



Reactive distillation: A review of optimal design using deterministic and stochastic techniques



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ABSTRACT

In the last years, the industries have shown interest in the development of reactive separation processes. Reactive distillation can be considered as reaction and distillation combined into one new unit operation and this integrated separation process is a good example of process intensification. This intensified process offers several important advantages that include the increment of the reaction yield and selectivity, the overcoming of thermodynamic restrictions and the considerable reduction in energy, water and solvent consumptions. Therefore, this process configuration has been applied in several chemical industries. However, due to the strong interactions of chemical reactions and heat and mass transfer, the design of this intensified separation process tends to be quite complex. The design of reactive distillation systems can be performed using single and multi-objective optimization approaches. This paper provides a comprehensive short review on current applications of deterministic and stochastic optimization techniques for the design of reactive distillation. Capabilities and limitations of optimization for reactive distillation design are discussed and topics for future research are provided.

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1. Introduction

Process intensification (PI) is an effective strategy to achieve increased energy efficiency. PI aims at reducing the mass and heat transfer resistances while overcoming thermodynamic limitations through the integrated design and operation. In recent years, PI has attracted considerable academic interest as a potential means for process improvement, to meet the increasing demands for

sustainable production [44,52,49]. A variety of intensified operations developed in the academia and industry creates a large number of options to potentially improve the process performance. However, the identification of the set of feasible solutions for PI in which the optimal condition can be found, may take considerable resources and it can be considered as a challenging task [48,10].

One of the most common examples of the process intensification field is the reactive distillation (RD), where the integration of reaction and separation is performed (Fig. 1). In all the cases where reactive distillation has been used, the variable cost, capital expenditure and energy requirement are reduced by 20% or more, when compared to the classic set-up of a reactor followed by

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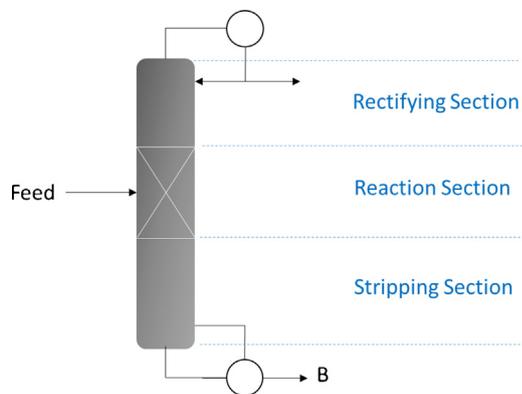


Fig. 1. Reactive distillation column.

distillation [27,64,59]. The first patents of RD, which were for the application of homogeneously catalyzed esterification, are of 1920s [5,6]. The first heterogeneously catalyzed process was patented for the production of methyl tert-butyl ether [61]. Although invented in 1921, the industrial application of reactive distillation did not take place before the 1980s [39]. Classic success stories in reactive distillation are the Eastman Chemical Co.'s methyl acetate reactive distillation process and the processes for the synthesis of fuel ethers. Some of the obtained improvements are so dramatic, for example, five times lower investment and five times lower energy use for the Eastman process [60]. The commercial success of reactive distillation for the production of MTBE was immediately followed by other remarkable achievements [63] and the last few years have seen a dramatic rise in the number of applications of RD. This useful technology is now being applied for any scale of operation from manufacture of fine chemicals to that of bulk chemicals. Applications for RD include esterification, transesterification, hydrolysis, etherification, hydrogenation, dehydrogenation, alkylation, metathesis and disproportionation, hydration and dehydration, carbonylation, production of polymers, alcoxysilanes and acyloxysilanes production, chlorination and amination, synthesis of carbonates, application for chiral separation, recovery of chemicals, and miscellaneous reactions such as those involved in the production of phenol, propylene oxide process, synthesis of vinyl acetate, among others [36].

Basically, RD is a process where the chemical reactor is also the separator. The concept of combining these two important functions for the enhancement of process performance is considered an important contribution in the chemical engineering community. Separation of the product from the reaction mixture does not need a separate distillation step, which saves energy (for heating) and materials [63]. This separation process is particularly attractive and useful for equilibrium-limited reactions. Therefore, it can be suitable for the disproportionate reactions because it eliminates conversion and phase equilibrium limitations. Note that conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone [63]. This helps to reduce the capital and investment costs and this process may be important for sustainable development due to a lower consumption of resources [41]. It is convenient to remark that the suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible [19–21]. Therefore, the exploring of the candidate reactions for RD is an area that needs considerable attention to expand the domain of RD processes for other promising industrial applications.

Being a relatively new field, the research on various aspects of RD design such as modeling and simulation, process synthesis,

column hardware design, non-linear dynamics and control is in progress. In particular, the design of RD columns focuses on the identification of the characteristics and operating conditions of the separation system to improve its performance, cost, profitability, safety, reliability and other attributes of interest. The design issues for reactive distillation systems are significantly more complex than those involved in ordinary distillation. For example, the catalyst selection, liquid holdup on each tray, and position of feeds become important design considerations. Reaction often occurs in the liquid holdup so that the reaction volume is a major design parameter, and constant molar overflow cannot be assumed. Also, a single feed may not be appropriate and a distributed feed must be considered. The design complexity increases with the configuration of the separation system (e.g., Petlyuk or thermally coupled columns) due to the increment on the degree of freedoms.

Results reported in the literature showed that the optimization strategies can be reliably used for facing this relevant design problem in chemical engineering. In particular, the optimization methods are important tools for process modeling, synthesis, design, operation and retrofitting of separation systems (Rangaiah and Bonilla-Petriciolet [74]). However, the design of RD columns is a complex optimization problem with challenging features for current optimization strategies. Overall, the design of RD systems involves several degrees of freedom with both continuous and discontinuous design variables and the presence of non-linear and potentially non-convex objective functions (i.e., characteristics or performance criteria to be maximized or minimized), which can be subjected to both equality and inequality constraints. Therefore, the research in the application of improved optimization methods for RD design has grown significantly during last years.

This review analyzes and describes the application of optimization techniques for the design of reactive distillation columns. This work provides a survey of different deterministic and stochastic optimization methods applied for solving this design problem. Capabilities and limitations of current numerical strategies have been discussed, including single and multi-objective optimization methods, and topics for further research are also described.

1.1. Formulation of the design of reactive distillation columns as an optimization problem

The objective of this section is to define the general formulation of the optimization problem for the design of RD columns. Overall, this design problem can be stated as follows

$$\text{Optimize } \{f_1(\vec{x}), f_2(\vec{x}), \dots, f_{n_{\text{obj}}}(\vec{x})\} \quad (1)$$

subject to

$$g_i(\vec{x}) \leq 0 \quad i = 1, 2, \dots, n_{\text{ine}} \quad (2)$$

$$h_i(\vec{x}) = 0 \quad i = 1, 2, \dots, n_e \quad (3)$$

$$\vec{x}_L < \vec{x} < \vec{x}_U \quad (4)$$

where f_i is the objective function i (i.e. attribute or characteristics) to be optimized (i.e., maximized or minimized) during the RD column design, n_{obj} is the number of objective functions involved in the RD design, \vec{x} is the vector of m decision variables (continuous and/or discontinuous) with lower (\vec{x}_L) and upper (\vec{x}_U) bounds, n_{ine} and n_e are the number of inequality (g) and equality (h) constraints, respectively. The feasible space for solving the design optimization

Table 1
Summary of some optimization tools applied to reactive distillation columns.

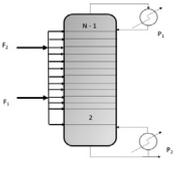
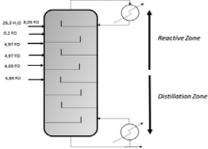
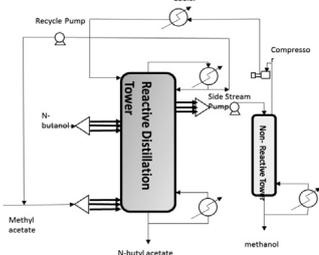
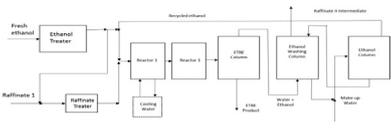
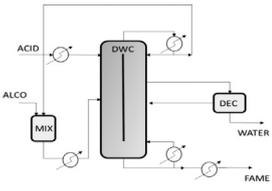
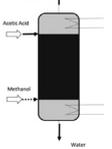
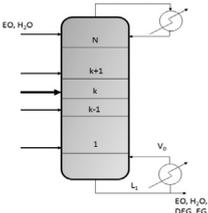
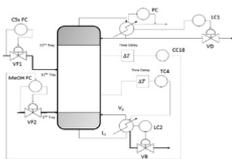
Scheme	Brief description of studied case	Variables to optimize	Objective function	Constrains	Optimization technique	Reference
	Distillation columns with multiple feed with different composition considering several mixtures	Feed stage (F_s) molar flow rate (M_{fr}) pressure at bottoms (P_b) pressure at top (P_t) amount of vapor (V_t)	Optimal feed location	Feed and their location amount of reflux ratio	Deterministic optimization, MINLP model solved using DICOPT ++	[71], Optimal feed locations and number of trays for distillation columns with multiple feeds, Ind. Eng. Chem. Res., 32, 2942.
	Production of ethylene glycol via ethylene oxide in a reactive distillation column	Number of trays (N_t) feed stage (F_s) temperature profile (T_p) composition profile (C_p) reflux ratio (R_r) column diameter (D)	Total annual cost minimization	Material balances V-L equilibrium mole fraction sum enthalpy balances kinetic and thermodynamic relationships	Deterministic Optimization, MINLP model solved using a generalized benders decomposition	[24], Synthesis of nonequilibrium reactive distillation processes by MINLP optimization, AIChE J., 40, 1479.
	Production of methanol and n-butyl acetate by the transesterification reaction of methyl acetate and n-butanol in a reactive distillation column with thermal coupling	Feed ratio (F_r) reflux ratio (R_r) met-acetate temperature (Mat) n-butanol temperature (Bt) stage of n-butanol feed (Sb) stage of methyl acetate (Sm) stage of side stream (S_{ns}) side sStream mol flow (M_{fss}) pressure of column (P)	Reboiler energy cost minimization RD productivity maximization nrdp productivity maximization	Methyl acetate temperature butanol temperature reflux ratio butanol feed stage molar flows column pressure	Stochastic optimization, using non-sorting genetic algorithm II (NSGAI)	[12] Multiobjective optimization of reactive distillation with thermal coupling using non-dominated sorting genetic algorithm-II, J. Nat. Gas Sci. Eng., 3, 365.
	Production of ETBE through the reaction of ethanol and isobutene in a reactive distillation column	Number of trays (N_t) feed stage (F_s) reactive section (R_s) reflux ratio (R_r) liquid bottom flowrate (L_{bf}) column pressure (P) diamater (D)	Gross annual profit maximization	Material balances thermodynamic relationships	Stochastic optimization, using genetic algorithms and particle swarm optimization	[28], Optimal design of reactive distillation systems: application to the production of ethyl tert-butyl ether (ETBE), Comput. Chem. Eng., 64, 81.
	Production of fatty acids methyl esters (FAME's) such as biodiesel based in a reactive dividing-wall column	Temperature (T) reactive stages (R_s) number of trays (N_t) distillate rate (D_r) side stream flowrate (S_{sfr}) boil up ratio (Br) recycle location (R_l) stage of side stream (S_{ss})	Reboiler duty minimization	Purities of products recoveries of products	Stochastic Optimization, using simulated annealing as optimization method	[42], Reactive DWC leading the way to FAME and fortune, Fuel, 95, 352.
	Production of methyl acetate in a reactive distillation column	Condenser duty (C_d) reboiler duty (R_d) temperature feed (T_f) number of stages (N_s) reactive stages	Total annual cost minimization	Reactive stages non reactive stages minimum product flowrate	Deterministic optimization, MINLP model solved using outer approximation/equaly-relaxatio/augmented-penalty algorithm	[31], MINLP optimization of reactive distillation columns, Comput. Aided Chem. Eng., 8,

Table 1 (Continued)

Scheme	Brief description of studied case	Variables to optimize	Objective function	Constraints	Optimization technique	Reference
	<p>Production of ethylene glycol from ethylene oxide and water in a reactive distillation column</p>	<p>(Rs) feed stages (Fs) number of trays (Nt) Column diameter (D) column height (H) reboiler area (Ra) condenser area (Ca)</p>	<p>Total annual cost minimization</p>	<p>Minimum purity of product bottoms rate distillate rate</p>	<p>deterministic optimization MINLP model solved using a modification of the logic-based outer approximation algorithm</p>	<p>115. [40], A disjunctive programming approach for the optimal design of reactive distillation columns, Comput. Chem. Eng., 25, 1661. [47], Reactive thermally coupled distillation sequences: pareto front, Ind. Eng. Chem. Res., 50, 926.</p>
	<p>Production of biodiesel through esterification process in a reactive distillation column with thermal coupling</p>	<p>Reflux ratio (Rr) feed stage (Fs) reactive stages (Rs) distillate rate (Dr1) interconnection flow (Fl, Fv)</p>	<p>Reboiler duty minimization</p>	<p>Purities of products recoveries of products</p>	<p>Stochastic optimization, using genetics algorithm as optimization method</p>	<p>[47], Reactive thermally coupled distillation sequences: pareto front, Ind. Eng. Chem. Res., 50, 926.</p>
	<p>Production of methyl tert-butyl ether produced from isobutene and n-butane in a reactive distillation column</p>	<p>Number of trays (Nt) feed stream (Fs) pressure (P) amount catalyst (Ac) reflux ratio (Rr) pressure (P)</p>	<p>Annual profit maximization</p>	<p>Purity product at top purity product at bottom</p>	<p>Hybrid optimization using a memetic algorithm as optimization method</p>	<p>[67] Optimization-based design of reactive distillation columns using a memetic algorithm, Comput. Chem. Eng., 35, 787.</p>
	<p>Production of ethylene glycol from ethylene oxide and water in optimization of steady a reactive distillation column</p>	<p>Temperature of tray (Tt) vapor flow rate (Vfr) liquid hold up (Lh) efficient reactive distillation optimization molar flow rate (Mfr) feed stream temperature (Tfs)</p>	<p>A performance index minimization</p>	<p>Liquid holdup of trays "vapor flow rates of trays liquid flow rates of trays mol purity of product</p>	<p>Stochastic optimization using an equation-oriented state chemical processes (SIMOP) deterministic optimization,</p>	<p>[43], SIMOP: using stochastic optimizers, Chem. Eng. Sci., 61, 1718. [62],</p>
	<p>Production of methyl tert-butyl ether from methanol and isobutylene</p>	<p>Reflux ratio (Rr) energy demand (ED) feed stage (Fs) reactive stages (Rs)</p>	<p>Total annual cost minimization</p>	<p></p>	<p>MINLP model solved using DICOPT ++</p>	<p>Mixed-integer nonlinear programming optimization of reactive distillation processes, Ind. Eng. Chem. Res., 40, 5978. [62],</p>
	<p>Production of ethylene glycol from ethylene oxide and water in a reactive distillation column</p>	<p>Vapor flow rate of tray (Vfrt) liquid flow rate of tray (Lfrt) liquid holdup (Lh) number of trays (NT) feed rate (FR) reboiler duty</p>	<p>Total annual cost minimization</p>	<p>Vapor flow rate of product liquid flowrate of product liquid hold up amount of trays</p>	<p>Stochastic optimization using differential evolution</p>	<p>[62], Mixed-integer nonlinear programming optimization of reactive distillation processes, Ind. and Eng.</p>

Table 1 (Continued)

Scheme	Brief description of studied case	Variables to optimize	Objective function	Constrains	Optimization technique	Reference
		(RD) condenser duty (CD) column diameter (D) height of the tower (H)				Chem. Res., 40, 5978.
	Production of t-amyl-methyl-ether from isoamylenes and methanol in a reactive distillation column	Molar flow (MF) temperature (T)	Controller overshoots minimization controller integral of absolute errors minimization	Gain of each controlled component integral time of each controller component	Stochastic optimization using non-dominated sorting genetic algorithm II (NSGAI)	[13], Control of TAME reactive distillation using non-dominated sorting genetic algorithm-II, J. Loss Prev. Process Ind., 25, 192.

problem is the set of vectors \vec{x} that satisfy all the constraints and bounds given by Eqs. (2)–(4).

The objective functions f_i involved in the design of RD columns measure the process performance and operation. They can be related to the metrics of separation effectiveness, economic indicators, safety and reliability, environmental impact, control properties and other attributes/characteristics of interest for the process including any combination of them. The RD design may involve only one objective to be optimized and the problem is solved as a straightforward optimization problem. If two or more objective functions should be optimized simultaneously, the problem is handled as a multi-objective optimization. Under this scenario, the objective functions used in the design may be conflicting, fully or partially, over the range of interest. The analysis of multi-objective design problems is performed via the Pareto fronts. Traditionally, the objective functions involved in RD design are highly non-linear, multivariable and potentially non-convex. Table 1 contains a survey of different objective functions employed for the design of reactive distillation columns. As expected, the complexity and difficulty of solving RD optimization problems, including the analysis of their solutions, are likely to increase with the number of objective functions considered in the design.

On the other hand, the decision variables in the optimization of RD columns are degrees of freedom that control the operation, configuration and physical characteristics of the separation system. The feed location, the operating temperature or pressure, the reflux ratios, the column stages, the feed location, and the interconnection flows are examples of the design variables involved in the optimization of RD columns. It is important to note that the RD column design implies both continuous and discrete variables. The presence of discrete variables (e.g., the stage number, the feed location) increases the problem complexity due to the design space is disjoint and potentially non-convex. Additionally, the constraints impose limits for the feasible values of design variables. The feasible search space of the design problem is determined by these constraints. The inequality and equality constraints may be derived from physical restrictions for the separation system or are defined considering an expected/desired process performance. For example, the target value for the recovery of a key component in the separation system can be handled by an inequality constraint: $x_A \geq 0.95$ or it can be

considered as an objective function for process design: the maximization of x_A . In general, the presence of these constraints increases the design problem complexity. Note that these constraints have different formulation for different configurations of the reactive distillation columns, see Table 1.

In summary, the difficulty and complexity of the RD design optimization problem are determined by the properties and mathematical relationships among the objectives or performance criteria to be optimized, the type of decision variables and the presence and properties of the constraints. For illustration, Table 1 contains the optimization problem formulation for the design of different types of reactive distillation columns. These characteristics also restrict the optimization strategy that should be used for its resolution Rangaiah and Bonilla-Petriciolet [74].

To date, a wide variety of optimization methods have been used to solve the design of RD columns. These methods include algorithms with local and global convergence properties for handling one or more objective functions. Table 1 summarizes several optimization methods used for designing reactive distillation columns. These methods include strategies for solving systems of non-linear equations or the direct optimization of the set of objective functions. The characteristics, convergence properties, capabilities and limitations of these optimization tools may vary significantly depending on the problem at hand. In the following section, an overview of several deterministic and stochastic optimization methods used for RD column design is provided.

2. Design of reactive distillation using deterministic optimization techniques

Several deterministic optimization methods for the design of equilibrium and non-equilibrium reactive distillation columns have been proposed that utilize mathematical programming models [25,35,14,8,7,11].

Ćirić and Gu [24] were first to present a rigorous, tray-by-tray model. Their MINLP model, which is solved with Generalized Benders Decomposition, is similar to the work by Viswanathan and Reddy [71] for optimizing a conventional distillation column, but ignores effects of liquid enthalpies. The number of trays is optimized in this model by multiplying related constraints with

a binary variable that represents the existence of a tray. This formulation introduces bilinearities that complicate the resolution and exhibits poor numerical behavior.

A design algorithm and software for a local optimization approach for reactive distillation are presented in the paper by Pekkanen [51]. Cervantes and Biegler [22] presented an efficient and stable decomposition method for solving differential algebraic equation optimization problems. Here, orthogonal collocation is used within a sparse rSQP framework in order to obtain the control profiles and the parameters given a fixed element placement. They have shown that the sparse decomposition of the discretized system is more efficient than in previous approaches. This new strategy also allows us to detect unstable modes automatically by a simple selection of pivots. Most of the works in reactive distillation has focused upon computing a single steady state solution to the material balances, but little work has been done with dynamic models, especially in the dynamic optimization area. In this work, Cervantes and Biegler [22] have formulated and solved dynamic index one optimization problems for both batch and continuous reactive distillation columns.

The optimization is based on directions in the concentration space. Frey and Stichlmair [31] have studied a MINLP model based on the concept of equilibrium stages in a reactive distillation scheme. To guarantee that the superstructure contains all physical relevant process alternatives, the definition of the superstructure is based on a thermodynamic background. The MINLP optimization can be performed with respect to minimum energy requirement or minimum total annual costs [46]. Poth et al. [53] presented a MINLP optimization of a kinetically controlled reactive distillation process (MTBE process), based on the concepts of equilibrium stage and tray efficiencies. The outer-approximation/equality-relaxation/augmented-penalty (OA/ER/AP) algorithm is used. Further, the proposed MINLP problem for methyl acetate production was solved using GAMS in combination with external function by Poth et al. [54].

Seferlis and Grievink [58] stated that an increase in the number of discrete variables typically leads to a substantial increase of the computational effort needed for the problem resolution in the design of a reactive distillation column. Under this scenario, the optimization strategies may face several difficulties for reaching convergence and finding the optimum configuration.

Jackson and Grossmann [40] have developed a new optimization model for the rigorous design of kinetically controlled reactive distillation columns. The proposed model is based on the Generalized Disjunctive Programming (GDP) framework developed by Yeomans and Grossmann [73] for the design and synthesis of distillation columns. The nonlinear tray-by-tray model is described, as well as the solution algorithm that is applied to two different problems. Burri and Manousiouthakis [16] presented a methodology for the global optimization of reactive distillation networks using the infinite dimensional state-space approach. This conceptual framework is realized through the solution of a series of finite dimensional linear programs. The proposed methodology is showed on a case study involving reactive distillation-based synthesis of methyl tert-butyl ether. Gomez et al. [34] proposed MINLP formulation for optimal design of catalytic distillation based on generic non-equilibrium model. The minimization of annualized cost in the case of ETBE catalytic distillation is studied.

For the optimization of reactive distillation columns, Barkmann et al. [9], Sand et al. [55] and other authors have shown that the quality of the solutions found by local nonlinear optimization could be significantly improved by the use of a scatter search based multi-start heuristic; but the price for this improvement was an increase of the computational effort.

An attempt to determine the global optimum was made by two methods namely, the multi-start algorithmic approach and the

deterministic polyhedral relaxation technique, for the design of reactive distillation columns for (a) isomerization of 2,3-dimethylbutene-2 to 2,3-dimethylbutene-1 and (b) synthesis of butyl acetate [32]. Due to complex interaction of reactions and distillation, the identification of an appropriate reactive distillation configuration for the known performance targets has been a challenge. Amte et al. [3] reported an MINLP optimization technique that would assist one to identify a suitable configuration for selectivity maximization at conceptual design level. An illustrative example of industrially important reaction of dimerization of isobutene for maximizing the selectivity toward diisobutene is considered. A survey of different resolution methods for the design optimization of reactive distillation columns can be found in Almeida-Rivera et al. [2] and Stichlmair and Frey [62].

The multi-objective design of complex reactive distillation columns has been analyzed by Filipe et al. [29,30]. The concept of feasible regions is employed to investigate the use of internal reaction distribution, as well as superheated and subcooled feeds. They obtained the Pareto surfaces relating the amount of reactive holdup, the number of stages and a cost indicator reflecting energy usage and column size. The ϵ -constraint method was used for solving the multi-objective optimization problem.

Butyl-levulinate (LBE) has been identified as a valuable fuel component for low emission combustion in diesel engines. Harwardt et al. [37] have studied a process for the production of LBE. They have formulated a rigorous column model. The reactive distillation column is modeled with a tray-by-tray model, assuming equilibrium on each tray, which is calculated using the NRTL model. The resulting mixed-integer nonlinear programming problem (MINLP) is reformulated as a continuous nonlinear programming problem (NLP) to achieve faster convergence. The SNOPT (sequential nonlinear optimiser) solver has been used to solve the nonlinear programs. The optimization results included an optimal column design and optimal operating conditions with respect to the provided economic model.

Several deterministic methods are able to achieve the global minimum on energy consumption, but they demand high mathematical efforts. Furthermore, the formulation of such design models is difficult and time consuming. In addition to the time and expertise needed to formulate these models, the synthesis and design of distillation sequences pose other difficulties. Finally, additional convergence problems are generated when discontinuous functions, such as complex cost functions, are introduced in the model. To compensate for these difficulties, it is often necessary to supply initial values for the optimization variables very close to the actual solution, something that is not always an easy task. Recent studies have employed simplifications for the design model, thermodynamics, hydraulics, or cost functions to obtain feasible solutions or to examine complex superstructures in the synthesis problems.

As stated, the optimal design of reactive distillation systems is a highly non-linear and multivariable problem, with the presence of both continuous and discontinuous design variables; also, the objective function used as optimization criterion is generally non-convex with several local optima and subject to several constraints. Due to the non-monotonic and local optimum properties of the search space, conventional derivative-based optimization algorithms turned out to be incapable of finding the global optimum design in most cases.

3. Design of reactive distillation using stochastic optimization techniques

Stochastic optimization algorithms are capable of solving, robustly and efficiently, the challenging multi-modal optimization problems, and they appear to be a suitable alternative for the

design and optimization of complex separation schemes. In this context, stochastic optimization methods are playing an important role in process intensification because they are generally robust numerical tools that present a reasonable computational effort in the optimization of multivariable functions, are applicable to unknown structure problems (i.e., black box models), require only calculations of the objective function, and can be used with all models without problem reformulation [65]. Based on these characteristics, several stochastic optimization methods have been reported for the design of RD columns.

Specifically, a simulated annealing-based algorithm (MSIMPISA) suitable for the optimization of mixed integer non-linear programming (MINLP) problems was applied to the synthesis of a non-equilibrium reactive distillation column in the work of Cardoso et al. [18]. In particular, MSIMPISA is a combination of simulated annealing metaheuristic and the simplex method of Nelder and Mead. The optimization was performed with non-ideal vapor–liquid equilibrium, considering either distributed feed and reaction trays or single feed and reaction tray. The results showed that the optimized objective function values were very similar, and mostly independent of the number of trays and of the reaction distribution. In addition, the performance of MSIMPISA was better than reported for adaptive random search algorithm. This approach can be applied to single and multiple reactions, ideal or non-ideal mixtures with vapor–liquid equilibrium and distributed or single-staged reaction zones. Herein, it is convenient to remark that these authors indicated that the objective function was flat and, consequently, optimization runs with starting random values for design variables generated different MINLP solutions. Therefore, this method can not guarantee the global optimality.

Due to their combinatorial nature, MINLP problems have been studied using evolutionary algorithms (e.g. genetic algorithm), which are effective population-based methods for solving mono and multi-objective problems [26]. Sand et al. [56] studied the conceptual design of reactive distillation column by application of MINLP based hybrid optimization methods extended by means of heuristic/stochastic algorithm for the global resolution of the optimization problems. On the other hand, Lima et al. [43] have proposed a methodology to improve the efficiency of stochastic methods applied to the optimization of reactive distillation columns with a large number of equality constraints. The methodology is based on the optimization of the simulation step, and the optimization of the nonlinear programming problem using stochastic methods. These methods are MSIMPISA and MSGA, which is an adaptive random search algorithm. Both stochastic methods have shown promising results for solving difficult NLP and MINLP problems. The results obtained suggest that in addition to the choice of design variables, the structure of subsystems associated to numerical procedures has a considerable impact on the performance of the optimizers. Authors have recognized that even though these stochastic optimizers showed a good performance for escaping from difficult local optima, these optimizers do not offer a theoretical guarantee for global optimization. Overall, MSGA algorithm offered a best performance, in terms of algorithm reliability and efficiency, than that obtained for MSIMPISA.

The optimization of reactive distillation processes using differential evolution strategies was studied by Babu and Khan [4]. The differential evolution algorithm was applied to find the minimum total annualized cost of the non-equilibrium reactive distillation for the synthesis of ethylene glycol, which is a MINLP optimization problem. Differential evolution is one of the most reliable population-based stochastic methods and it is considered as an improved version of genetic algorithms. It is shown that the proposed method with differential evolution strategy was capable of providing optimized solutions, which were close to the global

optimum. In fact, authors concluded that differential evolution is an easier and faster optimizer as compared to simulated annealing in the synthesis of reactive distillation columns.

Cheng et al. [23] studied a derivative-free optimization approach, simulated annealing, for the optimization of the reactive distillation column design. Simulated annealing employs the metropolis criterion and emulates the process in which melts freeze or metals grow crystals in the process of annealing. The simulated annealing-based optimization procedure found an equally good or better design than the optimal flowsheet obtained from the sequential design approach. More importantly, this was achieved with a significant reduction in computing time. However, high nonlinearity of the optimization problem caused that simulated annealing may be trapped at local minimum. Overall, authors concluded that simulated annealing is an efficient optimizer and may provide reasonable engineering design.

Miranda-Galindo et al. [47] introduced the application of a multi-objective optimization approach for the design of reactive distillation sequences with thermal coupling. The esterification of methanol and lauric acid was studied in direct and indirect reactive sequences, both conventional and thermally coupled. The optimal designs were obtained through a multi-objective genetic algorithm with constraints, which was based on NSGA-II method. This evolutionary algorithm was coupled with Aspen Plus to perform rigorous simulations of tested separation systems. Optimization targets analyzed in this study were the column stages, heat duties and the size of the reactive zone. The results showed that obtaining the ester with a purity of 99.9% was feasible in conventional and thermally coupled distillation sequences. However, lower energy consumptions, and consequently lower CO₂ emissions, were observed in the thermally coupled sequences.

As indicated, the design optimization of reactive distillation column is characterized by complex nonlinear constraints, nonlinear cost functions, and the presence of many local optima. Under these conditions, Urselmann et al. [67] have proposed a new approach combining evolutionary algorithms, which have the ability to escape from local optima and can handle integrality constraints and discontinuous cost functions, with a nonlinear solver, which can efficiently solve the continuous subproblems for given initial values but only provides a local solution. Note that a memetic algorithm is a population-based hybrid evolutionary algorithm, which is coupled with local refinement strategies. The application of the local search method allows to improve the quality solution and also to reduce the computer time. The computational effort needed to find the optimal solution with a success rate of 100% was reduced by more than one order of magnitude compared to a commercially available global search algorithm.

Recently, Kiss et al. [42] have proposed a novel biodiesel process based on a reactive dividing-wall column. The optimal scheme was established by using simulated annealing as optimization method implemented in Matlab, and coupled with rigorous simulations carried out in Aspen Plus. The novel design allowed savings by reducing the energy requirements with over 25% and by using less equipment units than conventional processes. Authors indicated that the CPU time involved in optimization is high due to the requirements of Aspen Plus for process simulation. However, simulated annealing offered a best performance than genetic algorithm and harmony search in the design of complex distillation sequences.

Vázquez-Ojeda et al. [68] have studied the design of reactive distillation with thermal coupling with minimum number of reboilers, for esterification of lauric acid and methanol, using differential evolution with restrictions coupled to Aspen Plus. The results indicated that the energy consumption and total annual cost of the complex distillation sequence with minimum number

of reboilers were reduced significantly in comparison with conventional reactive distillation process.

In a recent study, Behroozsarand and Shafiei [75] reported the multi-objective optimization of transesterification reactive distillation column with thermal coupling using non-sorting genetic algorithm. A visual C++ (VC++) code for real-parameter NSGA-II and HYSYS software for thermodynamic calculation of reactive distillation column have been linked to optimize the effective parameters of reactive distillation column. The NSGA-II proposed multiple solutions set as optimal solutions, but from these results, three sets gave better results than the others.

An optimization system, which hybridized a genetic algorithm application and a process simulator, was developed for the design of a reactive distillation process [66]. Based on the fact that genetic algorithms usually show a slow rate convergence and premature convergence, this study used a niche genetic algorithm technique to improve the diversity within the population and, consequently, its numerical performance. The application of multi-niche crowding algorithm allowed the search to yield various design solutions without causing remarkable performance degradation when searching for the best design in a case study on a distillation process involving the esterification of acetyl acetate.

Behroozsarand and Shafiei [13] have studied the optimization of dynamic state of *t*-amyl-methyl-ether in reactive distillation process using non-dominated sorting genetic algorithm-II (NSGA-II). This paper presented the tuning of proportional–integral–derivative controllers by minimization of two objective functions through the NSGA-II. Results showed that genetic algorithm is a suitable method for optimal control of the TAME reactive distillation columns.

Domingues et al. [28] have studied the design of reactive distillation columns to produce ETBE. An evolutionary algorithm was used to generate a sequence of feasible designs with improved characteristics in a sequential solution-optimization strategy. Two classes of optimization algorithms were compared: genetic algorithms and particle swarm optimization. The objective function considered was the gross annual profit where the optimization variables were the number of trays, the feed location, the reactive section height and location, liquid bottom flowrate and column pressure and diameter. The results showed that both algorithms are adequate to solve this design problem. However, particle swarm optimization solved the design problem faster than genetic algorithm.

The dehydration of 1-pentanol to yield di-*n*-pentyl ether (DNPE) is catalyzed by thermally stable resins. So, Bildea et al. [15] analyzed two process options: a reaction-separation-recycle system based on an adiabatic tubular reactor and a catalytic distillation process. Both processes were optimized using differential evolution with tabu list in terms of total annual costs. The new DNPE process alternatives (with catalytic distillation) were better process candidates, requiring simpler units leading to much smaller investment costs, while also having good controllability.

It is clear that the design of reactive distillation columns is a complex problem and there are still a limited number of studies concerning the applications of techniques using stochastic optimization methods, in order to make “easier” solving the associated mathematical problem. In fact, the stochastic optimization methods offer several advantages for solving design optimization problems for RD. On the other, reported studies indicate that population-based methods such as differential evolution, genetic algorithms and particle swarm optimization are the traditional options for single and multi-objective optimization of reactive separation schemes. Simulated annealing, a point-to-point method, is also a reliable strategy for the optimization and design of reactive separation systems.

4. Perspectives of future research and challenges in the design optimization of reactive distillation

Traditionally, chemical processes are designed by a sequential approach involving a sequence of decisions. The process is initially designed based on steady-state economic calculations followed by the synthesis of a control structure. This approach sometimes may lead to iterations between the process design and the control system design, and may also lead to poor dynamic operability in face of disturbances and uncertainties. Therefore, it is valuable and important to investigate the interactions between the process design and process control and process operability to improve the dynamic performance of chemical processes at the early design stage [72,69]. The need to simultaneously design, evaluate and control chemical process systems is important. The importance of this challenge, in the case of the reactive distillation, is evident. The work in the area of integration of design and control in reactive distillation systems is very limited. Heath et al. [38] studied the interactions of design and control in an ethylene glycol reactive distillation system assuming that the process structure is fixed (e.g., number of trays, feed tray location, etc). Schenk et al. [57] and Georgiadis et al. [33] compared sequential and simultaneous approaches to design and control of a reactive distillation system using advanced optimization techniques. Again, the process and control structure were assumed fixed. The design and control of a methyl acetate reactive distillation column have been studied, and several steady-state multiplicities have been reported by Al-Arfaj and Luyben [1]. The impact of these multiplicities on the open loop stabilities is discussed. The systems that are open loop unstable are harder to control than open loop stable systems. Several control structures have been studied. The interaction between the design and control is examined by changing the conversion level. Low-conversion designs are less nonlinear and are easier to control. It is important to consider both design and control together in the design stage. Design and control of two alternative processes for the production of butyl acetate from methyl acetate have studied by Luyben et al. [45]. Both processes are capable of producing high purity butyl acetate and methanol without the use of an extractive agent. The reactive distillation process is more economical. Both processes can be effectively controlled using conventional PI controllers by using an appropriate plant-wide control structure that manages the addition of fresh feeds and stabilizes recycle flow rates. Other example of design and optimal control of a reactive distillation system is the paper of Panjwani et al. [50]. A mixed-integer dynamic optimization (MIDO) model and solution strategy to study the interactions between process design and process control-operability of an ethyl acetate reactive distillation system is presented. It is clear that the resolution of the simultaneous design and control problems using rigorous models and leaving all optimization variables unfixed for design and control is an issue of great challenges.

Herein, it is important to note that stochastic methods are being increasingly used for solving complex, nonlinear, and nonconvex optimization control problems. For example, Venkateswarlu and Reddy [70] using optimization based nonlinear model predictive controllers (NMPCs), namely, GANMPC and SANMPC, applied to control a reactive distillation column. The results demonstrated the better performance of the stochastic optimization based NMPCs over a conventional PI controller, a linear model predictive controller (LMPC), and a nonlinear model predictive controller (NMPC) based on sequential quadratic programming (SQP). The stochastic optimizers, because of their stochastic nature, may not provide a rigorous guaranty for global optimality, but the problem formulation along with the constraints is simple and straightforward. With the availability of low-cost computing, these methods can be applied to solve even larger optimization problems.

Recently, Cabrera-Ruiz et al. [17] have developed a software tool that realizes global optimization through stochastic methods where the dynamic control behavior is considered. The methodology was proved in complex distillation sequence using a simulated annealing-based method as stochastic optimization algorithm. The results showed that the proposed objective function is acceptable for the search of global optimum of the best control structure. As can be seen a challenge in the future, on the topic of reactive distillation, is the generation of new approach to define and embed an objective function that can be solved through stochastic optimization techniques and gives an insight into design and dynamic behavior for the intensification of these complex distillation schemes. This objective function for analyzing control properties of RD schemes can be also incorporated in multi-objective design problems using other performance indicators related to economics, eco-indicators, safety, etc.

With respect to the convergence properties and reliability of current optimization methods, authors have identified that the stochastic optimization methods are promising numerical tools for RD column design. However, it is important to develop new optimization methods with better convergence properties for solving multivariable and non-convex RD design problems. In particular, new stochastic methods that require a reduced computer time are required for process intensification of RD sequences. Results reported in several studies showed that the performance of current meta-heuristics may be poor for complex design problem and the global optimality is not guaranteed. In addition, more studies on multi-objective optimization of RD sequences should be performed. This type of studies is relevant for developing robust design methodologies for RD columns.

In summary, there is a large area of research available in the field of RD design using optimization methods. In particular, the application of the non-equilibrium models, hybrids and intensified processes, bioprocess applications, and other topics are relevant for this field. Future studies should be focused on these topics for developing effective and low-cost RD processes.

5. Conclusions

Scores of advances in different aspects within the design of reactive distillation using deterministic and stochastic optimization techniques have been analyzed. Reactive distillation, an example of process intensification, has emerged as an economical unit operation. The main reason for employing this process is that reactive distillation overcomes the reaction equilibrium limitation found in traditional separation – reaction schemes. Reactive distillation can naturally use the heat of reaction as a heating or cooling source. Furthermore, reducing the initial investment and operating costs for an azeotropic system has a dramatic economic effect. Despite the recent advances, it can be claimed the complexity in the design of reactive distillation. One important reason is the difficulty associated with the modeling and non-linear and multivariable equation systems of these processes and the parametric uncertainty of the model parameters. As a result, reliable and consistent models (for property prediction, reaction kinetics, and process simulation) are not available, and the dependence of the model parameters is unknown. Stochastic optimization algorithms are capable of solving, robustly and efficiently, the challenging multi-modal optimization problem, and they appear to be a suitable alternative for the design and optimization of complex separation schemes taking into account one or several objective functions. Few studies have focused on the optimal design of reactive distillation columns, and it is an emerging field of great importance to explore in the area of process design. This is because of numerical robustness and computational efficiency achieved by stochastic optimization techniques.

Additionally, the next step in the area of reactive distillation is the simultaneous optimal design and control: a problem of great numerical scale and where stochastic optimization techniques could be a viable option for solving the above problem in an efficient alternative. Also, it is important to improve the convergence properties and robustness of stochastic optimization methods for assuring the global optimality in both one objective and multi-objective optimization problems involved in the process intensification of RD systems.

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