes can have a controllability comparable to or even better than the conventional schemes. This verification implies that one scheme can have a greater economical profit, be less energy-demanding, and have safer processes with a lower environmental impact and with equal or better control properties. Patraşcu et al.,[44] confirm the excellent controllability of the DWC configuration, as the product flow rates follow the amounts of acetone, ethanol, and butanol in the feed with practically unchanged purities. Although Patraşcu et al.,[44] also incorporate an intensified scheme, their work differs from this work in the variety of intensified schemes and the study of the effect of DWC positioning, which, as we can observe, changes the control properties of the ABE mixture separation process.

5. CONCLUSIONS

A control study of eight different processes for the purification of the ABE mixture is presented. The purpose was to obtain the optimum parameters of the controllers, as well as to quantify their performance by means of the integral of absolute error (IAE). It was observed that the degree of intensification and the location of the intensified equipment play an important role in the control properties. The schemes with a conventional column at the beginning of the separation were the alternatives with better control properties. On the other hand, the fully intensified scheme starting the separation with a DWC is one of the alternatives with worse dynamic behaviors. In this case, alternative B, consisting of a conventional column followed by a DWC, showed the best control properties compared to all sequences. Similar results have been reported for (ideal) hydrocarbon mixtures related to the degree of intensification and the location of the DWC in the separation train.[31]

Particularly, results show that acetone loops are well conditioned when subjected to disturbances. Strictly speaking, there are differences in the IAE and settling time values; however, almost all of the intensified alternatives have shown good control behaviors with a better dynamic behavior than the conventional scheme. This generalization of controllability results opens the possibility of generating a deeper analysis in terms of other indicators and globally evaluating the process schemes presented in this work. It is significant to allude that this work is a complement of the previous work proposed by Errico et al.,[12] where a multiobjective optimization was performed, considering the economics, environmental impact, and open-loop control. Thus, this control study was finished by performing the study of closed-loop control properties. These intensified purification processes were found to be more economical, with a lower environmental impact, and with good control properties due to their good stability during operation. In general, the results for the open-loop control study of this work corroborate, complement, and extend the study about the design and control properties of the studied configurations. Likewise, the information on the separation schemes is extended in an integral way for possible industrial implementation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c02417.

Design parameters for scheme (A); design parameters for DWC1 (B); hybrid liquid−liquid extraction−distillation to purify the ABE mixture; flowchart used to determine the optimal parameters of the PI controllers considering the IAE as performance criteria (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Juan Gabriel Segovia-Hernández − *Departamento de Ingeniería Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Guanajuato, Guanajuato 36050, Mexico*; orcid.org/0000-0003-4175-9809; Email: gsegovia@ugto.mx

Authors

Ernesto Flores-Cordero − *División de Ciencias de la Salud e Ingenierías, Universidad de Guanajuato, Celaya, Guanajuato 38110, Mexico*

Eduardo Sánchez-Ramírez − *Departamento de Ingeniería Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Guanajuato, Guanajuato 36050, Mexico*; orcid.org/0000-0002-4326-4837

Gabriel Contreras-Zarazúa − *Departamento de Ingeniería Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Guanajuato, Guanajuato 36050, Mexico*

https://doi.org/10.1021/acs.iecr.2c02417
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César Ramírez-Márquez − *Departamento de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacán 58060, Mexico*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.iecr.2c02417

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge CONACyT (Mexico).

■ NOMENCLATURE

ABE acetone−butanol−ethanol mixtures
ATJ alcohol-to-Jet
BTX mixtures of benzene, toluene, and the three xylene isomers
CN condition number
DWC dividing-wall column
IAE integral of the absolute error
ISE square-error criterion
Kc proportional gain
kPa kilopascal
kW kilowatts
LV liquid stream of reflux rate (L) and the vapor boil-up rate (V)
m meters
PA1 control loops, with eight control loops corresponding to the butanol stream, while the remainder eight control loops corresponding to acetone
PA2 other control loops, with eight loops for butanol and eight loops for acetone
PI process intensification
PI proportional−integral
PID proportional−integral−derivative
$\boldsymbol{\varepsilon(t)}$ function of integral time
$\boldsymbol{\tau_i}$ integral time constant

■ REFERENCES

(1) Stankiewicz, A.; Moulijn, J. A. Process intensification. *Ind. Eng. Chem. Res.* **2002**, *41*, 1920−1924.
(2) Baldea, M. From process integration to process intensification. *Comput. Chem. Eng.* **2015**, *81*, 104−114.
(3) Moulijn, J. A.; Stankiewicz, A.Process Intensification. In *Encyclopedia of Sustainable Technologies*; Elsevier Inc., 2017; pp 509−518.
(4) Stankiewicz, A. I.; Moulijn, J. A. Process Intensification Transforming Chemical Engineering. *Chem. Eng. Prog.* **2000**, *96*, 22−34.
(5) Wang, J.; Li, F.; Lakerveld, R. Process intensification for pharmaceutical crystallization. *Chem. Eng. Process.* **2018**, *127*, 111−126.
(6) Laird, T. Special Feature Section: Process Intensification/Continuous Processing in the Fine Chemicals Arena. *Org. Process Res. Dev.* **2001**, *5*, 612.
(7) Woodley, J. M. Bioprocess intensification for the effective production of chemical products. *Comput. Chem. Eng.* **2017**, *105*, 297−307.
(8) Pérez-Cisneros, E. S.; Mena-Espino, X.; Rodríguez-López, V.; Sales-Cruz, M.; Viveros-García, T.; Lobo-Oehmichen, R. An integrated reactive distillation process for biodiesel production. *Comput. Chem. Eng.* **2016**, *91*, 233−246.
(9) Simasatitkul, L.; Siricharnsakunchai, P.; Patcharavorachot, Y.; Assabumrungrat, S.; Arpornwichanop, A. Reactive distillation for biodiesel production from soybean oil. *Korean J. Chem. Eng.* **2011**, *28*, 649−655.
(10) Contreras-Zarazúa, G.; Jasso-Villegas, M. E.; Ramírez-Márquez, C.; Sánchez-Ramírez, E.; Vázquez-Castillo, J. A.; Segovia-Hernandez, J. G. Design and intensification of distillation processes for furfural and co-products purification considering economic, environmental, safety and control issues. *Chem. Eng. Process.* **2021**, *159*, No. 108218.
(11) Contreras-Zarazúa, G.; Sánchez-Ramírez, E.; Vázquez-Castillo, J. A.; Ponce-Ortega, J. M.; Errico, M.; Kiss, A. A.; Segovia-Hernández, J. G. Inherently Safer Design and Optimization of Intensified Separation Processes for Furfural Production. *Ind. Eng. Chem. Res.* **2019**, *58*, 6105−6120.
(12) Errico, M.; Sanchez-Ramirez, E.; Quiroz-Ramìrez, J. J.; Rong, B. G.; Segovia-Hernandez, J. G. Multiobjective Optimal Acetone-Butanol-Ethanol Separation Systems Using Liquid-Liquid Extraction-Assisted Divided Wall Columns. *Ind. Eng. Chem. Res.* **2017**, *56*, 11575−11583.
(13) Kumakiri, I.; Yokota, M.; Tanaka, R.; Shimada, Y.; Kiatkittipong, W.; Lim, J. W.; Yamada, M. Process Intensification in Bio-Ethanol Production−Recent Developments in Membrane Separation. *Processes* **2021**, *9*, No. 1028.
(14) Romero-Izquierdo, A. G.; Gómez-Castro, F. I.; Gutiérrez-Antonio, C.; Hernández, S.; Errico, M. Intensification of the alcohol-to-jet process to produce renewable aviation fuel. *Chem. Eng. Process.* **2021**, *160*, No. 108270.
(15) Etchells, J. C. Process intensification: Safety pros and cons. *Process Saf. Environ. Prot.* **2005**, *83*, 85−89.
(16) Nikačević, N. M.; Huesman, A. E. M.; Van den Hof, P. M. J.; Stankiewicz, A. I. Opportunities and challenges for process control in process intensification. *Chem. Eng. Process.* **2012**, *52*, 1−15.
(17) Hendershot, D. C. Conflicts and decisions in the search for inherently safer process options. *Process Saf. Prog.* **1995**, *14*, 52−56.
(18) Tian, Y.; Pistikopoulos, E. N. Operability and safety considerations in process intensification. *IFAC-PapersOnLine* **2020**, *53*, 11434−11439.
(19) Ling, H.; Luyben, W. L. New control structure for divided-wall Columns. *Ind. Eng. Chem. Res.* **2009**, *48*, 6034−6049.
(20) Joglekar, G. S. In *Dynamic Modeling and Optimization of Thermally Coupled Dividing Wall Column Batch Distillation Processes*, Spring National Meeting, 2009.
(21) Wojsznis, W.; Mehta, A.; Wojsznis, P.; Thiele, D.; Blevins, T. Multi-objective optimization for model predictive control. *ISA Trans.* **2007**, *46*, 351−361.
(22) Donahue, M. M.; Roach, B. J.; Downs, J. J.; Blevins, T.; Baldea, M.; Eldridge, R. B. Dividing wall column control: Common practices and key findings. *Chem. Eng. Process.* **2016**, *107*, 106−115.
(23) Lukač, G.; Halvorsen, I. J.; Olujic, Z.; Dejanovic, I. On controllability of a fully thermally coupled four-product dividing wall column. *Chem. Eng. Res. Des.* **2019**, *147*, 367−377.
(24) Rewagad, R. R.; Kiss, A. A. Dynamic optimization of a dividing-wall column using model predictive control. *Chem. Eng. Sci.* **2012**, *68*, 132−142.
(25) Yu, J.; Wang, S. J.; Huang, K.; Yuan, Y.; Chen, H.; Shi, L. Improving the Performance of Extractive Dividing-Wall Columns with Intermediate Heating. *Ind. Eng. Chem. Res.* **2015**, *54*, 2709−2723.
(26) Jiménez, A.; Hernandez, S.; Montoy, F. A.; Zavala-García, M. Analysis of control properties of conventional and nonconventional distillation sequences. *Ind. Eng. Chem. Res.* **2001**, *40*, 3757−3761.
(27) Segovia-Hernández, J.; Hernandez, S.; Jimenez, A. Control behaviour of thermally coupled distillation sequences. *Chem. Eng. Res. Des.* **2002**, *80*, 783−789.
(28) Segovia-Hernández, J. G.; Hernandez, S.; Jimenez, A. Analysis of dynamic properties of alternative sequences to the Petlyuk column. *Comput. Chem. Eng.* **2005**, *29*, 1389−1399.
(29) Segovia-Hernández, J. G.; Hernandez, S.; Femat, R.; Jimenez, A. Control of thermally coupled distillation arrangements with dynamic estimation of load disturbances. *Ind. Eng. Chem. Res.* **2007**, *46*, 546−558.

(30) Zavala-Guzmán, A. M.; Hernandez-Escoto, H.; Hernandez, S.; Barroso-Munoz, F. O.; Segovia-Hernandez, J. G. Conventional Proportional-Integral Control of a Dividing Wall Distillation Column with Discrete Measurements. *Chem. Eng. Technol.* **2016**, *39*, 2238−2250.

(31) Lucero-Robles, E.; Gómez-Castro, F. I.; Ramírez-Márquez, C.; Segovia-Hernández, J. G. Petlyuk Columns in Multicomponent Distillation Trains: Effect of its Location for the Separation of Hydrocarbon Mixtures. *Chem. Eng. Technol.* **2016**, *39*, 2207−2216.

(32) Tututi-Avila, S.; Domínguez-Díaz, L. A.; Medina-Herrera, N.; Jimenez-Gutierrez, A.; Hahn, J. Dividing-wall columns: Design and control of a Kaibel and a satellite distillation column for BTX separation. *Chem. Eng. Process.* **2017**, *114*, 1−15.

(33) Ponce-Ortega, J. M.; Al-Thubaiti, J. M.; El-Halwagi, M. M. Process intensification: new understanding and systematic approach. *Chem. Eng. Process.* **2012**, *53*, 63−75.

(34) Jiménez-González, C.; Constable, D. J.*Green Chemistry and Engineering: A Practical Design Approach*; John Wiley & Sons, 2011.

(35) Skogestad, S. The Dos and Don'ts of Distillation Column Control. *Chem. Eng. Res. Des.* **2007**, *85*, 13−23.

(36) Wolff, E. A.; Skogestad, S. Operation of integrated three-product (Petlyuk) distillation columns. *Ind. Eng. Chem. Res.* **1995**, *34*, 2094−2103.

(37) Luyben, W. L.*Practical distillation control*; Springer Science & Business Media, 2012.

(38) Marzoughi, A.; Selamat, H.; Rahmat, M. F.; Rahim, H. A. Optimized proportional integral derivative (PID) controller for the exhaust temperature control of a gas turbine system using particle swarm optimization. *Int. J. Phys. Sci.* **2012**, *7*, 720−729.

(39) Hussain, K. M.; Zepherin, R. A. R.; Kumar, M. S.; Kumar, S. M. G. Comparison of PID controller tuning methods with genetic algorithm for FOPTD system. *Int. J. Eng. Res. Appl.* **2014**, *4*, 308.

(40) Liu, X.; Zhou, Y.; Cong, L.; Ding, F. High-purity control of internal thermally coupled distillation columns based on nonlinear wave model. *J. Process Control* **2011**, *21*, 920−926.

(41) Wu, N.; Huang, K.; Luan, S. Operation of dividing-wall distillation columns. 2. A double temperature difference control scheme. *Ind. Eng. Chem. Res.* **2013**, *52*, 5365−5383.

(42) Sánchez-Ramírez, E.; Alcocer-García, H.; Quiroz-Ramírez, J. J.; Ramírez-Márquez, C.; Segovia-Hernández, J. G.; Hernández, S.; Errico, M.; Castro-Montoya, A. J. Control properties of hybrid distillation processes for the separation of biobutanol. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 959−970.

(43) Kiss, A. A.; Suszwalak, D.J.-P.C. Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns. *Sep. Purif. Technol* **2012**, *86*, 70−78.

(44) Patraşcu, I.; Bîldea, C. S.; Kiss, A. A. Eco-efficient butanol separation in the ABE fermentation process. *Sep. Purif. Technol.* **2017**, *177*, 49−61.

(45) Patraşcu, I.; Bîldea, C. S.; Kiss, A. A. Dynamics and control of a heat pump assisted azeotropic dividing-wall column for biobutanol purification. *Chem. Eng. Res. Des.* **2019**, *146*, 416−426.

(46) Kaymak, D. B. Design and control of an alternative process for biobutanol purification from ABE fermentation. *Ind. Eng. Chem. Res.* **2019**, *58*, 1957−1965.

https://doi.org/10.1021/acs.iecr.2c02417
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