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Multi-objective optimization involving cost and control properties in reactive distillation processes to produce diphenyl carbonate

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ABSTRACT

Polycarbonate has a very extensive commercial application thanks to its multiple physical properties. The environmental problems associated with the conventional process to obtain polycarbonate by the phosgene route has stimulated the research of intensified schemes as is the case of the reactive distillation for the synthesis of Diphenyl Carbonate (DPC). These intensified processes are complex in their structure because of the several degrees of freedom and are subject to be optimized in terms of crucial criteria such as the cost and the control properties. This work presents the multi-objective optimization involving cost and control properties of four intensified systems configurations to produce DPC: a conventional reactive distillation (CRD), a thermally coupled reactive distillation (TCRD), and two novel configurations which uses vapor recompression technology, a reactive distillation with heat integration (RDHI) through vapor recompression, and a reactive distillation with thermally coupling and heat integration (THRD) through vapor recompression. The results of the multi-objective optimization show that the tray holdups and diameter values of the columns strongly influence the control properties; thus, for large values of the tray holdups and diameters, the control properties were better. The control properties also were influenced by the presence of the interlinking streams in the reactive and separation columns, in particular, the presence of one interlinking stream tend to favor the control properties of a configuration. To close it is important to remark that the TCRD configuration was the most attractive arrangement to be implemented to produce DPC, mainly because the optimized designs showed the best control properties, and also the optimized designs achieved significant energy savings because they did not require electric power.

1. Introduction

Polycarbonate is an important thermoplastic in the chemical industry and very common in daily life; that is because it had excellent optic properties, besides the excellent properties of resistance to heat and electricity. A traditional process involving phosgene, which uses carbon monoxide and chlorine as raw material, produces a huge share in the market production of polycarbonate. Nevertheless, this process involving phosgene comes with a series of environmental problems. Particularly, the highly toxic phosgene is used as a monomer, alongside a huge quantity of methylene chlorine, just as toxic as phosgene, used during the polymerization reaction. This brings as a consequence that during the separation process, a huge quantity of water will be used for phosgene and chlorine separation, this for the phenyl carbonate production. Great efforts have been paid for developing new routes for the production of polycarbonate that can overcome the above-mentioned environmental difficulties (Cheng et al., 2013).

The creation of a *'green route'* for polycarbonate production, is the dimethyl carbonate reaction to produce diphenyl carbonate (DPC) which then reacts with bisphenol-A and as a result, it gives the polycarbonate. There are several pathways for DPC production, the one used by Tuinstra and Rand (1994) is the more promising of all, which consist of an esterification reaction between dimethyl carbonate (DMC) and phenyl acetate (PA) giving DPC and methyl acetate (MA) as products, the reaction is showed in Eq. (1).

$$DMC + PA \rightleftarrows DPC + 2MA \quad (1)$$

The advantages in using this reaction are:

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Nomenclature

CRD	Conventional reactive distillation
TCRD	Thermally coupled reactive distillation
RDHI	Reactive distillation with heat integration
THRD	Reactive distillation with thermally coupling and heat integration
RC	Recovery column
RDC	Reactive distillation column
TAC	Total annual cost
γ	Condition number
σ^*	Maximum singular value
σ_*	Minimum singular value
W_{VR}	Energy of the compressor
Top_{RDC}	Distillate from RC of the CRD configuration
MIX	Feed of DMC stream to RDC
$DMC_{recycle}$	Recycling stream of DMC
In.Steam	Vapor interlinking stream from RDC to RC in TCRD and THRD configuration
In.Liquid	Liquid interlinking stream from RC to RDC in TCRD and THRD configuration
$Liquid_{Top}$	Liquid stream fed at the top of RDC in RDHI configuration
$Feed_{RC}$	Feed stream of RC in RDHI configuration
$Steam_{top}$	Vapor interlinking stream from RDC to RC in RDHI configuration

(1) high equilibrium constant of reaction, (2) no formation of azeotropes, and (3) no existence of lateral reactions. Thus, the consequent purification process of DPC simplifies because it does not require extractive distillation for the azeotrope separation. It is important to mention that the reactive distillation processes studied here are free of any toxic material. The raw materials also may be produced by a *'green route'*, however, the generation of these reactants is out of the scope of this study.

Throughout the years there have been several studies about strategies to minimize energy consumption, operational costs and improve environmental benefits in chemical process plants. In a specific way, one of these strategies is the process intensification (PI) applied to column distillation with the so-called energy integration. PI and its strategies have emerged as a necessity for the creation of smaller, cleaner and more efficient technologies. It was recently defined as *"any engineer of development that substantially leads unto a smaller, cleaner, safer and energetically efficient technology"*, (Stankiewicz and Moulijn, 2000). A good example of PI is Reactive Distillation (RD), which combines reaction and separation in a single equipment (Moulijn et al., 2008). This intensified process has been a point of attention for researchers in recent decades, due to the benefits that it represents as an intensification process. The first industrial column of reactive distillation that has been recorded, it probably corresponds to the Eastman Corporation, on 1980 produced methyl acetate on an 80 m high by 4 m wide column mounted with a condenser and a reboiler. The advantages were highly clear because this column replaced a conventional multiunit process that consumed 5 times more energy and whose capital investment was 5 times that of the reactive column (Siirola, 1996). The reduction in the consumed energy also offers great potential due to a reduction of greenhouse emissions resulting from using fuel sources to convert the thermal energy supplied at the column reboiler, which derives in a friendlier environmental process. However, the limited investigation has directed the design and optimization only to reversible reactions.

Different general studies about synthesis and design of reactive distillation columns had been proposed (Barbosa and Doherty, 1988a,b; Ung and Doherty, 1995), afterward some works focused on the reaction kinetics and his effects under design; some had studied the reactive distillation under no conventional schemes like the dividing wall column (Kiss and Suszwalak, 2012). There has been a numerous growth regarding experimental and pilot plants works (Fernandez et al., 2013; Keller et al., 2013; Shah et al., 2012). Kumar et al. (2013) propose a novel design about reactive distillation with vapor recompression analogous to the internally Heat-Integrated Distillation Column (HIDiC) design but limiting the internal integration for exclusive means of reactive distillation.

In the context of proposals of reactive distillation processes for the production of important and valuable chemical compounds such as carbonates, only a few works have been published, for instance: Processes involving conventional reactive distillation for the synthesis of glycerol carbonate have been presented (Lertlukkanasuk et al., 2013; Wang et al., 2015); also reactive distillation processes for the synthesis of diethyl carbonate as the main product have been presented, Wei et al. (2011) proposed a conventional reactive distillation for the synthesis of diethyl carbonate, conventional and thermally coupled reactive distillation processes have also been proposed by Wang et al. (2014) and Zheng et al. (2016); reactive distillation has also been utilized in order to produce dimethyl carbonate, relevant works concerning this product refer to Huang et al. (2014) who introduced a heat-integrated reactive distillation process in order to synthesize DMC, Holtbruegge et al. (2014) proposed a membrane-assisted reactive distillation process in order to produce dimethyl carbonate and propylene glycol, more recently Holtbruegge et al. (2015) studied some reactive distillation alternatives to produce dimethyl carbonate and propylene glycol, the analyzed alternatives included conventional, membrane-assisted and thermally coupled reactive distillation columns. In the case of diphenyl carbonate synthesis through reactive distillation only the work by Cheng et al. (2013) is currently available, these authors introduced two reactive distillation configurations in order to synthesize this product, a conventional and a thermally coupled configuration.

Although it is true that intensification represents an attractive alternative to improve an actual process scheme, to lower its cost, environmental impact, and increases its process security, the intensified schemes are generally more complex if they are compared with their conventional counterparts. The process design of intensified schemes is ultimately more complex, due to a large number of degrees of freedom, which convert it into a large optimization problem, that it is not solved by trivial means. This major complexity also has a hugely important impact on the controllability of intensified systems. That is why the study of the control properties by means of analysis such as the singular value decomposition (SVD), relative gain array (RGA) and analysis through dynamic rigorous simulation has a special interest (Stephanopoulos, 1984).

The optimization problems can be classified in two different solution strategies, under deterministic or stochastic way (Cavazzuti, 2013; Dréo et al., 2006; Rao, 1996). The deterministic way is the most rigorous because it works with the mathematical model at issue and tries to solve it following different types of strategies. The result given by a deterministic method guarantee the global optimum solution if the problem is convex. On the other hand, the stochastic way consists of extenuating methodologies, which are given by aleatory searches of the optimum solution. The advantages regarding deterministic ways lie in that it is not necessary the resolution of the equations making easier the solving of the optimization problem. On the other hand, the natural disadvantage of the stochastic way is that it cannot guarantee that the solution found is actually the global optimum (Collet, 2007; Collet and Rennard, 2007). On both ways there exist a vast bibliography about the uses and applications of these strategies in the different areas of knowledge (Collet, 2007; Rangaiah, 2010; Uryasev and

Pardalos, 2013). The metaheuristic (stochastic) strategies have also reached a high impact on Chemical Engineering due not only to its implementation simplicity but also to its reliability.

It is important to mention that most of the global optimization works applied to distillation processes, both mono and multi-objective, have mainly used parameters such as total annual cost (TAC), the energy consumption, greenhouse gasses emissions, eco-indicators and conversions (Errico et al., 2016). On reactive distillation, it could be mentioned the work by Babu and Khan (2007), where they implement the differential evolution algorithm to optimize a mixed integer non-linear programming (MINLP) problem derived from the synthesis and design of a reactive distillation column for the production of ethylene glycol using the cost as the objective function. Some studies have done column optimization only under one variable modification at a time (number of stages and reactive stages) using the total annual cost as objective function (Xu et al., 2014). Vega et al. (2014) presented a complete analysis of the design and optimization of chemical processes and underlined the strong necessity of creating a multi-objective optimization that includes the control criteria properties such as an additional objective function to optimize the rest of design variables.

In this work a multi-objective optimization study involving cost and control properties on four reactive distillation configurations for the diphenyl carbonate (DPC) process production by reactive distillation from dimethyl carbonate (DMC) and phenyl acetate (PA) is presented, the utilized algorithm was the Multi-Objective Differential Evolution with Tabu List (MODE-TL) optimization algorithm (Sharma and Rangaiah, 2010), which is a *meta*-heuristic optimization algorithm. The reactive distillation configurations involve two novel configurations which use vapor recompression technology, these are: reactive distillation with heat integration (RDHI) through vapor recompression, and a reactive distillation with thermally coupling and heat integration (THRD) through vapor recompression. In addition, a conventional reactive distillation (CRD), a thermally coupled reactive distillation (TCRD) were studied. According to the knowledge of the authors, currently, there is not a paper that approaches a comparative study involving cost and control properties through a multi-objective optimization strategy in reactive distillation processes to produce diphenyl carbonate as the one presented in this work. This paper is organized as follows: Section 2 provides the modeling fundamentals of the reactive process and the reactive configurations, Section 3 presents the formulation of the multi-objective optimization problem, Section 4 provides the results, and finally Section 5 presents the conclusions of this study.

2. Modeling fundamentals

For the correct development of this study, it was necessary to take into account all the fundamentals, constraints and specifications of the reactive process to produce DPC and its implementation in reactive distillation configurations in order to develop the simultaneous cost and control multi-objective optimization problem. Thus, a suitable kinetic model for the chemical reactions in the process and a proper thermodynamic model that adequately describes phase equilibria of the reactive systems were selected.

2.1. Reaction scheme to produce diphenyl carbonate

The reaction scheme involves a transesterification reaction between dimethyl carbonate (DMC) and phenyl acetate (PA) to produce methyl acetate (MA), and the intermediary methyl phenyl carbonate (MPC), which reacts with PA or himself to produce diphenyl carbonate (DPC). The reaction sequence is showed by Eqs. (2)–(4). In each step, the reaction involved is reversible.

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

$$DMC + PA \rightleftarrows MPC + MA \quad (2)$$

$$MPC + PA \rightleftarrows DPC + MA \quad (3)$$

$$2MPC \rightleftarrows DPC + DMC \quad (4)$$

Cheng et al. (2013) proposed the rate expressions corresponding to the reactions of in Eqs. (2)–(4). These kinetics expressions are represented by Eqs. (5)–(7)

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

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

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

The kinetic parameters, which fit to the Arrhenius equation, were taken from Cheng et al. (2013). Table 1 shows the values of the pre-exponential factor, k_0, and the activation energy, E_a, of each reaction rates.

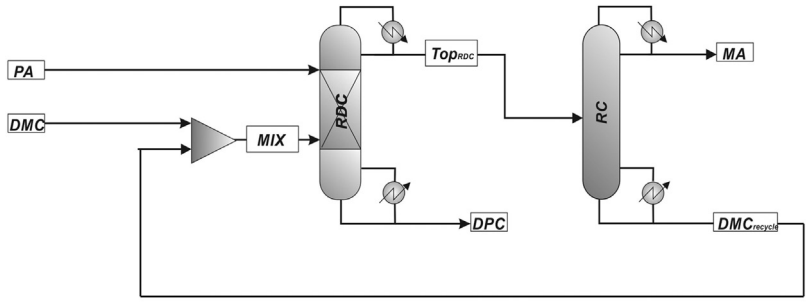
2.2. Thermodynamic model

The reactive system consists of five components, DPC, MPC, PA, DMC, and MA; Cheng et al. (2013) reported that there is not the existence of azeotropes among these components due to the boiling point temperature difference of any combination of two components in the system is large enough.

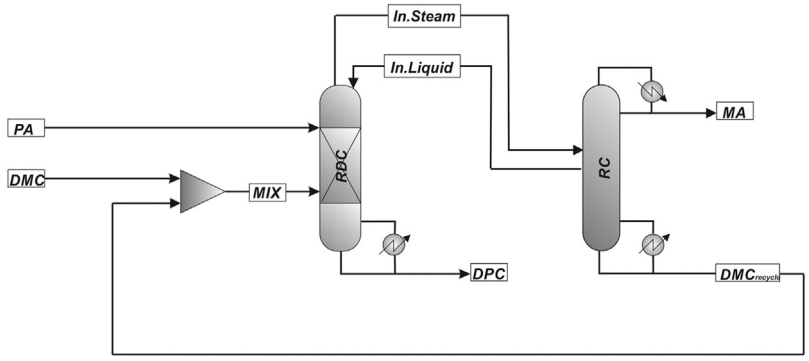
Yao (2012) showed experimentally that an ideal solution can describe the equilibrium data of the system with a very satisfactory fit. Therefore, the mixture can be properly modeled by an ideal thermodynamic model for the estimation of the vapor-liquid equilibrium.

2.3. Intensified reactive distillation configurations to produce DPC

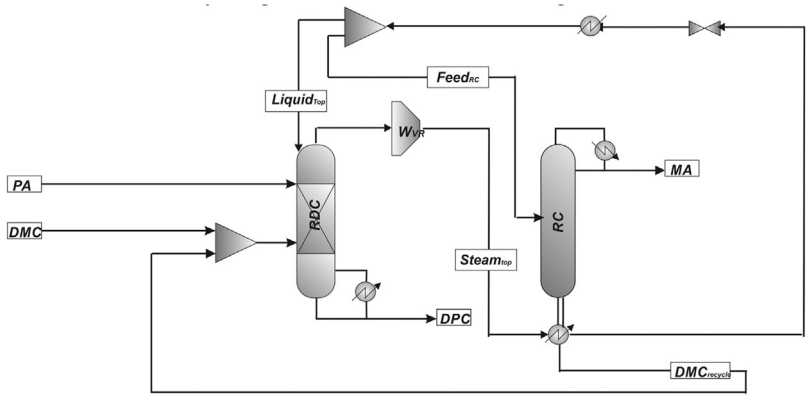
In the present work four different reactive distillation configurations to produce DPC are studied. The alternatives consist in: Conventional Reactive Distillation (CRD); a Thermally Coupled Reactive Distillation (TCRD); and two novel configurations: Reactive Distillation With heat Integration (RDHI) and Reactive Distillation with Thermally Coupled and heat Integration (THRD), these last configurations use vapor recompression in order to implement heat integration, the schemes of these configurations are shown in Fig. 1. All sequences consist of two columns, the first is the reactive distillation column (RDC). the reagent with higher boiling point (PA) is fed near the top of the RDC while the reagent with lower boiling point (DMC) is fed near the bottom. The second column is the recovery column (RC) of the by-product MA, and the reagent DMC is returned from the bottom of the RC column to the RDC column. In all cases, the feed flow of PA and DMC were 10 kmol h^{-1} and 5.06 kmol h^{-1}, respectively. The purity required for DPC and MA is 99.5 mol%. The topology of the designs of CRD and TCRD were taken from the previous work by Cheng et al. (2013). The RDHI and the THRD process were designed from the CRD and TCRD



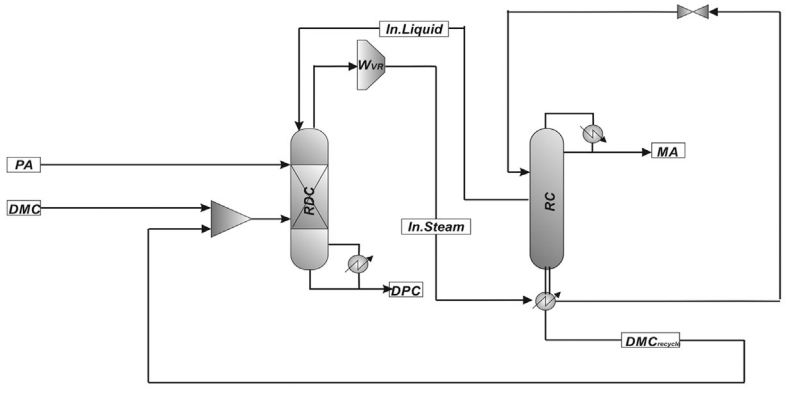
a). Conventional Reactive Distillation Configuration (CRD).



b). Thermally Coupled Reactive Distillation configuration (TCRD).



c). Reactive Distillation With heat Integration (RDHI).



d). Reactive Distillation with Thermally Coupled and heat Integration (THRD).

Fig. 1. Intensified reactive distillation configurations to produce DPC.

respectively. The main target in the reactive distillation sequence with heat integration is to upgrade and reuse the heat of vapor streams leaving the top of the RDC to mitigate the duty in the RC reboiler; the heat integration causes important energy savings in the reactive distillation process. The function of the compressor is to increase the temperature of vapor streams in order to guarantee

that its temperature is higher than the temperature of the bottom of the RC.

3. Formulation of the multi-objective optimization problem

The multi-objective optimization problem involving cost and control properties of the reactive distillation configurations for the synthesis of Diphenyl Carbonate leads to a large-scale optimization problem because of the large number of discrete and continuous variables, which include phase equilibrium and the kinetic relationships. Thus, it is important to utilize a suitable multi-objective optimization strategy for simultaneously relating the economic and controllability properties in the designs of these intensified configurations. In this study, the Condition Number has been established as the index to evaluate the control properties of the designs, whereas the cost is evaluated by calculating the Total Annual Cost.

The calculation of the Condition Number has been carried out through the singular value decomposition technique of the relative gain matrix of the design in the nominal point (e.g. the design that fulfills the restrictions of molar purity and recovery); lower values of the Condition Number of a design are preferable over upper values (Morari et al., 1985), because the condition number is a sensitivity measure of the system to any parameter perturbation (Lau and Jensen, 1985), it is a suitable index in order to have a qualitative assessment of the control properties of the designs in steady-state, the condition number has been used in Chemical Engineering processes for achieving such purpose (Lenhoff and Morari, 1982; Segovia-Hernández et al., 2006; Skogestad and Havre, 1996; Youngwoon and En Sup Yoon, 1996). For further details on the calculation of the Condition Number using the singular value decomposition of the relative gain matrix, the reader is referred to a previous work by Vázquez-Castillo et al. (2015).

On the other hand, the Total Annual Cost (TAC) of each reactive distillation configuration has been estimated as follows:

$$\text{TAC} = \frac{\text{Capital cost}}{\text{Payback time}} + \text{Operating cost} \tag{8}$$

The capital cost of each reactive configuration was calculated by using the modular method (Guthrie, 1969; Ulrich, 1984), the capital cost includes the cost 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. (2009). Carbon steel was the assumed construction material for all the equipment, and the payback time was considered to be five years. The operating cost includes cooling utilities, heating utilities, and 8400 h of yearly operation for each configuration. Furthermore, the utilities considered were: oil for heating with a cost of $ 6.28/GJ (Douglas, 1988), low-pressure steam (6 bar, 87 psia, 160 °C/320 °F) with a cost of $ 7.78/GJ, electric power 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 (Luyben, 2011).

Optimal designs of the reactive distillation configurations mean having solutions with Condition Number, γ, and TAC as minimum as possible, but satisfying the required molar purities and flowrates. The multi-objective optimization problem can be mathematically expressed as in Eq. (9):

$$\min \quad Z = \{TAC; \gamma\} \tag{9}$$

$$TAC = f\left(N_S, C_d, R_a, C_a, h_u, c_o, k, e_p\right)$$

$$\gamma = f\left(\sigma_*, \sigma^*\right)$$

Subject to:

$$\vec{y}_{i,PC} \geq \vec{x}_{i,PC}$$
$$\vec{w}_{i,FC} \geq \vec{u}_{i,FC} \tag{10}$$

The Total Annual Cost of a reactive distillation configuration depends on the number of stages N_S, column diameters C_d, the area of condensers C_a, the area of reboilers R_a, the cost of heating utilities h_u and cooling utilities c_o, compressor capacity k, electric power e_p; whereas the Condition Number relates the minimum singular value σ_* and the maximum singular value σ^*. The objective function is restricted to the fulfillment of the purity vectors and the molar flowrate vectors for the components in the mixture, e.g., the values of the purities for the components obtained during the optimization process $\vec{y}_{i,PC}$ must be either greater or equal to the specified values of purities for the components $\vec{x}_{i,PC}$, furthermore the molar flowrates obtained $\vec{w}_{i,FC}$ must also be either greater or equal to the specified values of the molar flowrates $\vec{u}_{i,FC}$. The decision variables in the optimization of Eq. (9) for the studied reactive distillation configurations (see Fig. 1) involve a combination of discrete and continuous variables. For the CRD, a total of 13 decision variables must be determined. Similarly, for TCRD a total of 13 decision variables must also be determined. However, for RDHI and THRD, 14 variables must be determined in the optimization process. Table 2 offers the detailed information of the decision variables for each reactive configuration subject to the multi-objective optimization procedure.

The multi-objective optimization problem states an important degree of difficulty so that a suitable optimization strategy must be used. In this work, it has been used the multi-objective optimization hybrid method namely the Multi-Objective Differential Evolution With Tabu List Algorithm (MODE-TL) proposed by Sharma and Rangaiah (2010), in the MODE-TL (see the flowchart given in Fig. 2) a population of NP individuals is randomly initialized within the bounds of the decision variables. Then, values of the objectives and constraints are calculated for each individual of the initial population. The size of TLS (Tabu List Size) is half of the population size, and Tabu List (TL) is randomly filled with 50% individuals of the initial population, initial individuals are also identified as target individuals (i). A trial individual is generated for each target individual by mutation and crossover on three randomly selected individuals from initial/current/parent population. The elements of the mutant vector compete with those of the target vector, with a Cr probability to generate a trial vector. Tabu check is implemented in the generation step of the trial vector of MODE-TL, and the trial individual is repeatedly generated until it is away from each individual in the TL by a specified distance called Tabu Radius (Tr). Euclidean distance between the trial individual and each individual in TL is calculated in the normalized decision variables space for accepting the trial individual. After that, objectives and constraints are calculated for the temporarily accepted trial individual. The trial individual is stored in the child population and added to TL. After generating the trial individuals for all the target individuals of the current population, non-dominated sorting of the combined current and child populations followed by crowding distance calculation, then if required is performed to select the individuals for the next generation (G). The best NP individuals are used as the population in the subsequent generation. For further details about the MODE-TL, the reader is referred to the work by Sharma and Rangaiah (2010).

The implementation of the multi-objective optimization strategy involved a hybrid platform which linked Aspen Plus™, Microsoft Excel™, and Matlab™ through the implementation of a COM Technology (see Fig. 3). During the optimization process, a decision vector of design variables is sent from Excel ™ to Aspen Plus™, in which rigorous calculations for the data that identify a particular design of the reactive distillation configurations

Table 2
Discrete and continuous decision variables for the reactive distillation configurations in Fig. 1.

Decision Variables	CRD		TCRD		RDHI		THRD	
	Continuous	Discrete	Continuous	Discrete	Continuous	Discrete	Continuous	Discrete
Number of stages, RDC		X		X		X		X
Number of stages, RC		X		X		X		X
Feed stage of PA		X		X		X		X
Feed stage of DMC		X		X		X		X
Reflux ratio of RDC	X				X			
Reflux ratio of RC	X		X		X		X	
Feed stage, RC		X		X		X		X
Heat duty of RDC, kW	X		X		X		X	
Heat duty of RC, kW	X		X		X		X	
Diameter of RDC, m	X		X		X		X	
Diameter of RC, m	X		X		X		X	
Top pressure RDC, atm	X		X		X		X	
Top pressure RC, atm	X		X		X		X	
Discharge pressure of compressor, atm					X		X	
Interlinking flow, kmol h^{-1}			X				X	
Total number of variables	13		13		14		14	

are obtained (e.g., temperature profile, molar composition profile, molar flow profile, etc.) via resolution of phase equilibria along with the complete set of MESH equations by using the RADFRAC™ module. These data are returned from Aspen Plus ™ and stored in Excel ™, perturbations of 1% are applied to the manipulated variables and new simulations are executed, after these simulations are completed the differences among the components molar purity in the nominal state and the components molar purity after the perturbations are estimated, these data along with the necessary data to estimate the Total Annual Cost are sent from Excel™ to Matlab™. In this software, the calculation of both objective functions is carried out, the values obtained for the objective functions are returned to Excel™ and new vectors of design variables are generated according to the stochastic procedure of this method. For the optimization process, in this study the values for the parameters associated with the used MODE-TL algorithm are the following: Population size (NP): 120 individuals, Generations Number (GenMax): 500, Tabu List size (TLS): 60 individuals, Tabu Radius (TR): 2.5×10^{-6}, Crossover fractions (Cr): 0.8, Mutation fractions (F): 0.6. The values of NP, GenMax and TLS were determined through a previous tuning process of the multi-objective optimization algorithm, whereas the values of Cr, TR and F were taken from the recommended values for these parameters in the work by Sharma and Rangaiah (2010).

4. Results

In this section, the results of the simultaneous cost and control multi-objective optimization for all the reactive distillation configurations is presented. The optimized results fulfill the molar purities set as 99.5% molar fraction of DPC and MA. In the optimization process, all the reactive sequences were rigorously modeled using the process simulator Aspen Plus™ through the RADFRAC™ module, which contains the complete set of mass and energy balances along with the phase equilibrium calculations. All the runs to carry out the multi-objective optimization were performed on an Intel (R) Core ™ i7-4790 CPU @ 3.6 GHz, 12 GB computer, the computing time for obtaining the Pareto optimal solutions was different according to the complexity of each reactive configuration: CRD required 175.2 h, TCRD required 201.6 h, RDHI required 247.2 h, and THRD required 295.2 h.

4.1. Pareto optimal solutions

As previously mentioned, the intensified reactive distillation configurations for the synthesis of Diphenyl Carbonate can provide significant advantages related to energy savings; however, the complex structure of these configuration poses a very complex problem in finding an optimum design through the implementation of a conventional optimization method due to the large number of variables involved, without mentioning that this complexity can degrade the controllability of the designs. The multi-objective optimization process allows for obtaining multiple solutions, which fulfill the restrictions imposed by the recovery and molar purities. The solutions of reactive distillation configurations found in the Pareto charts which offer the trade-offs between the two objective functions, namely the cost and the control properties of these intensified configurations are offered in the following sections.

4.2. Conventional reactive distillation (CRD)

Fig. 4, shows the Pareto chart for CRD, as observed in this figure, the values of the condition number are found between 715 and 10,000, whereas the TAC values from $ 1,700,000 to $ 5,000,000 per year. In order to compare the designs in different zones of the Pareto chart and to have a better understanding why the solutions in the extremes of the Pareto have important reductions in TAC, but bad control properties and the other way around, three different designs were selected, the first design is found on the upper left side of the Pareto where the highest value of condition number and minimum cost are present, this design is identified as PC in Fig. 4. the second design, PT, is in the opposite condition, this is with the highest cost and minimum condition number, and finally one design in the curve zone of the Pareto was selected, PO; the solutions in the Pareto chart can help in the decision-making process by showing the trade-offs involved in the objective functions, for example, in this study the selection of a design with one of the lowest values in the total annual cost will have an impact of some extent on the value of condition number and vice versa, this is, the selection of solutions in the extremes of the Pareto chart. Therefore, the solutions that offer the best trade-offs between the two objectives are those located in the curve zone of the Pareto Chart, in particular, the PO design is a good example of one design of this feature. The values of the design variables of PT, PO, and PC selected designs are offered in Table 3.

As it can be seen in Table 3, PO is the solution that offers the best trade-off between the two objectives. PC is the solution with the worst control properties, it has smaller values of the column diameters in RDC and RC respect to the PT solution, which has good control properties but the highest TAC. This difference in the diameters in RDC has a strong influence in the tray holdup for each design, in this way the values in the tray holdup for PO and PC are

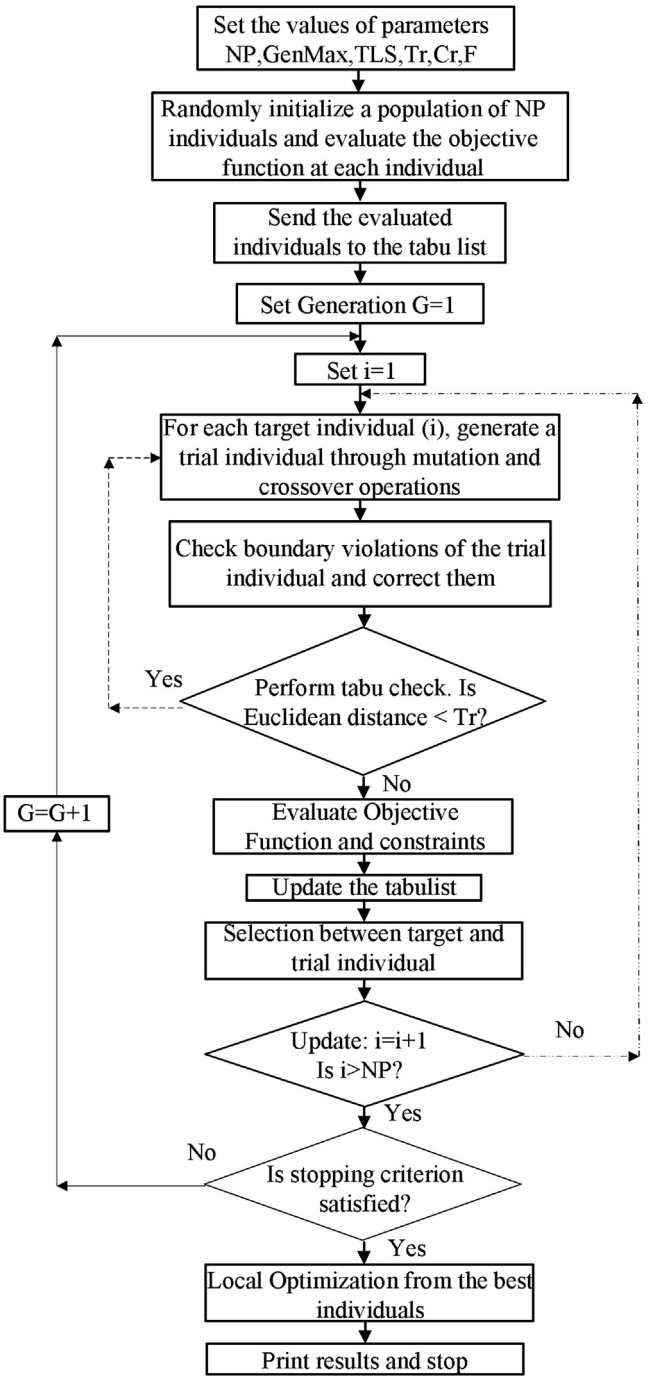


Fig. 2. Flowchart of the used multi-objective optimization algorithm (MODE-TL).

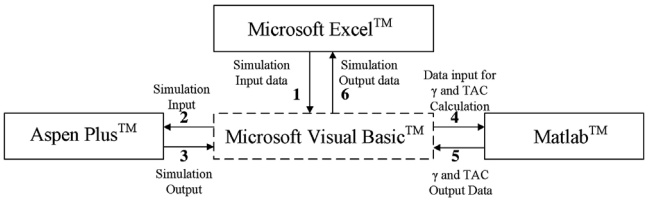


Fig. 3. Hybrid platform to implement the multi-objective optimization.

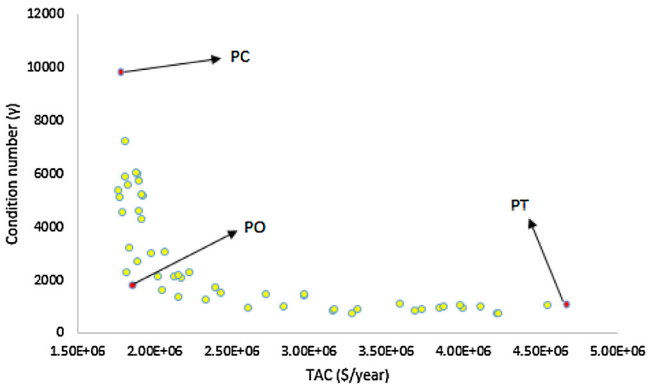


Fig. 4. Pareto chart of the optimized designs of CRD configuration.

significantly smaller than the tray holdup values in PT; from this, it can be inferred that for the CRD configuration the tray holdups and consequently the diameters of the columns RDC and RC might have some influence on the control properties, being the control properties of the PT design the best in these three representative designs. An explanation of these results can be suggested by stating that as bigger tray holdups values are present during the operation of the columns, these holdup volumes can serve as a surge capacity of the process in order to deal in a better way with the effects of the perturbations in the manipulated variables; So the effects of the perturbations are not so noticeable. But this has as consequence an increase in the values of the diameters of the columns, which has a direct impact in the increment of the energy consumption of the designs because a large amount of internal flowrate is present. This kind of conclusion relating the holdup volumes and the surge capacity of the column has been commented in studies of practical distillation control (Luyben, 1992).

With respect to the number of stages in the columns, it does not seem to have a noticeable influence on the control properties; there is not a clear trend in this aspect. However, it is clear that the number of stages of the design PT is larger than PO and PC. On the other hand, the reflux ratio values of the PO and PT solutions have values larger than PC, so, it can be inferred that the larger the values of the reflux ratio are the better the control properties are, but this is compensated with increments in the energy consumptions.

In the case of the molar purities, especially in the purity of the recycled component, DMC, the results indicate that it is not

Table 3
Design variables of optimized designs PC, PO, and PT of CRD configuration.

Design variables of CRD	PC	PO	PT
Number of stages, RDC	83	78	82
Number of stages, RC	29	26	35
Feed stage of PA	5	7	4
Feed stage of DMC	72	71	74
Feed stage, RC	20	11	28
Reflux ratio, RDC	1.21	2.59	2.02
Reflux ratio, RC	1.05	2.38	1.95
Heat duty of RDC (kW)	676.00	819.31	931.71
Heat duty of RC (kW)	176.90	160.89	291.28
Diameter of RDC (m)	0.90	1.14	2.67
Diameter of RC (m)	1.23	1.42	2.13
Top pressure RDC (atm)	1.07	2.38	1.08
Top pressure RC (atm)	1.00	1.00	1.01
Tray holdup (l)	260.54	346.31	970.45
Reactive stages, RDC	5–74	7–74	4–81
Total energy (kW)	852.80	979.62	1222.99
Purity of DPC (mol. fraction)	0.997	0.995	0.997
Purity of MA (mol. fraction)	0.995	0.995	0.997
Purity of DMC (mol. fraction)	0.677	0.478	0.995
Condition number	9768	1764.49	1091.31
Total Annual Cost ($/yr)	1,787,420	1,854,323.60	4,671,366.08

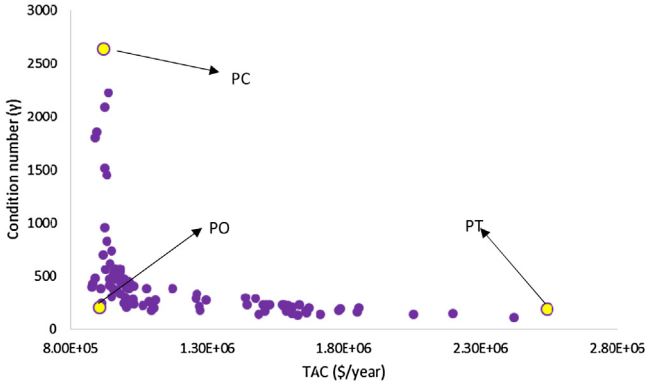


Fig. 5. Pareto chart of the optimized designs of TCRD configuration.

necessary a very high purity of the reactant in excess in the recycle stream.

4.3. Thermally coupled reactive distillation (TCRD)

The Pareto chart of TCRD is shown in Fig. 5, the values of the Condition numbers for this configuration range from 100 to 2750, whereas the Total Annual Cost values obtained were in the range from $ 800,000 to $ 2,600,000. The designs with the best trade-off between the two objectives are found in a narrow zone of the Pareto chart with condition numbers values that range from 150 to 700 and Total Annual Cost values from $ 890,000 to $ 1,100,000. It is important to notice that the values in the objective functions in the Pareto chart of TCRD are lower than the values in the Pareto chart of CRD. Therefore, it can be stated that the designs of TCRD are better in terms of cost and control. The results of cost reduction with respect to CRD can be explained because of the presence of a recycle stream in TCRD. Likewise in thermally coupled configurations without reaction, the recycle stream helps to mitigate the required heat duty in this configuration and also can be a factor to deaden the control response of the TCRD system.

Similar to the selected points in CRD configuration, three points have been selected in the optimal designs of TCRD configuration in Fig. 5, in this way the selected design, PC, has the minimum TAC and the worst control properties, the design PT has the minimum condition number and the worst TAC, and the PO design, which offers the best trade-off between the two objectives. The design variables of these selected designs are offered in Table 4.

In Table 4 can it be seen that the selected designs of TCRD have lower energy consumptions than the selected designs of CRD in Table 3. In the case of the PC design, it has low energy requirements in the RC, also in Table 4 it can be seen that the purity of the DCM recycled in PC is very low compared with the designs PO and PT. The way in which the low energy consumption affects the control properties mainly lies in the work done by the recycle stream, which is used to return the reactant DMC to the RDC, with the aim to achieve an excess of this reactant and to shift the equilibrium in the reaction towards the formation of the products. However, the low purity in the recycle stream of PC implies a low quantity of DMC in the recirculated stream, which negatively affects the formation of DPC; therefore, any small change in the energy duty of the column RC affects the DPC formation in RDC, and also the formation of MA. Finally, it is important to mention that the total annual cost savings of the design PO are a consequence of the low energy consumption.

In the designs PT and PO of TCRD, the results indicate that larger diameters and tray holdups tend to favor the control properties, likewise in CRD, the columns of TCRD with higher tray holdups and diameters can handle the perturbations in the manipulated variables. With respect to the values of the reflux ratios in TCRD, these

Table 4
Design variables of optimized designs PC, PO, and PT of TCRD configuration.

Design variables of TCRD	PC	PO	PT
Number of stages, RDC	85	82	85
Number of stages, RC	22	30	20
Feed stage of PA	10	8	6
Feed stage of DMC	80	72	75
Feed stage, RC	13	11	20
Reflux ratio, RC	8.30	11.34	10.56
Interlinking flow, kmol h^{-1}	36.05	21.28	30.93
Heat duty of RC (kW)	86.43	293.56	273.51
Heat duty of RDC (kW)	606.79	564.90	641.86
Diameter of RDC (m)	0.99	0.82	1.39
Diameter of RC (m)	0.74	0.82	0.85
Top pressure RDC (atm)	2.95	2.09	2.89
Top pressure RC (atm)	1.01	1.02	1.01
Tray holdup (l)	437.21	300.026	610.74
Reactive stages, RDC	10–81	8–78	6–81
Total energy (kW)	693.22	858.46	915.37
Purity of DPC (mol. fraction)	0.996	0.996	0.995
Purity of MA (mol. fraction)	0.997	0.997	0.998
Purity of DMC (mol. fraction)	0.0186	0.997	0.998
Condition number	2640.16	206.46	185.6
Total Annual Cost ($/yr)	906,241.1	905,863.6	2,542,406.5

are high in the recovery column, which is a consequence of the thermal coupling as the recovery column must provide liquid to the reactive column, RDC. In the case of other design parameters as the operating pressure or the interlinking flow there is no a clear trend to discern whether these have advantageous or disadvantageous effects on the control properties, but rather it seems that the effects of these would depend on the combination of these variables together with the other parameters of the design.

4.4. Reactive distillation with heat integration (RDHI)

For the reactive configuration with heat integration, the Pareto chart of this configuration is shown in Fig. 6, the values of the condition numbers of RDHI were in the range from 160 to 3000, and the Total Annual Cost values from $ 1,600,000 to $ 3,700,000. In comparison with the CRD results, the designs of RDHI are more promissory; it is very important to notice because the complexity in the structure of RDHI configuration seems not to degrade the control properties and the heat integration strongly mitigates the energy requirements of RDHI, affecting in a positive way the TAC.

Three representative points of the Pareto chart are shown in Fig. 6. The PC point represents the design with the highest condition number; the PT point represents the design with the highest TAC, and the PO point offers the best trade-off between the two objectives. The design variables of these designs are shown in Table 5.

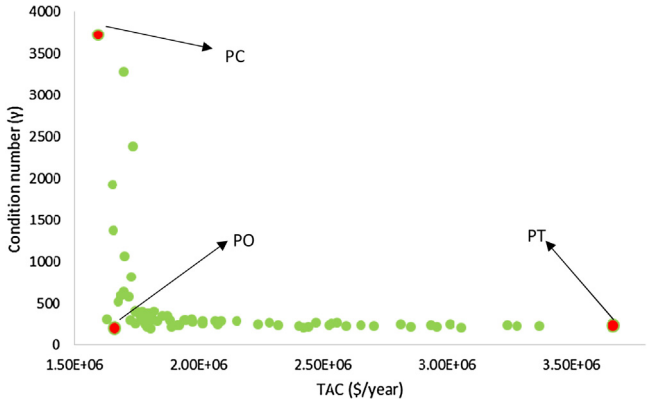


Fig. 6. Pareto chart of the optimized designs of RDHI configuration.

Table 5
Design variables of optimized designs PC, PO and PT of RDHI configuration.

Design variables of RDHI	PC	PO	PT
Number of stages, RDC	76	80	76
Number of stages, RC	26	26	26
Feed stage of PA	8	9	3
Feed stage of DMC	74	72	72
Feed stage, RC	23	8	8
Reflux ratio, RDC	0.97	1.63	2.65
Reflux ratio, RC	1.51	1.69	1.77
Heat duty of RDC (kW)	536.82	713.59	1133.72
Heat duty of RC (kW), Integrated	396.621	228.904	286.32
Diameter of RDC (m)	1.01	1.06	1.13
Diameter of RC (m)	1.13	1.29	1.29
Top pressure RDC (atm)	2.46	2.16	2.26
Top pressure RC (atm)	1.022	1.03	1.00
Tray holdup (l)	354.48	371.34	382.21
Reactive stages, RDC	8–75	9–76	3–74
Energy of Compresor (kW)	1.90	6.59	39.64
Discharge pressure of compressor (atm)	2.58	2.44	3.05
Total energy (kW)	538.73	720.18	1172.71
Purity of DPC (mol. fraction)	0.996	0.998	0.995
Purity of MA (mol. fraction)	0.996	0.998	0.997
Purity of DMC (mol. fraction)	0.998	0.571	0.998
Condition number	3730.0	246.0	236.2
Total Annual Cost ($/yr)	1,595,070.0	1,663,652.8	3,669,899.9

As can be seen in Table 5 the design of the three representative optimized designs of RDHI has a similar number of stages as those in RDC and RC. The increment of the columns diameters from PC to PT has an important positive impact on the control properties because they allow to the configuration to handle better the effects from the perturbations likewise the optimized designs in CRD and TCRD. There is a strong relationship between the holdup and the column diameter because large values of the holdup, as in the PT design having the highest possible value of holdup, result in longer residence time of reactants in each stage and therefore it is linked with the liquid flowrate and it also allows for the variation of others variables such as the heat duty and the reflux ratio. With respect to the values of the reflux ratio, as expected, lower values represent lower energy consumption, and these are reflected in lower TAC; however, this has a negative effect on the values of the condition numbers of RDHI configuration.

Another factor that can help in an important way to the improvement in the control properties is the heat duty, larger values in the energy consumption of the reboilers of the columns, as observed in Table 5, and analogously to bigger internal flowrate, a larger heat duty can better assimilate the perturbations doing the configuration to operate near the nominal point.

4.5. Reactive distillation with thermally coupled and heat integration (THRD)

For the last configuration, the THRD, the Pareto chart is shown in Fig. 7. As observed in this figure, the condition number values are found in the range from 1290 to 5500 whereas the TAC values are in the range from $ 1,600,000 to $ 2,500,000. Both values in the objective functions are close to those obtained in CRD, which indicates that the presence of more than one recycle stream as in RDHI does not benefit the control properties; on the other hand, the elevated cost of this configuration is because of the electric power required for the compressor and the operating pressure in the reactive column (See Table 6), this considerably increases the cost of the configuration because a considerable amount of electric power is required in order to achieve the pressure in the reactive column, this may be an unappealing motivation for the industrial implementation of THRD compared with TCRD and RDHI.

In the same way, three representative optimized points were selected, PC, PO, and PT, the design variables of these designs are

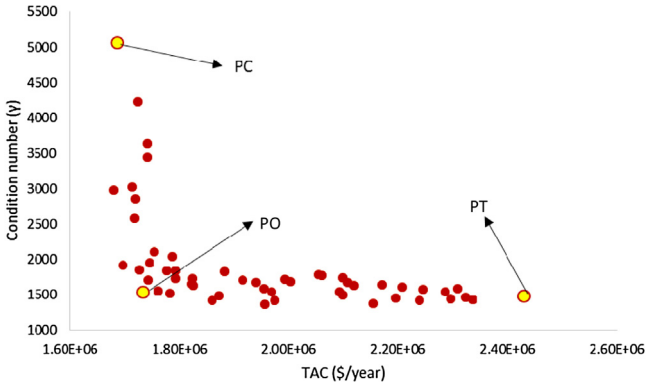


Fig. 7. Pareto chart of the optimized designs of THRD configuration.

shown in Table 6. The effects of the values of tray holdups and the diameters on the control properties are very noticeable helping to improve these properties, but with increments in the costs. The holdups are related with the diameters and then these follow the same trend.

With respect to the effect of the reflux ratio, and other designs parameters such as the number of stages, and the feed stages, there is not a clear trend about their effects on the control properties, as the selected and representative designs have similar values of the number of stages and feed stages. On the other hand, it seems that larger values in the interlinking flows may produce positive effects on the control properties, similar to the values of the diameters, but negatively affecting the cost.

On the basis of the values of the TAC of this configuration, it can be stated that the total annual cost is strongly affected by the energy utilized in the compressor, this is clear to be seen through the analysis of the disaggregated values of the energy. Another parameter that also affects the TAC is the top pressure in RDC because the larger this pressure is the larger the energy required by the compressor is. Also, it is important to note that the designs of THRD have lower energy consumptions compared to the designs of CRD, TCRD, and RDHI. However, the high requirement of electric power of THRD configuration decreases the economic benefits of the energy savings in RDC and RC.

Table 6
Design variables of optimized designs PC, PO, and PT of THRD configuration.

Design variables of THRD	PC	PO	PT
Number of stages, RDC	82	80	81
Number of stages, RC	24	23	26
Feed stage of PA	6	4	6
Feed stage of DMC	77	74	78
Feed stage, RC	18	2	22
Reflux ratio, RC	7.17	9.69	8.06
Heat duty of RDC (kW)	536.22	514.02	580.69
Heat duty of RC (kW), Integrated	182.31	819.21	931.59
Diameter of RDC (m)	0.53	1.07	2.16
Diameter of RC (m)	0.73	1.02	1.44
Top pressure RDC (atm)	2.56	2.03	1.23
Top pressure RC (atm)	1.0042	1.0423	1.031
Tray holdup (l)	115.12	213.23	675.66
Reactive stages, RDC	6–78	4–74	6–78
Interlinking flow, kmol h^{-1}	27.63	29.07	33.17
Energy of Compresor (kW)	4.08	30.36	66.79
Discharge pressure of compressor (atm)	2.82	3.20	2.98
Total energy (kW)	540.30	544.38	647.48
Purity of DPC (mol. fraction)	0.997	0.996	0.996
Purity of MA (mol. fraction)	0.997	0.995	0.996
Purity of DMC (mol. fraction)	0.795	0.027	0.118
Condition number	5058.9	1541.9	1486.6
Total Annual Cost ($/yr)	1,686,805.5	1,734,136.2	2,429,723.1

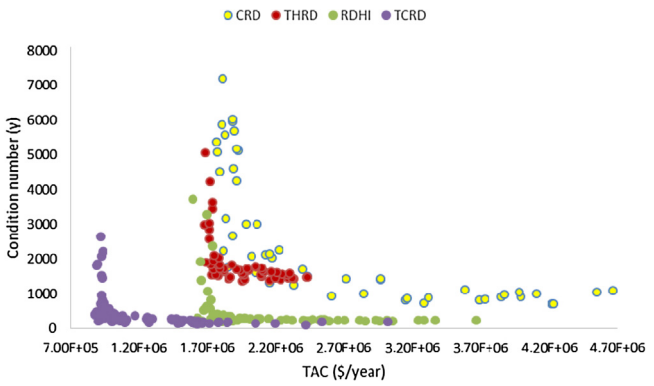


Fig. 8. Superposed Pareto chart of the optimized designs of reactive distillation configurations.

4.6. Analysis of the superposed Pareto charts for all the configurations

With the purpose to illustrate in a more comprehensible way, Fig. 8 shows the Pareto charts of all the configurations in Figs. 4–7. As it can be seen in Fig. 8 the designs of CRD, RDHI, and THRD have similar ranges in the values of the TAC, it is a fact that this last configuration, and, RDHI, have important energy savings and thus it would be expected a reduction in the TAC, however, the compressor energy requirement involves the use of electric power and increases in a significant way the cost of the configurations. On the other hand, the results indicate that the structure with more complexity and with more recycle streams, which is THRD, shows the worst control properties followed by the conventional configuration, CRD. The designs of RDHI and TCRD configurations are those that show the best control properties, however, the Total Annual Cost values of TCRD are lower than the values of RDHI, and in general with respect to the other configurations. Thus, it can be stated that the TCRD configuration has a significant advantage over the other configurations as the best alternative for the synthesis of Diphenyl Carbonate because of the control properties and the cost values. Table 7 shows the summary of design variables of the optimized designs of each configuration that offer the best trade-off between the control properties and the total annual cost; these are the "PO" points of each Pareto chart.

From the values of the design variables, it can be observed that the optimized designs are similar with respect to the number of stages of RDC and RC, in the case of the reactive distillation column designs, the number of stages and their heights are in concordance with the mechanical considerations in the design of distillation columns built so far (Górak and Olujic, 2014). As previously mentioned, the THRD configuration is not favored in its control properties because of the existence of more than one recycle stream in its structure, in addition the Total Annual Cost is also increased due to the cost of the electric power required for this configuration, a similar situation, in a lower degree, occurs in RDHI.

Table 7
Summary of the design variables of the best designs of the reactive configurations.

Design Variables and Parameters	CRD	TCRD	RDHI	THRD
Columns Topology				
Number of stages, RDC	78	82	80	80
Number of stages, RC	26	30	26	23
Feed stage of PA	7	8	9	4
Feed stage of DMC	71	72	72	74
Feed stage, RC	11	11	8	2
Diameter of RDC (m)	1.14174	0.821441	1.05766	1.07288
Diameter of RC (m)	1.42637	0.822119	1.29306	1.02118
Specifications				
Reflux ratio, RDC	2.59377	11.3423	1.63179	–
Reflux ratio, RC	2.3831	–	1.69531	9.6938
Heat duty of RDC (kW)	819.311	564.904	713.596	514.023
Heat duty of RC (kW)	160.892	293.565	228.904	819.213
Top pressure RDC (atm)	2.3831	2.09142	2.1598	2.03481
Tray holdup (l)	346.31	300.026	371.341	213.231
Reactive stages, RDC	7–74	8–78	9–76	4–74
Interlinking flow, kmol h^{-1}	–	21.2805	–	29.0766
Energy of Compresor (kW)	–	–	6.5918	30.359
Discharge pressure of compressor (atm)	–	–	2.43987	3.20148
Streams Mole Flow (kmol h^{-1} r)				
PA	10	10	10	10
DMC	5.06	5.06	5.06	5.06
$DMC_{Recycle}$	19.39	32.85	17.26	18.75
MA	10.05	8.93	9.97	9.69
DPC	5.01	5.011	4.99	5.016
TOP_{RDC}	29.43	–	–	–
In. Steam	–	64.18	–	57.93
In. Liquid	–	21.28	–	29.07
$Steam_{top}$	–	–	71.72	–
$Liquid_{top}$	–	–	44.47	–
$Feed_{RC}$	–	–	27.25	–
Purity of Products (mol. fraction)				
Purity of DPC	0.995005	0.996672	0.998265	0.996245
Purity of MA	0.99577	0.99749	0.998841	0.995566
Key performance indicators				
Energy per ton of DPC produced (GJ/Ton_{DPC})	3.41	2.89	2.20	1.67
Total energy (kW)	979.621	858.469	720.18	544.382
Condition number	1764.49	206.46	246.0	1541.9
Total Annual Cost ($/yr)	1,854,323.60	905,863.61	1,663,652.8	1,734,136.2

In the case of the optimized design of TCRD, and despite the energy consumption is larger than RDHI and THRD, the absence of a compressor in TCRD helps to reduce the Total Annual Cost. Also, it is important to mention that the influence of the recycle stream helps to improve the control properties. On the basis of all the results represented in the Pareto charts and the design variables of the optimized designs, it can be stated that TCRD is the most attractive configuration in economic terms and controllability properties for the synthesis of Diphenyl Carbonate.

The energy consumption (GJ/ton of DPC) per ton of DPC produced of each optimized design is shown in Table 7. It indicates that the highest required energy for the production of DPC corresponds to the CRD configuration, whereas significant and favorable differences in the requirements of energy for the other configurations, with respect to the CRD design, were obtained; for instance, the TCRD configuration required 17.99% less energy than CRD, RDHI configuration needs 55% less that the conventional configuration, whereas the lowest required energy corresponded to the THRD configuration with 104% less than CRD.

With respect to the total annual cost in configurations RDHI and THRD, the results did not indicate a direct relationship between energy consumptions and costs; where these configurations use electric power and it increased their TAC, this is easy to see by inspecting the values of the design variables reported in the optimal designs of these configurations, which have similar values in the number of stages and diameters. Therefore, it was possible to discard the reduction in the cost because of structural arrangement.

Finally, it is important to mention that the CRD configuration for the synthesis of Diphenyl Carbonate resulted in the most unappealing alternative for its formal implementation because it has the largest TAC, the worst control properties, and high energy consumptions, this last can be translated into high polluting emissions and a negative environmental impact.

5. Conclusions

This work presented a multi-objective optimization study involving cost and control properties of four reactive distillation configurations to produce Diphenyl Carbonate, the utilized multi-objective optimization algorithm has proven to be a powerful tool to deal with the complex structure of these configurations. These configurations corresponded to the conventional reactive distillation configuration, CRD, the thermally coupled reactive distillation configuration, TCRD, and two novel reactive distillation configurations using vapor recompression technology, these are, RDHI, and THRD.

From the optimized designs of the Pareto charts of each reactive configuration, it was found that the tray holdups values and consequently the diameter values of the columns strongly influence the control properties of the configurations; thus, for large values of the tray holdups and diameters, the control properties were better. The control properties also were influenced by the presence of the interlinking stream in the reactive and separation columns, in particular, the presence of one interlinking stream tend to favor the control properties of a configuration, as in RDHI; however, the presence of two interlinking streams negatively affected these properties as in THRD. Nevertheless, this configuration presented good energy savings.

From all the configurations, the results indicated that the TCRD configuration was the most attractive arrangement to be implemented to produce DPC, mainly because the optimized designs showed the best control properties, and also it is important to mention that significant energy savings were achieved at the optimal designs, and because it did not require electric power, significant reductions in the total annual cost were obtained.

Acknowledgements

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