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Comparison of intensified reactive distillation configurations for the synthesis of diphenyl carbonate

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A B S T R A C T

Reactive Distillation is one of the most representative examples of Process Intensification due this technology allows to simplify and to unify the reaction and separation processes in only one equipment, reducing in this way the total cost of the process. However, the RD technology can be improved through energy integration in order to reduce the energy consumption, increasing energy efficiency and economic benefits compared with conventional reactive distillation. In this paper, four intensified reactive distillation configurations for the Synthesis of Diphenyl Carbonate are compared. A conventional reactive distillation (CRD), a thermally coupled reactive distillation (TCRD) and two novel configurations with energy integration, which consist in a reactive distillation with vapor recompression (VRRD) and the second one in a hybrid process that involve thermally coupling in a reactive distillation with vapor recompression (VTCR). Economic and controllability aspects were evaluated for all of the configurations. The results show that the processes with energy integration provide significant energy savings compare with the CRD process. The result of the condition number shows that the control properties are better in the intensified process compare with the conventional process. In addition, the TCRD is the process that provides the best control properties and economic benefits.

1. Introduction

Polycarbonate is an important engineering plastic, and it is widely utilized because of its excellent properties in the manufacturing of a wide range of products such as those found in the automotive, consumer electronics, and packaging industries. In recent decades, significant research has been devoted to the search for environmentally friendly processes and new routes to produce polycarbonate; these processes are free from highly toxic compounds, e.g. phosgene and chlorine, found in the phosgene process for polycarbonate manufacturing. One of the most relevant green routes involves the reaction between dimethyl carbonate (DMC) and phenol to carry out the transformation of DMC into diphenyl carbonate (DPC), which reacts with bisphenol-A to produce polycarbonate. However, this route is limited because of low selectivity to DPC, side reactions, and azeotrope formation [1]. Some authors [2,3] have proposed an improved route to produce DPC and methyl acetate (MA) through the reaction between DMC and phenyl acetate (PA) to overcome the limitations mentioned above because the later route avoids azeotrope formation, and it provides a high equilibrium constant value in the reaction between DMC and PA.

In recent years, Process Intensification (PI) has become an attractive research area in academia and industry providing alternatives to develop and implement more efficient, sustainable and safe processes [4,5]. Reactive distillation (RD) is one of the best examples of PI, in RD it is possible to perform the reaction and separation operations simultaneously in a single device, this can offer significant advantages with respect to the traditional process of reaction and separation [6]. One of the most relevant advantages at the operational level of RD is the ability to increase the overall conversion and the selectivity by the continuous removal of

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reaction products from the reaction zone unit; this is particularly useful for reactions where the thermodynamic reaction equilibrium prevents high conversions. Literature offers relevant works that show the advantages that reactive distillation can provide including the potential to reduce capital investment and consumption of utilities [7–9]. In the context of PI, there is room for further development of RD by introducing more complexity in its operation. For example, by implementing heat-integrated reactive separation configurations, improvements in energy efficiency and further advantages in economic terms than conventional reactive distillation can be attained. It has been widely documented [10–13] that in separation configurations without reaction (e.g. heat-integrated configurations, thermally coupled distillation configurations) have proven to provide significant energy savings and higher energy efficiency than conventional separation configurations. However, the full implementation of these schemes has not been entirely achieved because of the operational and controllability issues and the complex control structures of these configurations, even conventional reactive distillation may pose a significant challenge when approaching a suitable control strategy.

Considering all the above, new proposals for improving RD by implementing heat integration should take into account not only economic aspects of the process but also a preliminary evaluation of controllability issues. To study the economic performance and to evaluate the controllability of intensified reactive distillation configurations through the introduction of heat integration in reactive distillation, this work compares four intensified reactive distillation configurations. The alternatives comprise two new reactive distillation configurations involving vapor recompression and thermally coupled vapor recompression, a thermally coupled reactive configuration, and a conventional reactive configuration without heat integration. To the best of our knowledge, there is no a study that involves vapor recompression and reactive distillation to synthesize DPC. The total annual cost and the calculation of a controllability index, namely the condition number for a preliminary evaluation of controllability of these designs were performed.

This paper is organized in the following sections. Section 2 provides the modeling fundamentals, including the chemical kinetics and thermodynamics of the reactive system, the details of the total annual cost calculation (TAC), and the description of the simulation of the intensified reactive distillation configurations. Section 3 contains the methodology utilized for the minimization of the TAC and condition number calculation; Section 4 offers the results of this study, and the conclusions of this work are stated in Section 5.

2. Modeling fundamentals

A comprehensive revision of the fundamentals, constraints, and specifications of the process was necessary. Thus, a proper thermodynamic model that adequately describes phase equilibria of the reactive systems was selected. Also, a suitable kinetic model for the chemical reactions in the process was selected. The simulation of each different reactive configuration was carried out using steady-state equilibrium-stage simulations using Aspen Plus V8.4® software. The raw materials and product specifications used during the simulations were the same for all the intensified reactive configurations under comparison.

2.1. Chemical kinetics

The synthesis of DPC from DMC and PA involves a homogenous catalyst tetra-*n*-butyl orthotitanate, the reaction has a two-step reaction that takes place through formation of the intermediate, MPC. The first step is the transesterification of DMC and PA to the intermediate Methyl Phenyl Carbonate (MPC) and the by-product MA as in Equation (1). Two possible routes exist for the second step: The transesterification of MPC and PA to DPC and MA (See Equation (2)) or the disproportion of MPC yielding DPC and DMC as in Equation (3):

$$DMC + PA \rightleftarrows MPC + MA \tag{1}$$

$$MPC + PA \rightleftarrows DPC + MA \tag{2}$$

$$2MPC \rightleftarrows DPC + DMC \tag{3}$$

The overall reaction is defined:

$$DMC + 2PA \rightleftarrows DPC + 2MA \tag{4}$$

The rate expressions for the reversible reactions of Equations (1)–(3) are respectively as follows:

$$r_1 = k_1 C_{PA} C_{DMC} - k_{-1} C_{MPC} C_{MA} \tag{5}$$

$$r_2 = k_2 C_{PA} C_{MPC} - k_{-2} C_{DPC} C_{MA} \tag{6}$$

$$r_3 = k_3 C_{MPC}^2 - k_{-3} C_{DPC} C_{DMC} \tag{7}$$

The kinetic constants of the three reversible reactions are related in Equation (8).

$$\frac{k_2}{k_{-2}} = \frac{k_1}{k_{-1}} \cdot \frac{k_3}{k_{-3}} \tag{8}$$

Table 1 shows the kinetic parameters that fit with the Arrhenius Equation, this data consist in the pre exponential factor k_0 and activation energy E_a, and are necessary to the calculation of kinetic constants k_n in function of the temperature. This data were taken from previous work of Cheng et al. [2].

2.2. Thermodynamics

The reactive system consists of five components, DPC, MPC, PA, DMC, and MA; Yao [14] showed experimentally that the equilibrium liquid-vapor can be fit with the ideal model, due the boiling point temperature difference of any combination of two components in the system is large enough. Therefore the mixture exhibits ideal behavior, which can be represented by an ideal thermodynamic, so an ideal model can be suitable for the estimation of the vapor-liquid equilibrium in this system.

2.3. Total annual cost calculation

In order to objectively compare the different reactive configurations, two relevant aspects were defined in this paper. The first is the process economics, this involves the Total Annual Cost (TAC) calculation; the second aspect is the evaluation of the

Table 1
Kinetic parameters for reaction rate coefficients.

	k_0(m^3/kmol s)	E_a(kJ/kmol)
k_1	135	5.42×10^4
k_{-1}	52	5.49×10^4
k_2	1210	6.15×10^4
k_{-2}	611	5.62×10^4
k_3	8.20×10^4	7.68×10^4
k_{-3}	1.09×10^5	7.08×10^4

configurations controllability through the singular value decomposition and the condition number calculation. The evaluation of the controllability is carried out after obtaining the reactive configurations with the minimum TAC. The implemented optimization procedure varied the designs parameters to minimize the TAC of VRRD and VTCR. For example, the number of total stages, the number of stages in the rectifying, the stripping, and reactive zone, and the feed location of each column among others.

The Total Annual Cost of each intensified reactive distillation configuration has been estimated as indicated in Equation (9):

$$\mathrm{TAC} = \frac{\text{Capital cost}}{\text{Time of investment}} + \text{Operating cost} \tag{9}$$

The capital cost of each reactive configuration was calculated by using the modular method [15,16], the capital cost includes the costs of distillation columns, trays, heat exchangers, and compressors. The parameters and equations to calculate the cost can be found in the publication by Turton et al. [17] Carbon steel was the assumed construction material for all the equipment, and the time of investment was considered to be ten years. The operating cost includes cooling and heating utilities, and 8400 h of yearly operation for each sequence. Furthermore, three utilities have been considered: low-pressure steam (6 bar, 87 psia, 160 °C/320 °F) with a cost of $ 7.78/GJ, electricity with a cost of $ 16.8/GJ, and cooling water received at 20 °C and returned to 30 °C with a unit cost of $ 0.72/GJ [18].

2.4. *Simulation of reactive distillation processes*

The simulation in this work was carried out in the software Aspen Plus® the Ideal base method for property estimation in the process was selected. The modulus Radfrac® was used to simulate the processes studied in this work, due this modulus contains a rigorous model with the complete set of MESH equations required to phase equilibrium calculations.

2.4.1. *Conventional reactive distillation CRD*

Fig. 1 shows the conventional reactive distillation configuration; it consists of a reactive distillation column, RDC and a separation column, RC. This configuration has been taken from the work reported by Cheng et al. [2], and a brief description of this the reactive distillation configuration is provided here; there are two zones in RDC: The rectifying zone and the reactive zone. The high-boiling reactant PA was fed at the top of the reactive zone whereas the DMC reactant was fed at the bottom of the reactive zone, the feed rate of the reactants PA and DMC were 10 kmol/h and 5.06 kmol/h respectively. A recirculation stream of DMC was fed to the RDC column in onder to create an excess of DMC and increase the reaction conversion of PA. The homogenous catalyst tetra-*n*-butyl orthotitanate were fed near on top of the RDC column in the same tray that PA, due the catalyst al PA were fed in the same tray the reaction a rectification zones are defined by the localization of PA feed tray with respect to the total stages in the RDC column.

The products MA, MPC, and DPC were produced in the reaction zone. The purity required for DPC is 99.5 mol% in the RC column is separated a mixtures that contain mostly DMC and MA and the purity required in this second column is 99.5 mol% of MA on the top and 99.5mol% of DMC by the bottom. The reactive column, RDC, and separation column, RC, were both operated at 1 atm. In the RDC column, two kinds of variables were defined: design variables and operating variables. The design variables included the total number of trays and the PA and DMC feed stage locations. The number of trays in the rectifying zone was determined from the top of RDC to the feed tray of PA reactant, the number of trays in the stripping zone of RDC was determined from the feed tray of DMC to the bottom of RDC. The total number of stages in the reactive zone was determined by the total number of stages that exist from PA feed tray to DMC feed tray.

The operating variables included the reflux ratio, the reboiler duty, and the DMC recycle flow rate. The variation of the reflux ratio was carried out to ensure that the PA reaction conversion exceeded 99.5 mol%, and the reboiler duty was also varied in order and to achieve the molar purity specification of DPC at the bottom of the column. In the separation column, RC, the design variables were the total number of stages and the feed stage; the operation variables were the reflux ratio and the reboiler duty. In this column, the reflux ratio was varied to achieve the MA purity at the top of the column whereas the reboiler duty was adjusted to ensure the DMC purity of the at the bottom tray of the column.

2.4.2. *Thermally coupled reactive distillation TCRD*

Fig. 2 shows thermally coupled reactive distillation configuration. It has also been taken from the paper by Cheng et al. [2] The configuration that involves thermally coupling between the RDC and RC uses the vapor stream from the top of RDC and directly connects to RC and a liquid stream from RC that connects to the top of RDC to eliminate the condenser of RDC. In this configuration, the reflux ratio of RC was manipulated to achieve the purity of MA at the top of RC, and the reboiler duty of RC was adjusted to achieve the purity of the DMC stream that recirculates to RDC. In this way, the design variables and the operation variables for this configuration were as follows: In RDC, the design variables included the total number of trays, the stage locations of PA and DMC. The operation variables included the reboiler duty and the DMC recycled flow rate. In RC, the design variables included the total number of stages and the feed stage of vapor and liquid interconnection streams, whereas the operation variables were the reflux ratio, the reboiler duty, and the liquid stream flow rate.

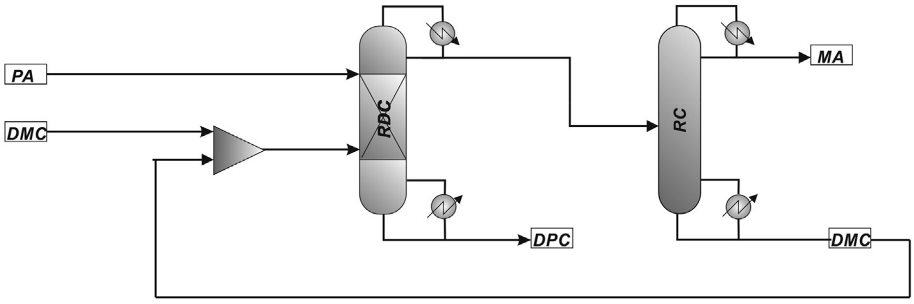

Fig. 1. Conventional reactive distillation configuration for the synthesis of DPC.

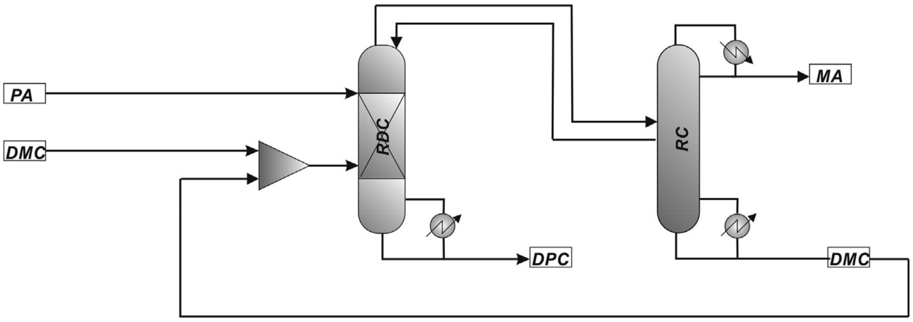

Fig. 2. Thermally coupled reactive distillation configuration for the synthesis of DPC.

2.4.3. Vapor recompression reactive distillation VRRD

The vapor recompression technology, VRT, has not been fully developed in intensified systems such as reactive distillation columns. This technology has been mostly utilized in conventional separation systems. The studies that adopt VRT have stated that vapor recompression technology can provide significant energy savings compared with systems without VRT. In particular, the processes that are highly favored in energy savings and increment in the energy efficiency are those where the components involved in the processes exhibit close boiling point mixtures [19–22]. Typically, the VRT uses a compressor in which electrical energy is converted into mechanical work to upgrade the enthalpy of a vapor stream by increasing its pressure and temperature; this stream can provide its latent heat to be used as the only heating source or as an auxiliary heating source. Thus, heat integration is possible.

The use of thermally coupling between streams in combination with the addition of a compressor through VRT can be challenging and can increase the complexity of reactive distillation configurations. However, it can also offer the possibility to establish the tradeoffs between the economics and the operational aspects of the process, for example, the utilization of a compressor implies a significant investment of capital, but it can attain important energy savings that can be translated into the reduction of operative costs. In addition to economic and energy criteria, the importance of the controllability assessment of these intensified systems must not be neglected. Two new vapor recompression configurations are introduced to implement VRT in reactive distillation for synthesizing DPC, the first of them is explained in this section. The methodology to the simulation of VRRD and TCRD processes were taken and adapted of a previous work of Alcantara-Avila et al. [23].

Fig. 3 shows the proposed vapor recompression reactive distillation configuration, VRRD, for synthesizing DPC in this work. The compressor utilized in this configuration is an isentropic and rotary type compressor; it has been assumed that the isentropic efficiency of this device is 0.8, a temperature difference of 10 K is assumed between the recompressed overhead vapor and the cold streams in order to have adequate temperature gradient to heat transfer [24]. The conceptual design of the vapor recompression configuration and the simulation were executed in Aspen Plus V8.4®, a distillation module in commercial process simulators does not have vapor recompression as a possibility. Thus, the simulation of vapor recompression part is executed separately from the main part. A detailed explanation of the simulation procedure for VRRD is given below.

The simulation procedure for VRRD was:

1. Fix the product specifications, the number of total stages of RDC and RC, feed stages of reactants and operating pressure in both columns.
2. Execute rigorous simulations in RadFrac® for the given conditions in step 1.
3. Obtain the reboiler duty of RC (Q_{RC}) from the rigorous simulation results. Up to step 3, the simulation for VRRD is completed. The procedure for the simulation of the vapor recompression part continues as follows:
4. Drag a pseudo stream that leaves the RDC column from first stage as vapor and connect it to the compressor. Then connect the stream leaving the compressor to the heat exchanger. The pseudo stream is only used in order to carry out the energy balances between Q_{VR} and Q_{RC} in a simplified way, therefore the effects of the complex interconnections among the columns and the streams are avoided during the simulation.
5. Set the temperature of the stream leaving the heat exchanger (T_{Out}^{VR}), which must be higher than that of the stream entering the reboiler of RC (T_{Qin}^{RC}).

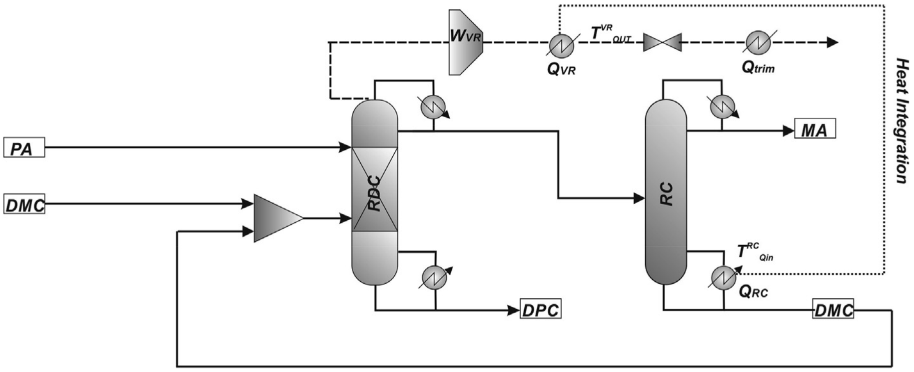

Fig. 3. Vapor recompression reactive distillation configuration for the synthesis of DPC.

6. Set a new design specification [25], which satisfies the energy balance $Q_{VR} - Q_{RC} = 0$ by varying the compressor outlet pressure (P_{Out}^{VR}).
7. Calculate the resulting compressor work duty (W_{VR}) and the heat exchanger duty (Q_{VR}).

The procedure until step 7 explains the methodology simulation for VRRD and the vapor recompression part. However, the stream leaving the heat exchanger Q_{VR} becomes a vapor-liquid mixture when depressurized. In such case, a trim condenser,Q_{Trim}, is necessary to send this stream to the RC column as a saturated liquid. In Fig. 3, the thick dotted line denotes the pseudo stream utilized for simulating the vapor recompression part in VRRD.

2.4.4. *Vapor recompression and thermally coupled reactive distillation VTCR*

Fig. 4 shows the proposed vapor recompression and thermally coupled reactive distillation configuration, VTCR. In this configuration, a vapor stream from the top of RDC column is directly compressed in order to realize heat integration between the RDC and the separation column, RC. The way to implement heat integration in this reactive configuration, and to provide the required reboiler duty in the separation column through the work of the compressor, is carried out through the adjustment of the pressure in the compressor until Q_{VR} is equal to Q_{RC}.

The procedure for the rigorous simulation of VTCR was:

1. Fix the product specifications, the number of total stages of RDC and RC, operating pressure in both columns, feed stages of reactants, feed stages of the liquid stream and vapor stream in RC.
2. Drag a vapor stream that leaves the RDC column from stage 1 and connect it to the compressor. Then connect the stream leaving the compressor to the heat exchanger and connect the stream leaving the heat exchanger to an expansion valve, finally connect this stream to RC.
3. Execute rigorous simulations in RadFrac® for the given conditions in step 1 and the vapor recompression in step 2.
4. Obtain the reboiler duty of RC (Q_{RC}), compressor work duty (W_{VR}) and the heat exchanger duty (Q_{VR}) from the rigorous simulation results.
5. Set the temperature of the stream leaving the heat exchanger (T_{Out}^{VR}), which must be higher than that of the stream entering the reboiler of RC (T_{Qin}^{RC}).
6. Set a new design specification [25] until satisfying the energy balance $Q_{VR} - Q_{RC} = 0$ by varying the compressor outlet pressure (P_{Out}^{VR}).
7. Calculate the resulting compressor work duty (W_{VR}) and the heat exchanger duty (Q_{VR}).

The procedure from steps 1 to 7 explains the methodology simulation for VTCR. The stream leaving the heat exchanger Q_{VR} needs to be expanded to increase its vapor fraction. In such case, an expansion valve is necessary to send this stream to the RC column as vapor feed.

3. Methodology

Several studies of control properties using the condition number have been reported [26–28] on cases where only the minimization of TAC or energy consumption have been approached, as these studies provide important information of the controllability around operating nominal conditions, for this reason this methodology is adequate for a first study based in control properties. Although it is true, the ideal strategy would be carry out this analysis of TAC and control properties simultaneously, the high mathematical complex make no easy the implementation of a simultaneous analysis, some works like the presented by Vazquez-Castillo et al. [29] integrate this simultaneous analysis.

3.1. *Minimization of TAC in the reactive processes*

In this work, the conventional reactive distillation configuration has been firstly optimized in order to achieve the minimum TAC. In the conventional reactive distillation configuration, there were four degrees of freedom in RDC: number of total stages, the PA and DMC feed stage locations, and DMC recycled flow rate, and two degrees of freedom in RC: number of total stages and feed stage location. Therefore, a total of six variables can be manipulated to achieve the minimum TAC of the conventional reactive distillation configuration. Fig. 5 displays the flowchart of the procedure to obtain the minimum TAC of the conventional reactive distillation configuration; the steps are as follows:

Step 1. Give the flow rate of DMC, F_{DMC}.
Step 2. Give the number of total stages of RDC, NT_{RDC}.
Step 3. Give the feed stage of Phenyl Acetate, NF_{PA}.
Step 4. Give the feed stage of DMC, NF_{DMC}
Step 5. Adjust the reflux ratio of RDC, R_{RDC}, and reboiler duty of RDC, Q_{RDC}, until achieving the PA reaction conversion and DPC product specification. Then calculate the TAC of RDC.
Step 6. Go back to step 4 and repeat step 5 until the minimum TAC of RDC is found.

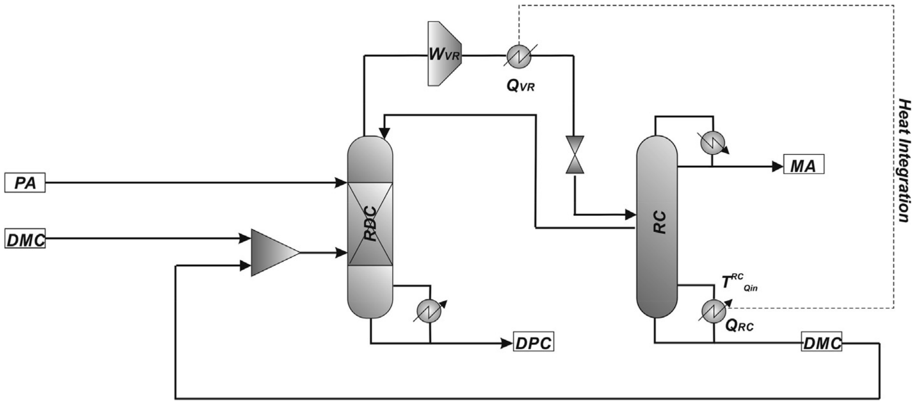

Fig. 4. Vapor recompression and thermally coupled reactive distillation configuration for the synthesis of DPC.

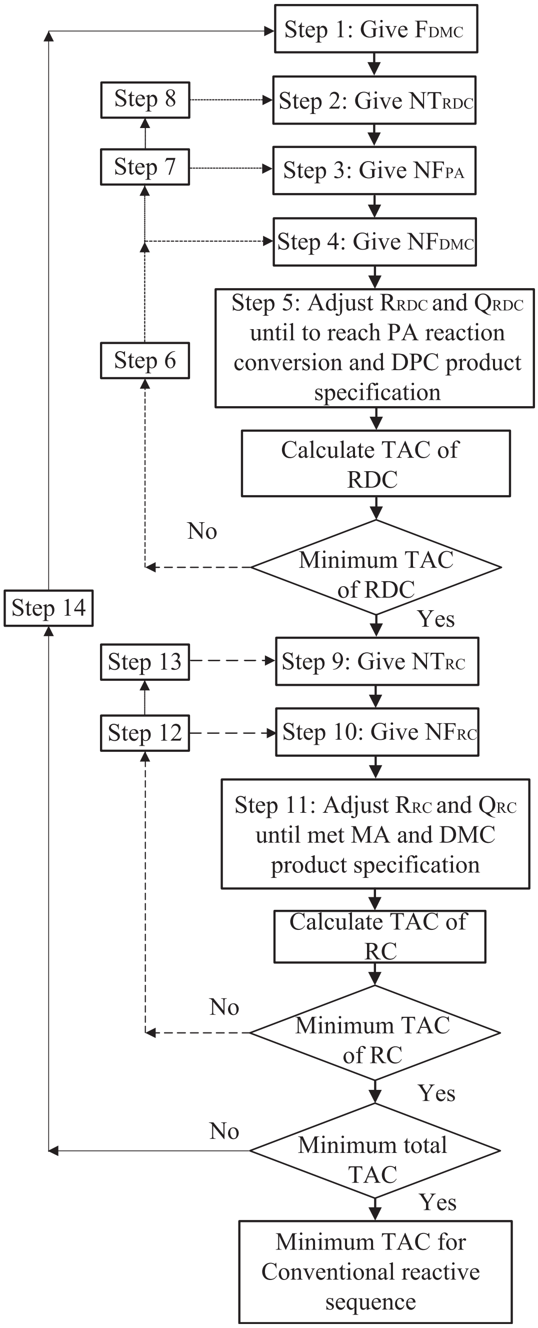

Fig. 5. Flowchart of the procedure to achieve minimum TAC in CRD.

Step 7. Go back to step 3 and repeat steps 4 and 5 until the minimum TAC of RDC is found.
Step 8. Go back to step 2 and repeat steps 3–5 until the minimum TAC of the RDC is found.
Step 9. Give the number of total stages of RC, NT_{RC}.
Step 10. Give the feed stage of RC, NF_{RC}.
Step 11. Adjust the reflux ratio of RC, R_{RC} and reboiler duty of RC, Q_{RC}, until meeting the MA and DMC product specification. Then calculate the TAC of RC.
Step 12. Go back to step 10 and repeat step 11 until the minimum TAC of RC is found.
Step 13. Go back to step 9 and repeat steps 10 and 11 until the minimum TAC of RC is found.
Step 14. Go back to step 1 and repeat the steps for minimizing the TAC of the RD and RC, respectively, until the total TAC is the minimum.

3.2. Evaluation of controllability of reactive distillation configurations

The condition number has been established as the index to evaluate the control properties of the intensified reactive configurations; the condition number has been utilized in qualitative assessments of the control properties of a design [30–33]. The calculation of the condition number has been carried out through the singular value decomposition, SVD, of the relative gain matrix of the design in the nominal point, e.g. the design that had achieved the minimum TAC. In the reactive distillation process for the synthesis of DPC, there are three variables to be controlled: the mole purities of Diphenyl Carbonate (DPC), Methyl Acetate (MA), and Dimethyl Carbonate (DMC). Also, three manipulated variables: the reboiler duty of the reactive column (Reboiler Duty RDC), the reflux ratio of the separation column (Reflux Ratio RC) and the reboiler duty of the separation column (Reboiler Duty RC). It was defined that the DPC mole purity is controlled by the reboiler duty of RDC, whereas the MA mole purity is controlled by the reflux ratio of RC, and the DMC mole purity is controlled by the reboiler duty of RC. The singular value decomposition is a study that provides useful information on the stability of a multivariable system; it is applied on the inputs and outputs of a multivariable system in such a way that the changes in the inputs and the corresponding variations on the outputs are related through the transfer function matrix [34,35]. In the case of the reactive distillation configurations the SVD have been successfully implemented in order to evaluate the dynamic open loop behavior of these systems [36,37], in order to carry out the SVD decomposition of the reactive configurations under comparison in this paper, it has been defined that the changes in the nominal values of molar purities should be related with the changes of the manipulated variables through the respective transfer function, and in this study the manipulated variables were stablished according to the traditional arrangement to the control of distillation columns reported by Luyben [25] and other authors [26,27].

Previous to the calculation of the condition number, the singular values are obtained. For example, consider the mathematical expression in Equation (10), which represents the relative gain matrix of a linear system

$$K = W\sum V^T \tag{10}$$

where W and V are unitary matrixes and Σ is a matrix whose diagonal elements are the singular values, σ. Assuming that K is not singular, then the condition number of K, γ is a positive number which relates the minimum singular value, σ_* and the maximum singular value, σ^* being none of these two zero, the condition number, γ, can be estimated as in Equation (11):

$$\gamma = \frac{\sigma^*}{\sigma_*} \tag{11}$$

Large values of σ_* and small values of σ^* are desirable so that the process may assimilate the perturbations without system destabilization [30]. Therefore, low values of the condition number in a design are preferable over high values. In this study, the condition number of the relative gain matrix obtained in an open loop control strategy for each design is estimated by generating the relative gain matrix in a nominal state of each intensified reactive configuration, the elements of this matrix are calculated through the introduction of perturbations in the manipulated variables. The magnitude of the perturbations was set as a 1% negative change in the values of the manipulated variables in the nominal state, this negative change in the perturbation is due to the high purity of 99.5 mol%, because it does not allow positive perturbations, which could fall into a singularity with a purity of 100 mol%. The level of these perturbations is low enough, so that it is assumed that the response of the system can be approximated as a first order response. Equation (12) shows the relative gain matrix for the conventional reactive distillation configuration under comparison.

$$\begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix} = \begin{bmatrix} \dfrac{\left(x_{DPC}^{Q_{RDC}} - x_{DPC}^{sp}\right)}{\frac{1}{2}p} & \dfrac{\left(x_{DPC}^{R_{RC}} - x_{DPC}^{sp}\right)}{\frac{1}{2}p} & \dfrac{\left(x_{DPC}^{Q_{RC}} - x_{DPC}^{sp}\right)}{\frac{1}{2}p} \\ \dfrac{\left(x_{MA}^{Q_{RDC}} - x_{MA}^{sp}\right)}{\frac{1}{2}p} & \dfrac{\left(x_{MA}^{R_{RC}} - x_{MA}^{sp}\right)}{\frac{1}{2}p} & \dfrac{\left(x_{MA}^{Q_{RC}} - x_{MA}^{sp}\right)}{\frac{1}{2}p} \\ \dfrac{\left(x_{DMC}^{Q_{RDC}} - x_{DMC}^{sp}\right)}{\frac{1}{2}p} & \dfrac{\left(x_{DMC}^{R_{RC}} - x_{DMC}^{sp}\right)}{\frac{1}{2}p} & \dfrac{\left(x_{DMC}^{Q_{RC}} - x_{DMC}^{sp}\right)}{\frac{1}{2}p} \end{bmatrix} \tag{12}$$

The elements on the left side of Equation (12), K_{ij}, are the elements of the relative gain matrix. Moreover, the elements of the first row on the right side correspond to the differences in the molar purity of the component DPC in the nominal state, x_{DPC}^{sp}, and the molar purities after that the perturbations, p, are introduced. $x_{DPC}^{Q_{RDC}}$ is the molar purity of DPC after the perturbation of the reboiler duty in the reactive column, $x_{DPC}^{R_{RC}}$ is the molar purity of DPC after the perturbation of the reflux ratio in the separation column, $x_{DPC}^{Q_{RC}}$ is the molar purity of DPC after the perturbation of the reboiler duty of the separation column. Fig. 6 exhibits the procedure utilized for the calculation of the relative gain matrix elements for the conventional reactive distillation configuration while Fig. 7 shows the values utilized for the calculation of the condition number in this configuration. The values of the controlled variables and manipulated variables are the ones in the nominal state. The values of molar purities of DPC, MA and DMC after that the perturbations are also shown in Fig. 7.

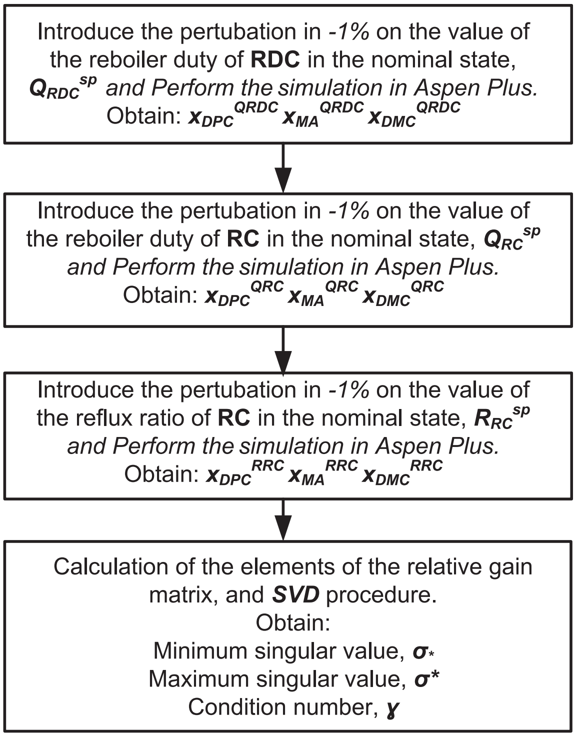

Fig. 6. Procedure for the calculation of the elements of the relative gain matrix of CRD configuration.

One drawback of the singular value decomposition is the fact that the singular values depend on the system of units used. Applying the singular value decomposition to the relative gain matrix will include the effects of such units. Therefore, it is important to use a scaling method to remove this dependency and to provide reliability in the results as well as a physical meaning. Some authors [38,39] have proposed scaling methods for the manipulated variables and the control variables to obtain reliable values. For the reactive distillation configurations in this study, there are three important control variables, which are the molar purities of DPC, MA and DMC. Furthermore, these are naturally bounded between 0 and 1. There are three manipulated variables for each reactive distillation configuration; they are the reboiler duty in the reactive column, the reflux ratio in the separation column and the reboiler duty in the separation column, these manipulated variables have units and are not bounded naturally.

To eliminate the drawback mentioned above, it is proposed to limit the manipulated variables considering that the maximum aperture that can reach the control valves is twice the nominal value of the steady state; therefore, in principle, the valves are open to 50%. This value of valve opening implies that for the relative gain matrix, the step change is implemented in the manipulated variable to be divided by twice the steady state to have the same range of variation in both the closing and opening operations of the control valves. This allows for a physical interpretation to the way of scaling of the manipulated variables, to link the amount of change of the manipulated variables with the magnitude of change of the position of the corresponding valve stem, which can only vary between 0 and 100% open (0 and 1). With this form of scaling it is achieved simultaneously dimensionless standardization and manipulated variables, the term $\frac{1}{2}p$ has been included in Equation (12) to achieve this purpose.

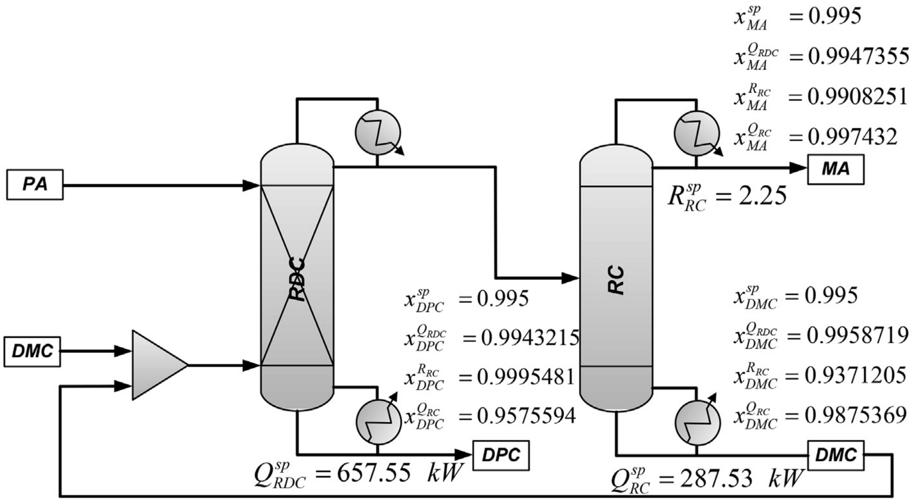

Fig. 7. Values of the manipulated variables and the controlled variables of CRD for the calculation of the condition number.

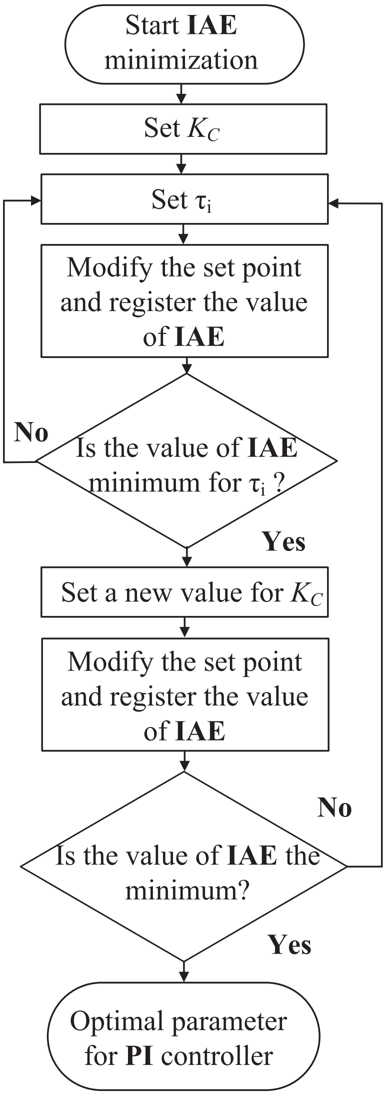

Fig. 8. Flowchart to tunning parameters of the controller.

Finally in order to validate this methodology a study of close loop was carried out. This study is based in the implementation of feedback control with proportional-integral controllers (PI) due this kind of controller is the most used by the industry. The tuning of the parameters of the controllers, gain (K_c) and integral time (τ_i), were realized using the criterion of minimization of integral of absolute error (IAE). Where the IAE is mathematically defined according to Equations (13) and (14) as:

$$IAE = \int_0^\infty |\varepsilon(t)| dt \tag{13}$$

where $\varepsilon(t)$ is the error in the time, which is given by:

$$\varepsilon(t) = y_d - y(t) \tag{14}$$

Where y_d is the value of the purity in set point and $y(t)$ is the value of the purity in the time.

This methodology has been reported by some authors [40,41], and it provides a good tuning and fast response of the controllers where the process presents any perturbation. The parameters obtained inside the tuning process, such as the controller gains and integral time are within the industrial values reported by Luyben [42]. The methodology of tuning is showed in Fig. 8. The Aspen Dynamics® simulator was used in this study because of the easy with which the rigorous simulation can be exported from Aspen Plus to Aspen Dynamics®. The control loops are the same that the manipulate variables, this means that DPC purity is controlled by Reboiler duty of RDC column and MA purity by reflux ratio of RC column. Finally, perturbations of 1% in the feeds of DMC and PA was made in order to see the dynamic responds in the DPC stream with the tuned parameters to the controller previously obtained.

4. Results

This section offers the results for all the reactive distillation configurations under comparison. It is important to stress that the values of the design variables for the optimized conventional reactive distillation, CRD, and Thermally coupled reactive distillation, TCRD, have been taken from the work by Cheng et al. [2] and adapted into this work to compare them with the VRRD and VTCR configurations. The fixed purities of the products were defined as follows: 99.5 mol% for DPC, 99.5 mol% DMC, 99.5 mol% MA. The TAC and the condition number of all the reactive distillation configurations were calculated with the design variables shown in Table 2.

Table 2
Design variables of the reactive distillation configurations to synthesize DPC.

Configuration	CRD		TCRD		VRRD		VTCR	
	RDC	RC	RDC	RC	RDC	RC	RDC	RC
Columns Topology								
Number of stages	80	25	76	25	80	25	76	25
Reactive stages	4–80	–	4–76	–	4–80	–	4–76	–
Feed stage								
DMC Stream	74	–	70	–	74	–	70	–
PA Stream	4	–	4	–	4	–	4	–
Liquid stream	–	11	–	–	–	11	–	–
Vapor stream	–	–	–	11	–	–	–	11
Specifications								
Reflux ratio	1.25	2.25	–	9.51	1.25	2.5	–	7.9
Top pressure, atm	1.0	1.0	1.1	1.0	1.0	1.0	1.1	1.0
Diameter, m	1.06	0.46	1.00	0.81	1.10	0.47	1	0.74
Reboiler duty, kW	657.55	287.53	610.55	184.25	735.84	–	615.57	–
Compressor Power, kW	–	–	–	–	31.1		38.13	
Discharge pressure, atm	–	–	–	–	2		1.75	
Tray hold up, l	531.02	–	531.02	–	531.02	–	530.5	–
Streams Mole Flow, kmol h^{-1}								
PA	10	–	10	–	10	–	10	–
DMC	5.057	–	5.057	–	5.057	–	5.057	–
$DMC_{Recycle}$	26.78	–	29.083	–	30.35	–	29.48	–
MA	–	10.02	–	10.04	–	9.992	–	9.995
DPC	5.02	–	5.01	–	4.988	–	4.987	–
TOP_{RDC}	36.83	–	77.13	–	40.56	–	77.65	–
In. Steam	–	–	–	77.13	–	–	–	77.65
In. Liquid	–	–	38	–	–	40.55	38.13	–
Temperature of DPC stream, °C	316.53	–	319.18	–	316.53	–	319.18	–
Temperature of MA stream, °C	–	57.52	–	57.15	–	57.15	–	57.15
Temperature of DMC stream, °C	–	93.67	–	93.18	–	93.67	–	93.18
Purity of Products (mol. fraction)								
Purity of DPC	0.995	–	0.9965	–	0.995	–	0.9965	–
Purity of MA	–	0.995	–	0.994	–	0.9939	–	0.9939

Table 3
TAC, energy consumption and condition number of reactive distillation configurations to synthesize DPC.

Configuration	TAC $/y	Energy consumption kW	Condition number γ
CRD	899,317.82	945.08	2179.96
TCRD	786,435.71	794.8	45.32
VRRD	1,035,794.6	766.94	284.17
VTCR	887,478.64	653.7	164.5

Without loss of generality, it has been established in this work that the same number of stages and the feed stages of reactants in RDC and RC of CRD are utilized in VRRD, and in a similar way the same number of stages of TCRD are utilized in VTCR.

Very close values of reflux ratios in both columns RDC and RC were obtained in the reactive configurations VRRD and CRD. The energy consumption in the reboiler of RDC is larger than the energy required in RDC of the CRD configuration. However, with the vapor recompression implementation, it is possible to eliminate a reboiler

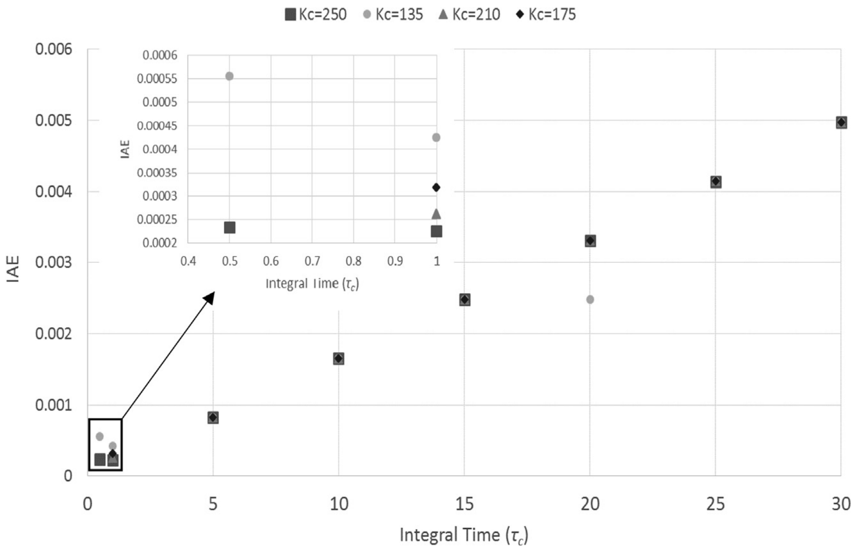

Fig. 9. Tuning of controller parameters to DPC loop of TCRD process.

Table 4
Parameters of PI controllers to CRD and TCRD sequences.

	CRD		TCRD	
	DPC loop	MA loop	DPC loop	MA loop
Integral Time (τ_c)	9	16	1	37.5
Gain (K_c)	250	14	250	125
IAE	1.52E-03	2.89E-03	2.25335E-04	6.22E-03

of RC in VRRD. Thus, the energy for RC is provided by the work of the compressor, the pressure of discharge of this device was 2 atm. For the TCRD and VTCR configurations, it is possible to eliminate the condenser of the reactive column, RDC, through the thermally coupling. The reflux ratio of the separation column in TCRD is slightly larger than the reflux ratio of the separation column in VTCR, and the reflux ratios of VTCR and TCRD are larger than the reflux ratios of the separation columns in CRD and VRRD. The previous situation results in the increase in the diameters of the separation columns in TCRD and VTCR in comparison with the diameters of the separation columns in VRRD and CRD, respectively. With the vapor recompression and thermally coupling in VTCR, it is possible to eliminate the reboiler of RC column. Thus, the energy necessary for the separation column is provided by the work of the compressor. The energy required for the compressor in the VTCR configuration was set as 38.13 kW, and the discharge pressure was 1.75 atm.

Table 3 provides the summary of the results for the reactive distillation configurations regarding TAC, energy consumption, and condition number. The VRRD configuration presents the highest TAC, $1,035,794.6 per year, of all the configurations, the CRD configuration has a TAC of $899,317.82 per year, whereas VTCR presents a TAC of $887,478.64 per year. The configuration with the lowest TAC is the TCRD configuration with $786,435.71 per year. The results of the TAC in these reactive distillation configurations can be explained in terms of the capital cost investment that represents the purchase of the compressor in the VRRD and VTCR reactive configurations. Despite the energy savings in the VTCR and VRRD, the TAC in VRRD was higher than that in CRD, the best reactive configuration in terms of the TAC was the thermally coupled reactive distillation configuration.

The reactive distillation configuration with the lowest energy consumption is the VTCR, with 653.7 kW; the VRRD has a consumption of 766.94 kW, thermally coupled reactive distillation presents an energy consumption of 794.8 kW, and the configuration with the highest energy consumption is the conventional

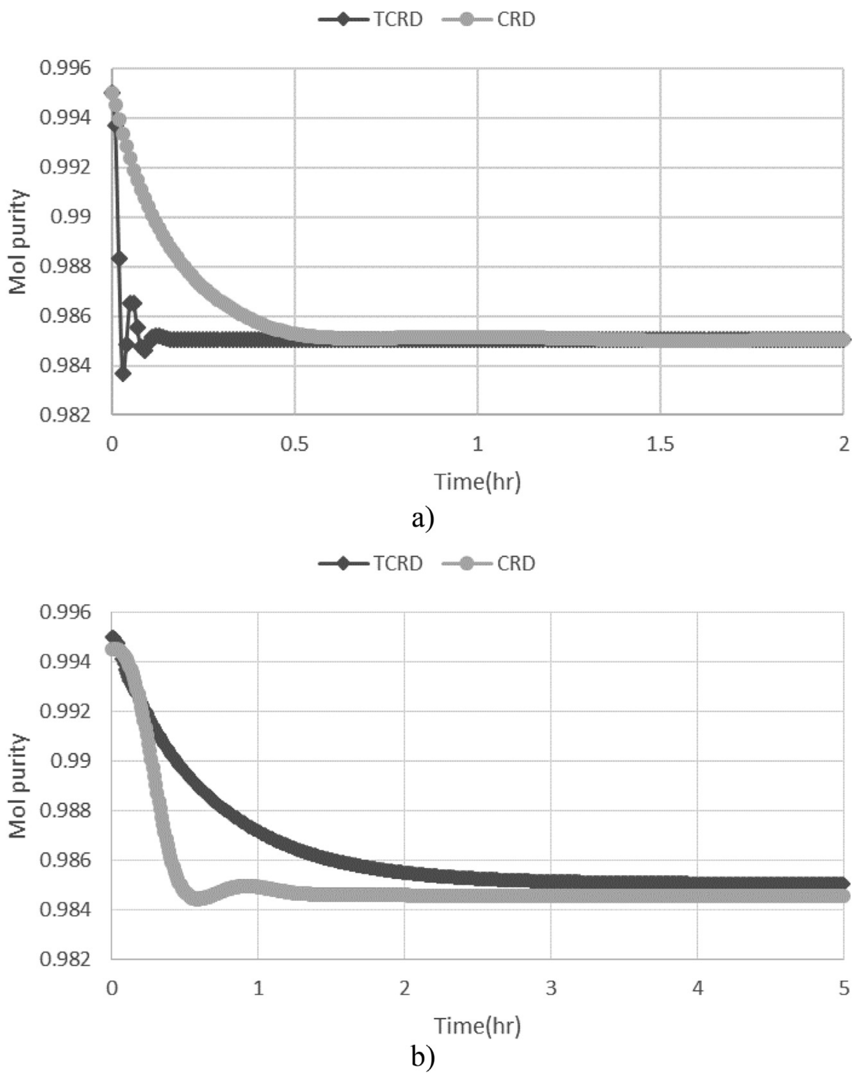

Fig. 10. a) Dynamic response to DPC loop. b) Dynamic response to MA loop.

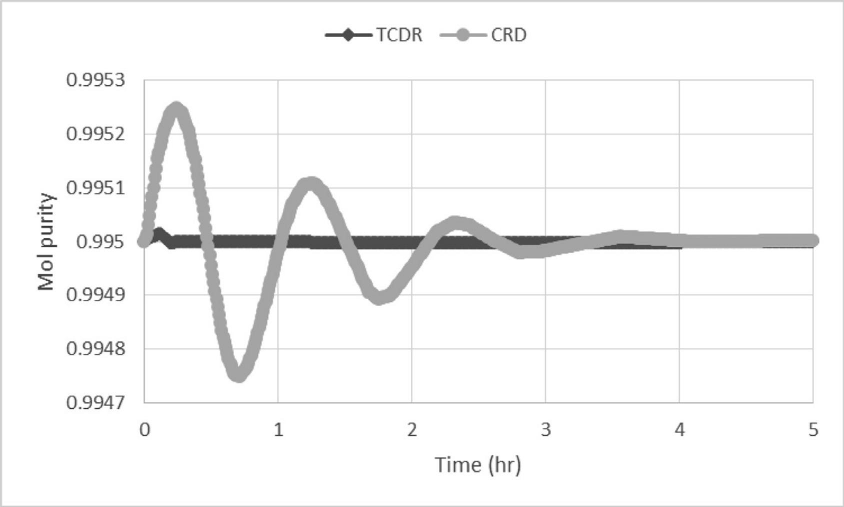

Fig. 11. Perturbation in PA feed dynamic response to DPC loop.

reactive distillation configuration with 945.08 kW. As expected, the vapor recompression implementation provided significant energy savings. For example, the VTCR configuration provided 30.8% energy savings with respect to the conventional reactive configuration, whereas the VRRD offered 18.8% energy savings with respect to CRD. Thermally coupled reactive distillation configuration also presented energy savings of 15.9% with respect to CRD.

The evaluation of controllability in the reactive distillation configurations through the condition number calculation offers a good assessment of the operation of these complex intensified reaction-separation schemes; the results in this work show that the TCRD configuration offers the best control properties with the lowest condition number. On the other hand, the configurations with vapor recompression also offer the intermediate values for the condition number. Significant differences are found between the condition number values of these configurations, for example, VTCR has a value of the condition number lower than VRRD. The reactive distillation configuration with the worst control properties is the conventional reactive configuration.

In the obtained results of the evaluation of controllability, the heat-integrated reaction-separation schemes showed better control properties than the conventional reactive distillation configuration. The results indicate that there is not degradation of the control properties due complex topology in these processes, Several works where the interconnection and recycle streams can provide good control properties has been documented in some works that studied separations systems without chemical reactions [43,44]. This fact is attributed to the interconnections of liquid and vapor in the columns, and because the remixing of streams is avoided. In this way, the thermally coupled configuration is less unstable because of the gradients in the concentration of species in the mixture tend to be minimized in some regions of the columns.

As the last point, in order to validate the results of a singular value decomposition analysis, the dynamic responses of CRD and TCRD are presented. These results are offered due the CRD and TCRD presented the worst and the best condition number respectively. The results of the controller tuning for the loop of DPC of TCRD sequence is showed in Fig. 9, the results tuning for the other loops are analogous. The values of the RDC and MA loops are showed in Table 4, likewise the dynamic response are presented in Fig. 10. As can be seen in Table 4 the values of IAE are lower in the TCRD sequence indicating that the dynamic responses or TCRD presents smaller variations with respect to the set point, validating in this way the results predicted by the condition number.

Perturbations in the PA feed was realized as representative example of the dynamic response with the values for the controller previously obtained by the tuning method, the dynamic responses of the main product are showed in Fig. 11. In order to determinate which response is better, the IAE was used, the values of IAE are reported in Table 5. As can be seen in Fig. 11 the dynamic response to CRD process present more oscillations and it is reflected in a greater value of IAE reported in Table 5 with respect to TCRD, these results are consistent with the singular value decomposition where it was found that TCRD had better control properties.

Table 5
IAE values of DPC loop for perturbations on DMC and PA feed.

	IAE to CRD	IAE to TCRD
Perturbation on PA feed	2.69E-04	6.11E-06

5. Conclusions

In this work four reactive distillation configurations for the synthesis of DPC were compared in terms of the total annual cost and the evaluation of controllability through the condition number calculation. Two new reactive distillation configuration involving vapor recompression, VRRD, and vapor recompression and thermally coupling, VTCR, were presented and compared with a conventional reactive distillation configuration, CRD, and a thermally coupling reactive distillation configuration, TCRD. On the basis of the results, significant energy savings were obtained from the vapor recompression implementation in reactive distillation for the DPC synthesis, the VTCR configuration provided 30.8% of energy savings with respect to the CRD configuration, whereas VRRD offered an 18.8% of energy savings compared with CRD. The TCRD configuration also offered energy savings of 15.9% respect to the conventional reactive configuration. The total annual cost of the VTCR and VRRD configurations had increments associated with the purchase of the compressor, and it may be an unappealing motivation for their implementation. TCRD exhibited the minimum TAC of all the reactive distillation configurations. The reactive distillation configurations with heat integration showed better control properties than the conventional reactive configuration; it is important to highlight that the thermally coupled reactive configuration offered the best control properties in all of the reactive distillation configurations. These control properties were validated by the study in close loop for two representative schemes, where the results show that the TCRD presents a lower IAE value compared with the CRD configuration.

Acknowledgements

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Nomenclature

CRD	Conventional reactive distillation
TCRD	Thermally coupled reactive distillation
VRRD	Vapor recompression reactive distillation
VTCR	Vapor recompression and thermally coupled reactive distillation
RDC	Reactive distillation column
RC	Recovery/separation column
TAC	Total Annual Cost
γ	Condition number
σ_*	Minimum singular value
σ^*	Maximum singular value
P	Magnitude of the perturbations on the manipulated variables, −1%
Q_{RDC}^{sp}	Reboiler duty of RDC in the nominal state
R_{RC}^{sp}	Reflux ratio of RC in the nominal state
Q_{RC}^{sp}	Reboiler duty of RC in the nominal state
x_{MA}^{sp}	Molar purity of component MA in the nominal state
$x_{MA}^{Q_{RDC}}$	Molar purity of component MA after the perturbation of the reboiler duty in RDC
$x_{MA}^{R_{RC}}$	Molar purity of component MA after the perturbation of the reflux ratio in RC
$x_{MA}^{Q_{RC}}$	Molar purity of component MA after the perturbation of the reboiler duty in RC
x_{DMC}^{sp}	Molar purity of component DMC in the nominal state
$x_{DMC}^{Q_{RDC}}$	Molar purity of component DMC after the perturbation of the reboiler duty in RDC
$x_{DMC}^{R_{RC}}$	Molar purity of component DMC after the perturbation of the reflux ratio in RC
$x_{DMC}^{Q_{RC}}$	Molar purity of component DMC after the perturbation of the reboiler duty in RC
PI	Proportional-Integral controller
IAE	Integral of absolute error
K_c	Gain of the controller
$\varepsilon(t)$	Error in the time.
y_d	Value of the purity in set point
$y(t)$	is the value of the purity in the time.

References

[1] Tundo P, Trotta F, Moraglio G, Ligorati F. Continuous-flow processes under gas–liquid phase-transfer catalysis (GL-PTC) conditions: the reaction of dialkyl carbonates with phenols, alcohols, and mercaptans. Ind Eng Chem Res 1988;27:1565–71.

[2] Cheng K, Wang SJ, Wong DSH. Steady-state design of thermally coupled reactive distillation process for the synthesis of diphenyl carbonate. Comput Chem Eng 2013;52:262–71.

[3] Tuinstra, H.; Rand, C. L. Process for the preparation of phenyl carbonate or polycarbonates. U. S Patent 5349102. 1994.

[4] Ponce-Ortega JM, Al-Thubaiti MM, El-Halwagi MM. Process intensification: new understanding and systematic approach. Chem Eng Process Process Intensif 2012;53:63–75.

[5] Lutze P, Gani R, Woodley JM. Process intensification: a perspective on process synthesis. Chem Eng Process Process Intensif 2010;49:547–58.

[6] Noeres C, Kenig EY, Górak A. Modelling of reactive separation processes: reactive absorption and reactive distillation. Chem Eng Process Process Intensif 2003;42:157–78.

[7] Stankiewicz A. Reactive separations for process intensification: an industrial perspective. Chem Eng Process Process Intensif 2003;42:137–44.

[8] Wang SJ, Hao-Yeh L, Jui-Hung H, Cheng-Ching Y, Huang HP, Ming-Jer L. Plantwide design of ideal reactive distillation processes with thermal coupling. Ind Eng Chem Res 2010;49:3262–74.

[9] Jan Harmsen G. Reactive distillation: the front-runner of industrial process intensification: a full review of commercial applications, research, scale-up, design and operation. Chem Eng Process Process Intensif 2013;67:111–9.

[10] Triantafyllou C, Smith R. The design and optimization of fully thermally coupled distillation columns. Trans IChemE Part A. Chem Eng Res Des 1992;70:118–24.

[11] Amminudin KA, Smith R, Thong DY-C, Towler GP. Design and optimization of fully thermally coupled distillation columns. Part 1: preliminary Design and Optimization Methodology. Trans IChemE 2001;79:701–15.

[12] Dunnebier G, Pantelides CC. Optimal design of thermally coupled distillation columns. Ind Eng Chem Res 1999;38:162–76.

[13] Agrawal R, Fidkowski ZT. Are thermally coupled distillation columns always thermodynamically more efficient for ternary distillations? Ind Eng Chem Res 1998;37:3444.

[14] Yao CT. VLE and boiling point of binary system of methyl acetate, dimethyl carbonate, phenyl acetate and diphenyl carbonate. Taiwan: I-Shou University; 2012. Diss. Master Thesis.

[15] Guthrie KM. Capital cost estimating. Chem Eng 1969;24(March):114.

[16] Ulrich GD. A guide to chemical engineering process design and economics. New York: Wiley; 1984.

[17] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. Analysis, synthesis and design of chemical process. third ed. USA: Prentice Hall; 2009 [Appendix A].

[18] Luyben WL. Principles and case studies of simultaneous design. USA: Wiley; 2011.

[19] Carta R, Kovacic A, Tola G. Separation of ethylbenzene–xylenes mixtures by distillation: a possible application of the vapour recompression concept. Chem Eng Commun 1982;19:157–65.

[20] Cheng HC, Luyben WL. Heat-integrated distillation columns for ternary separations. Ind Eng Chem Proc Des Dev 1985;24:707–13.

[21] Gao X, Ma Z, Ma J. Application of three-vapor recompression heat-pump concepts to a dimethylformamide–water distillation column for energy savings. Energy Technol 2014;2:250–6.

[22] Enweremadu C, Waheed A, Ojediran J. Parametric study of an ethanol–water distillation column with direct vapour recompression heat pump. Energy sustain Dev 2009;13:96–105.

[23] Alcántara-Avila JR, Gómez-Castro FI, Segovia-Hernández JG, Sotowa KI, Horikawa T. Optimal design of cryogenic distillation columns with side heat pumps for the propylene/propane separation. Chem Eng Process Process Intensif 2014;82:112–22.

[24] Shi L, Huang K, Wang SJ, Yu J, Yuan Y, Chen H, et al. Application of vapor recompression to heterogeneous azeotropic dividing-wall distillation columns. Ind. Eng Chem Res 2015;54(46):11592–609.

[25] Luyben WL. Distillation design and control using ASPEN simulation. USA: Wiley; 2006.

[26] Torres-Ortega CE, Segovia-Hernández JG, Gómez-Castro FI, Hernández S, Bonilla-Petriciolet A, Rong BG, et al. Design, optimization and controllability of an alternative process based on extractive distillation for an ethane–carbon dioxide mixture. Chem Eng Process Process Intensif 2013;74:55–68.

[27] Acosta-Solórzano AD, Guerrero-Farfán O, Ramírez-Márquez C, Gómez-Castro FI, Segovia-Hernández JG, Hernández S, et al. Controllability analysis of distillation sequences for the separation of bio-jet fuel and green diesel fractions. Chem Eng Technol 2016;39(12):2273–83.

[28] Angelina-Martínez AY, Sánchez-Ramírez E, Quiroz-Ramírez JJ, Segovia Hernández JG. Controllability analysis of process alternatives for biobutanol purification. Chem Eng Technol 2015;38(9):1591–8.

[29] Vazquez-Castillo JA, Segovia-Hernandez JG, Ponce-Ortega JM. Multiobjective optimization approach for integrating design and control in multicomponent distillation sequences. Ind. Eng Chem Res 2015;54(49):12320–30.

[30] Lenhoff AM, Morari M. Design of resilient processing plants-1 Process design under consideration of dynamic aspects. Chem Eng Sci 1982;37:245–58.

[31] Skogestad S, Havre K. The use of RGA and condition number as robustness measures. Comput Chem Eng 1996;20:S1005–10.

[32] Youngwoon K, En Sup Yoon ES. A method for improving condition number of chemical processes by sensitivity analysis. Comput Chem Eng 1996;20:S841–6.

[33] Morari M, Grimm W, Oglesby MJ, Prosser ID. Design of resilient processing plants-VII. Design of energy management system for unstable reactors-new insights. Chem Eng Sci 1985;40:187–98.

[34] Klema VC, Laub AJ. The singular value decomposition: its computation and Some Applications. IEEE Trans Automat. Control 1980;25:164–76.

[35] Lau H, Alvarez J, Jensen KF. Synthesis of control structures by singular value analysis: dynamic measures of sensitivity and interaction. AIChE J 1985;31:427–39.

[36] Murrieta-Dueñas R, Gutiérrez-Guerra R, Segovia-Hernández JG, Hernández S.

Analysis of control properties of intensified distillation sequences: reactive and extractive cases. Chem Eng Res Des 2011;89:2215–27.

[37] Ramírez-Márquez C, Sánchez-Ramírez E, Quiroz-Ramírez JJ, Gómez-Castro FI, Ramírez-Corona N, Cervantes-Jauregui JA, et al. Dynamic behavior of a multitasking reactive distillation column for production of silane, dichlorosilane and monochlorosilane. Chem Eng Process Process Intensif 2016;108:125–38.

[38] Lau H, Jensen KF. Evaluation of changeover control policies by singular value analysis-Effects of scaling. AIChE J 1985;31:135–46.

[39] Johnston RD, Barton GW. Structural interaction analysis. Int J Control 1985;41:1005–13.

[40] Acosta-Solórzano AD, Guerrero-Farfán O, Ramírez-Márquez C, Gómez-Castro FI, Segovia-Hernández JG, Hernández S, et al. Controllability analysis of distillation sequences for the separation of bio-jet fuel and green diesel fractions. Chem Eng Technol 2016;39(12):2273–83.

[41] Ramírez-Márquez C, Cabrera-Ruiz J, Segovia-Hernández JG, Hernández S, Errico M, Rong BG. Dynamic behavior of the intensified alternative configurations for quaternary distillation. Chem Eng Process Process Intensif 2016;108:151–63.

[42] Luyben WL. Practical distillation control. New York, USA: Van Nostrand Reinhold; 1992.

[43] Hernández S, Jiménez A. Controllability analysis of thermally coupled distillation systems. Ind Eng Chem Res 1999;38:3957–63.

[44] Kencse H, Mizsey P. Comprehensive process investigation methodology for energy-integrated distillation. Comput Aided Chem Eng 2007;17:883–8.