I&EC research
Industrial & Engineering Chemistry Research

ARTICLE

pubs.acs.org/IECR

Optimization and Controllability Analysis of Thermally Coupled Reactive Distillation Arrangements with Minimum Use of Reboilers

María Vázquez-Ojeda,[†] Juan Gabriel Segovia-Hernández,*[,†] Salvador Hernández,[†]
Arturo Hernández-Aguirre,[‡] and Rafael Maya-Yescas[§]

[†]Departamento de Ingeniería Química, Campus Guanajuato, Universidad de Guanajuato, Noria Alta s/n, 36050, Guanajuato, Gto., Mexico

[‡]Departamento de Ciencias Computacionales, CIMAT, A.C., Callejón de Jalisco s/n, 36240, Mineral de Valenciana, Guanajuato, Gto., México

[§]Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás Hidalgo, Santiago Tapia 403, Morelia, Mich., México

ABSTRACT: The optimal design of reactive complex distillation systems is a highly nonlinear and multivariable problem, and the objective function used as optimization criterion is generally nonconvex with several local optimums and subject to several constraints. The esterification of lauric acid and methanol is explored using thermally coupled distillation sequences with side columns and with a minimum number of reboilers. The product of the esterification can be used as biodiesel. This is a major step forward since thermally coupled reactive distillation sequences with side columns and with a minimum number of reboilers offer significant benefits, such as the following: reductions on both capital investment and operating costs due to the absence of the reboilers and higher conversion and selectivity since products are removed as they are produced as well as no occurrence of thermal degradation of the products due to a lower temperature profile in the column. In this work, we have studied the design of reactive distillation with thermal coupling with a minimum number of reboilers, using differential evolution with restrictions coupled to AspenONE Aspen Plus. Also, we have analyzed the control properties of the reactive distillation schemes studied, and the results indicate that the energy requirements and the total annual cost of the complex distillation sequences with a minimum number of reboilers are reduced significantly in comparison with the conventional reactive distillation process and can be also achieved without significant control problems.

1. INTRODUCTION

The world is presently confronted with the twin crises of fossil fuel depletion and environmental degradation. Indiscriminate extraction and lavish consumption of fossil fuels have led to a reduction in underground-based carbon resources. The search for alternative fuels, which promise a harmonious correlation with sustainable development, energy conservation, efficiency, and environmental preservation, has become highly pronounced in the present context. The fuels of bio-origin can provide a feasible solution to this worldwide petroleum crisis. Gasoline and diesel-driven automobiles are the major sources of greenhouse gases emission.[1−3] Scientists around the world have explored several alternative energy resources, which have the potential to quench the ever-increasing energy thirst of today's population. Various biofuel energy resources explored include biomass, biogas,[4] primary alcohols, vegetable oils, biodiesel, etc. These alternative energy resources are largely environment-friendly, but they need to be evaluated on a case-to-case basis for their advantages, disadvantages, and specific applications. Some of these fuels can be used directly, while others need to be formulated to bring the relevant properties closer to conventional fuels.[5]

Biodiesel, the common name for fatty acid methyl esters (FAMEs), is a liquid fuel obtained from the transesterification of vegetable (or animal) oils. It involves simply the reaction, under very mild conditions, between vegetable oil and typically a large excess of alcohol of methanol, in the presence of an acid or basic catalyst, which produces FAMEs as the main product and glycerol as a byproduct.[6] Biodiesel has drawn significant attention due to increasing environmental concern and diminishing petroleum reserves. Biodiesel is a renewable and environmentally friendly energy. Application of this energy not only can significantly reduce the pollution generated from petroleum based diesel oil but also can lessen the dependence on petroleum. Presently, biodiesel is produced commercially in Europe and USA to reduce air pollution and the net emission of greenhouse gas. Surplus edible oils, such as rapeseed oil, soybean oil, or castor oil, used cooking oil, rice bran oil, and algae, among others, are used as raw materials for biodiesel.[7−10] Outstanding benefits of biodiesel are the high cetane numbers that it naturally achieves and the lack of polluting heteroatoms like sulfur or nitrogen. Cetane number increase and sulfur/nitrogen content reduction are the most capital intensive hydrotreatment processes that a conventional refinery has to handle, a fact that lays the ground for the biodiesel niche in the near-future refining business.[11] Also, biodiesel is safe, renewable, nontoxic, and biodegradable; it contains no sulfur and is a better lubricant.

Special Issue: AMIDIQ 2011

Received: May 3, 2011
Accepted: December 21, 2011
Revised: December 19, 2011
Published: December 21, 2011

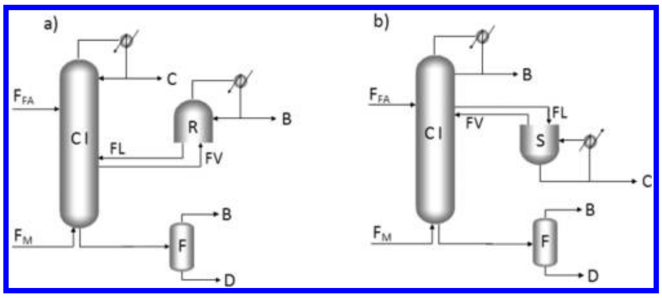


Figure 1. Thermally coupled arrangement with minimum use of reboilers: (a) with side rectifier (TCRDS-SR) and (b) with side stripper (TCRDS-SS).

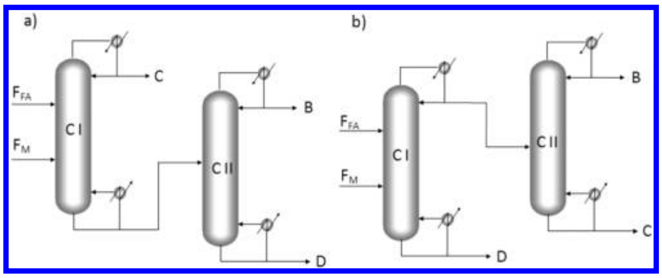


Figure 2. Conventional reactive distillation sequences: (a) direct (DRDS) and (b) indirect (IRDS).

The current manufacturing biodiesel processes, however, have several disadvantages: shifting the equilibrium to fatty esters by using an excess of alcohol that must be separated and recycled, making use of homogeneous catalysts that require neutralization (causing salt waste streams), expensive separation of products from the reaction mixture, and high costs due to relatively complex processes involving one to two reactors and several separation units. Therefore, to solve these problems, some authors have recently developed a biodiesel production process development based on reactive distillation using solid acid catalysts.[12−16] Recent studies show the synthesis of fatty esters by reactive distillation with a novel heat-integrated process.[17] Solid acid catalysts are also used in other processes of intensification such as the reactive adsorption;[18] these works in addition to its economic attractiveness include a study of control and dynamics.[19,20]

Reactive distillation integrates reaction and separation in one unit. This intensifies mass transfer and allows in situ energy integration while simplifying the process flowsheet and operation. However, combining the two operations is possible only if the reactions show reasonable conversion and selectivity data at pressures and temperatures that are compatible with the distillation conditions. The reduction in the number of processing units and the direct heat integration between reaction and separation can reduce capital investment as well as utility costs. Increased overall conversion as well as improved selectivity in competing reactions can be achieved in reactive distillation by the continuous removal of products from the reaction zone of equilibrium limited reactions.[21] Other process improvements can be realized such as reducing byproduct formation, improving raw material usage, and overcoming chemical equilibrium limitations.

Fatty esters are important fine chemicals used in the manufacturing of cosmetics, detergents, and surfactants. Particularly, methyl ester could play a significant role in the future as a major component of biodiesel fuels. Thus, in this paper, the esterification of methanol and lauric acid is studied using thermally coupled distillation sequences with a side column including the cases with a minimum number of reboilers (Figure 1) and conventional reactive distillation sequences (Figure 2). We have generalized, for the reactive distillation case, a differential evolution stochastic algorithm with restrictions coupled to the Aspen ONE Aspen Plus process simulator for the evaluation of the objective function and attributes to be optimized simultaneously.

2. DESIGN OF REACTIVE COMPLEX DISTILLATION SYSTEMS

Design issues for reactive distillation systems are significantly more complex than those involved in ordinary distillation.[22] 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. Several optimization methods for the design of nonequilibrium reactive distillation columns have been proposed that utilize mathematical programming models. Ciric and Gu[21] were the 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 Grossmann[23] and Viswanathan and Grossmann[24] for optimizing a conventional distillation column but ignores the 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 introduces bilinearities which complicates the solution and exhibits poor numerical behavior. Jackson and Grossmann[25] 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[26] 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.

These methods are able to achieve the global minimum on energy requirements, but they demand high mathematical efforts. Furthermore, the formulation of such 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. Even recent studies have employed simplifications for the design model, thermodynamics, hydraulics, or cost functions to obtain feasible solutions or to examine complex superstructures in synthesis problems.

In general, the optimal design of reactive complex distillation systems is a highly nonlinear and multivariable problem, with the presence of both continuous and discontinuous design variables; also, the objective function used as optimization criterion is generally nonconvex with several local optimums and subject to several constraints. Due to the nonmonotonic 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. Stochastic optimization algorithms are capable of solving, robustly and efficiently, the challenging multimodal optimization problem, and they appear to be a suitable alternative for the design and optimization of complex separation schemes.

Among stochastic algorithms, differential evolution (DE) has shown their merits in approaching the global optimum quickly and steadily. DE is a population-based method that has found several applications in science and engineering, including chemical engineering and for parameter estimation.[27−31] This is a method that optimizes a problem by iteratively trying to improve a candidate solution with regard to a given measure of quality. DE optimizes a problem by maintaining a population of candidate solutions and creating new candidate solutions by combining existing ones according to its simple formulas and then keeping whichever candidate solution has the best score or fitness on the optimization problem at hand. In this way the optimization problem is treated as a black box that merely provides a measure of quality given a candidate solution, and the gradient is therefore not needed. Differential evolution has several features that make it attractive for solving optimization problems with modular simulators, where the model of each unit is only available in an implicit form (black-box model).

3. CASE STUDY

Fatty esters are important fine chemicals used in the manufacturing of cosmetics, detergents, and surfactants. Particularly, methyl ester could play a significant role in the future as a major component of biodiesel fuels.[32] Then, the esterification reaction to generate biodiesel can be conceptually represented by the following equation

$$\text{Alcohol} + \text{FattyAcid} \leftrightarrow \text{Ester} + \text{Water} \tag{1}$$

Particularly, the esterification of methanol and lauric acid is studied using the reactive thermally coupled systems with a minimum number of reboilers, Figure 1, and reactive conventional, Figure 2, distillation sequences. In this reaction, lauric acid is the limiting reactive, so a mixture integrated by methanol, water, and the ester (biodiesel) is generated. The equilibrium of this reaction can be favored if the products are removed as the reaction proceeds. Due to this, we are considering that the reaction just occurs in a section of the first distillation column and not in the second one.

An additional problem may present itself; depending on the acid and the alcohol used, binary or ternary homogeneous azeotropes can be formed in the reactive system. For highly nonideal systems, heterogeneous azeotropes can be formed.[32] These key factors must be considered in order to select the appropriate thermodynamic model when the system is studied with process simulators. For this class of reactive systems, thermodynamic models such as NRTL, can be used to calculate vapor−liquid or vapor−liquid−liquid equilibrium, as required in this case study.

The systems include two feed streams; the first is lauric acid with a flow of 45.4 kmol/h as saturated liquid at 1 atm, and the second is methanol with a flow of 54.48 kmol/h as saturated vapor at 1 atm. The design objective is a process for high-purity fatty ester, over 99.9% mass fraction, suitable for applications in cosmetics, detergents, surfactants, or biodiesel application. It is important to highlight that this equilibrium reaction is usually catalyzed using sulfuric acid or p-toluensulfonic acid. The kinetic model (see Table 1) reported in Steinigeweg and Gmehling[33] was used. In this case it is important to note that using a homogeneous catalyst in the reactive distillation setup has significant drawbacks, such as requiring neutralization and separation, while producing salt waste streams. The use of solid acid catalysts can be an alternative.[12−16]

Table 1. Kinetic Parameters for the Pseudohomogeneous Kinetic Model of the Esterification Reaction

reaction	k°_{i}(mol/g s)	$E_{A,i}$ (kJ/mol)
esterification	9.1164×10^{5}	68.71
hydrolysis	1.4998×10^{4}	64.66

4. OPTIMIZATION STRATEGY

The optimization problem is established for each distillation sequence, considering the objectives, constraints, and variables included. For all schemes presented here, methanol is fed in excess to the reaction that is performed with lauric acid. We considered as initial guess a complete conversion of the lauric acid, and that excess methanol is only obtained as a product. Considering this, we performed the material balances for the products of the reaction. Thereby, the recoveries and mass purities of unreacted methanol and water are calculated with respect to the results of the material balances. For the ester, we specify 99.9% for the mass purity. It is worth mentioning that the conversion of the reaction is not an optimization objective itself; however, we specify the recoveries of the unreacted compound, methanol, and of the principal product, ester, as constraints of the problem. Thereby, indirectly the conversion is considered as an objective.

In the reactive direct and indirect conventional distillation sequences, the objective to minimize is the cost of steam plus the cost of the cooling water in each column. The minimization of this objective is subject to the required recoveries and purities in each product stream

$$\mathrm{Min}(C_U) = f(RR_I, R_{DI}, S_I, S_{FAI}, S_{MI}, S_{IN}, S_{SRI}, S_{ERI}, RR_{II}, R_{DII}, S_{II})$$

$$\text{subject to}$$

$$\vec{y}_m \geq \vec{x}_m \tag{2}$$

where C_U is the cost of steam plus the cost of the cooling water in all columns, RR_I and R_{DI} are the reflux ratio and distillate flow rate in column I, S_I is the number of stages of the column I, S_{FAI} and S_{MI} are the stages of feeds, S_{SRI} and S_{ERI} are the sizes of the reactive sections in the first columns of the conventional reactive distillation sequences (Figure 2), S_{IN} is the feed stage in the column II, RR_{II} and R_{DII} are the reflux ratio and distillate flow rate in column II, S_{II} is the number of stages of column II, and y_m and x_m are the vectors of obtained and required purities and recoveries for the m components, respectively. This minimization implies the manipulation of 11 variables as continuous as integer. Note that since the product streams flows are manipulated, the recoveries of the key components in each product stream must be included as a restriction.

On the other hand, for the reactive thermally coupled distillation sequences with minimum use of reboilers, there is one objective to minimize: the cost of steam and the cost of the cooling water in the columns plus the cost of the utilities in the

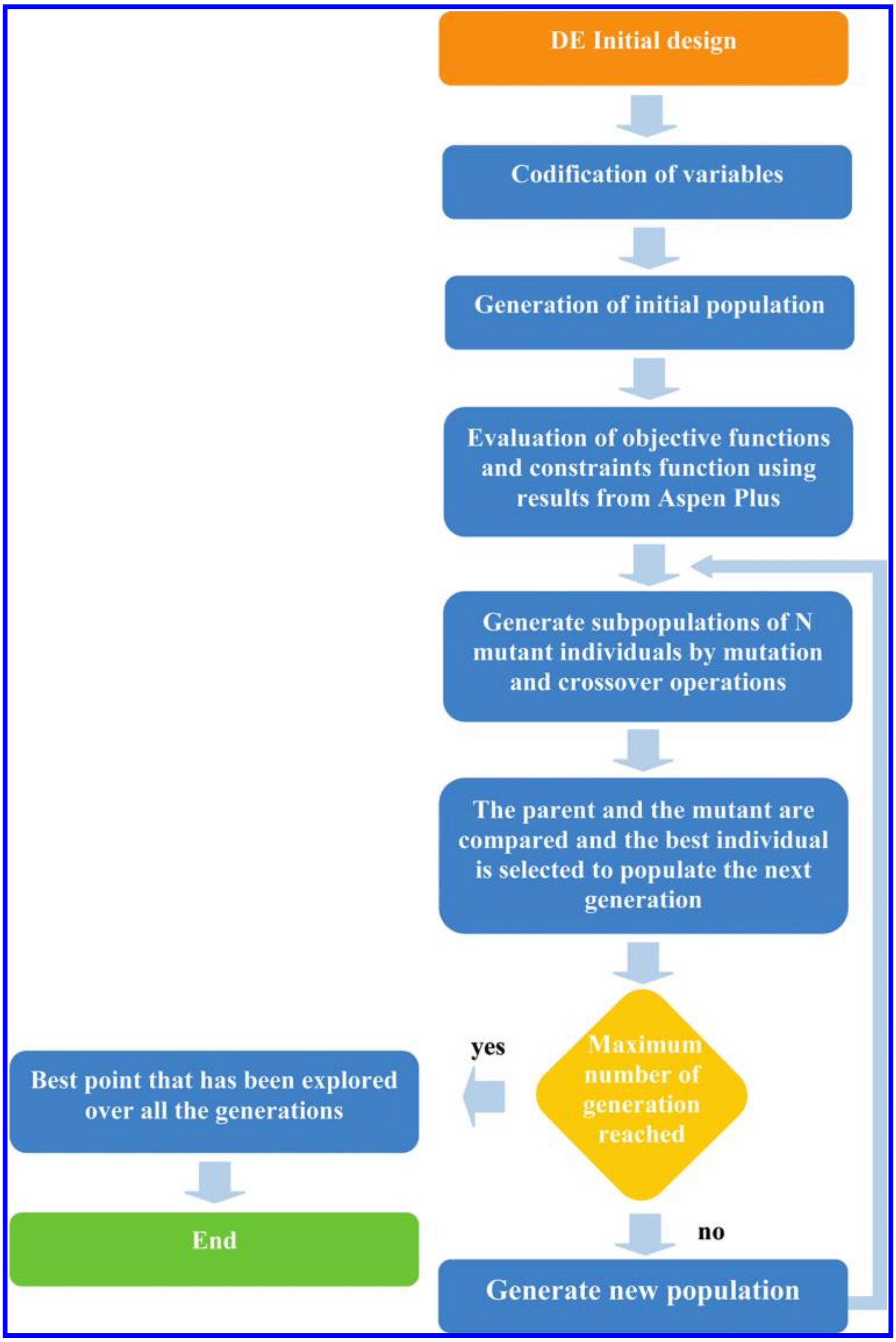


Figure 3. Flowchart for the differential evolution algorithm.

flash tank. The minimization problem can be expressed as

$$\text{Min}(C_U) = f(RR_I, S_I, S_{FAI}, S_{FVI}, S_{FLI}, S_{SRI}, S_{ERI}, S, F_F, R)$$

subject to

$$\vec{y}_m \geq \vec{x}_m \tag{3}$$

where C_U is the cost of steam and the cost of the cooling water in the columns plus the cost of the utilities in the flash tank, RR_I is the reflux ratio in the column I, S_I is the number of stages of the column I, S_{FAI} is the stage of the feed, S_{SRI} and S_{ERI} are the sizes of the reactive sections in the first columns of the complex reactive distillation sequences (Figure 1), S_{FVI} and S_{FLI} are the stages of the interconnectig flow rates in column I, S is the number of stages of the column II, F_F is the flow rate of the thermally coupling, R is the reflux ratio or bottoms flow rate of column II, and y_m and x_m are the vectors of obtained and required purities and recoveries for the m components, respectively.

This minimization implies the manipulation of 10 variables as continuous as integer.

Then, in order to optimize the reactive sequences we used a differential evolution algorithm with constraints coupled to AspenONE Aspen Plus. This link allows obtaining the optimal and rigorous designs of the reactive schemes that satisfied the purities and recoveries required. The term "rigorous" means that all designs presented were obtained considering the complete set of MESH equations along with the phase equilibrium calculations, using the Radfrac module of AspenONE Aspen Plus. The differential evolution algorithm works as follows: an initial population is randomly generated using uniformly distributed random numbers spanning the entire feasible space. The individuals are checked for boundary violation (check if any individual is generated in the infeasible region; the infeasible points are replaced by generating new individuals until they are feasible). The first step is to compute the objective function value of every individual. Then, for each individual in the population, named "parent", a "mutant" is produced by applying the particular reproduction operator of differential evolution. Mutants created by the reproduction operator have two characteristics: 1) keep exploration and diversity of the population, escaping from local minima, and 2) convergence to the optimum by adaptive mutations. Mutations obey the actual distribution of the population on the search space. A mutant is created from three vectors chosen randomly from the population. For every dimension X_1, X_2, X_3, X_4, ..., X_n, the difference of two vectors is computed and multiplied by a factor F, $(0 < F < 1)$, then the scaled difference is added to respective component of the third vector, and finally it is stored in the mutant. This process is repeated n times, filling one component of the n-dimensional mutant in each step. Selection is deterministic and applied when the mutant is ready. The objective function value of the parent and the mutant are compared, and the best individual, either the parent or the mutant, is copied to populate the next generation. Once all parents have been traversed, the next population thus created simply replaces the old one, and a new generation can start. One iteration (generation) of the differential evolution algorithm traverses all parents. For each parent a mutant vector is created as explained before. The iterations are stopped until a termination criterion is satisfied. The algorithm then terminates providing the best point that has been explored over all the generations (Figure 3). For the optimization of reactive distillation sequences, we used 100 individuals and 150 generations as parameters of the differential evolution algorithm, with 0.80 and 0.40 for crossover and mutation factor, respectively.[34] These parameters were obtained through a tuning process. The simulation ware performed on a Dell computer with processor Intel Core i7CPU 930 2.80 GHz, 6.00 GB memory, Windows 7 Ultimate, Matlab version 7.8.0.347 (R2009a) and Aspen One V7.0.

5. SINGULAR VALUE DECOMPOSITION (SVD)

We complement this work, analyzing the control properties of the design obtained. Open loop dynamic responses to set point changes around the assumed operating point were obtained. The responses were obtained through the use of Aspen Dynamics. Transfer function matrices (G) were then collected for each case, and they were subjected to singular value decomposition (SVD)

$$G = V \sum W^H \tag{4}$$

where $\Sigma = \text{diag}\ (\sigma_1,.....,\sigma_n)$, σ_i = singular value of $G = (\lambda_i)^{1/2}(GG^H)$; $V = (v_1, v_2,.....)$ matrix of left singular vectors; and $W = (w_1, w_{2,}....)$ matrix of right singular vectors. Two parameters of interest are the minimum singular value, σ_*, and the ratio maximum to minimum singular values, or condition number

$$\gamma = \sigma^*/\sigma_* \tag{5}$$

The minimum singular value is a measure of the invertibility of the system and represents a measure of potential problems of the system under feedback control. The condition number reflects the sensitivity of the system under uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with higher minimum singular values and lower condition numbers are expected to show the best dynamic performance under feedback control.[35] In this case we cover a sufficiently complete range of frequencies. Similar studies have been reported by Jantes-Jaramillo et al.,[36] Gómez-Castro et al.,[37] Ibarra-Sánchez and Segovia-Hernández[38] among

Table 2. Product Streams in Distillation Reactive Sequences

	mole flow [kmol/h]			mass frac		
sequences	biodiesel	water	methanol	biodiesel	water	methanol
DRDS	45.35	45.35	8.95	0.9994	0.9999	1.0000
IRDS	45.35	45.21	8.77	0.9993	0.9970	0.9907
TCRDS-SR	39.25	45.35	2.71	0.9991	0.9861	1.0000
TCRDS-SS	41.79	45.31	5.3295	0.9991	0.9869	0.9950

Table 3. Parameters of the Configurations of Conventional Schemes

	distillation sequences			
	DRDS		IRDS	
design specifications	column I	column II	column I	column II
RR	2.26	0.10	2.02	8.71
R_D [kmol/h]	45.35	8.96	54.14	8.99
R_B [kmol/h]	54.44	45.48	45.58	45.29
F_{FA} [kmol/h]	45.35	-	45.35	-
F_M [kmol/h]	54.43	-	54.43	-
S	36	28	40	49
S_{FA}	8	-	27	-
S_M	36	-	10	-
S_{IN}	-	16	-	22
S_{SR}	18	-	14	-
S_{ER}	28	-	38	-
P [atm]	1.00	1.00	1.00	1.00
P_B [atm]	1.68	1.68	1.68	1.68
T_C [°C]	83.73	64.66	99.26	64.72
T_B [°C]	269.65	115.00	291.42	265.51
Q_C [kW]	−1676.36	−98.05	−1871.97	−848.98
Q_B [kW]	37.52	1106.46	1145.92	880.52
ER [kWh/Ton FAME][a]	172.36		263.09	

[a] Utilities is also considered to bring the methanol of liquid to vapor saturated.

others, for control analysis in studies of thermally coupled distillation systems.

Table 4. Parameters of Thermally Coupled Distillation Schemes with a Minimum Number of Reboilers

	distillation sequences			
	TCRDS-SR		TCRDS-SS	
operating specifications	column I	rectifier	column I	stripper
RR	1.52	7.99	28.80	4.14
R_D [kmol/h]	45.72	2.71	5.2644	14.19
R_B [kmol/h]	51.35	19.36	48.88	45.65
F_{FA} [kmol/h]	45.36	-	45.36	-
F_M [kmol/h]	54.43	-	54.43	-
S	28	18	22	5
S_{FA}	13	-	14	-
S_M	28	-	22	-
S_{FV}	28	18	7	1
S_{FL}	28	18	14	1
F_{FV}[kmol/h]	22.08		14.19	
F_{LV} [kmol/h]	19.36		59.83	
S_{SR}	19	-	10	-
S_{ER}	25	-	21	-
P [atm]	1.00	1.00	1.00	1.00
P_B [atm]	1.68	1.68	1.68	1.68
T_C [°C]	98.56	64.54	69.50	
T_B [°C]	151.53	-	177.22	113.75
Q_C [kW]	−1306.34	−238.91	−1523.08	-
Q_B [kW]	776.95[a]	-	538.41[a]	169.07
ER [kWh/Ton FAME][b]	155.49		138.31	

[a] Heat duty in the flash tank. [b] Utilities are also considered to bring the methanol of liquid to vapor saturated.

Table 5. Total Annual Cost of the Distillation Sequences

distillation sequences	equipment [UDS/year]	energy consumption [UDS/year]	total annual cost [UDS/year]
DRDS	512,162	339,459	851,621
IRDS	693,781	475,301	1,169,082
TCRDS-SR	351,879	185,077	536,955
TCRDS-SS	281,759	155,049	436,808

6. RESULTS

The results are presented in two sections; in the first section, the two thermally coupled distillation sequences with a minimum number of reboilers are compared in terms of energy requirements, cost of cooling water plus cost of vapor and total annual costs (calculated using the method of Guthrie Appendix A of Turton et al.[39]). The second section presents the theoretical control properties obtained in the SVD analysis derived from open-loop dynamic simulation in Aspen Dynamics.

6.1. Steady State Analysis. Table 2 shows the molar flows and mass fraction purities for the products obtained in all distillation sequences. The tray arrangements and some important design variables for all sequences after the optimization task are given in Tables 3 and 4. It can be seen that the total number of stages in the conventional reactive distillation sequence is higher in comparison with thermally coupled reactive distillation sequences with a minimum number of reboilers, which are topologically more complex than conventional systems.

Table 5 presents the energy requirements, the cost of equipment, and the total annual costs for the four reactive distillation sequences after the optimization procedure. The optimized designs comply with the restrictions of the purities and recoveries in all components. Figures 4 and 5 show the composition profiles for the distillation columns TCRDS-SR and TCRDS-SS. These composition profiles show that the composition of the biodiesel in the bottoms product does not fit the desired value of 99.9 mass fraction, for that reason, an additional flash tank is used.

The conventional designs present up to 59.38% more equipment cost, 67.37% more energy requirements, and 62.60% more total annual costs than the complex reactive distillation sequences, despite the presence of the flash tank, which involves additional equipment that is not present in conventional distillation arrangements. According to the results presented in Table 5, the best option in economic terms is the design TCRDS-SS. The total annual cost of this designs that turns out to be the cheapest is 436,808 $/yr. Given these results, it is possible to conclude that the best design among the four case studies reviewed is the system TCRDS-SS with a minimum number of reboilers. Additionally, this design has the lowest total number of stages when compared with the other configurations studied.

6.2. Controllability Results. In order to conduct the SVD analysis, open-loop transfer functions are required (see the Appendix). In this study, step changes in the input variables were implemented, and the open-loop dynamic responses were registered. The dynamic responses were adjusted to transfer functions and

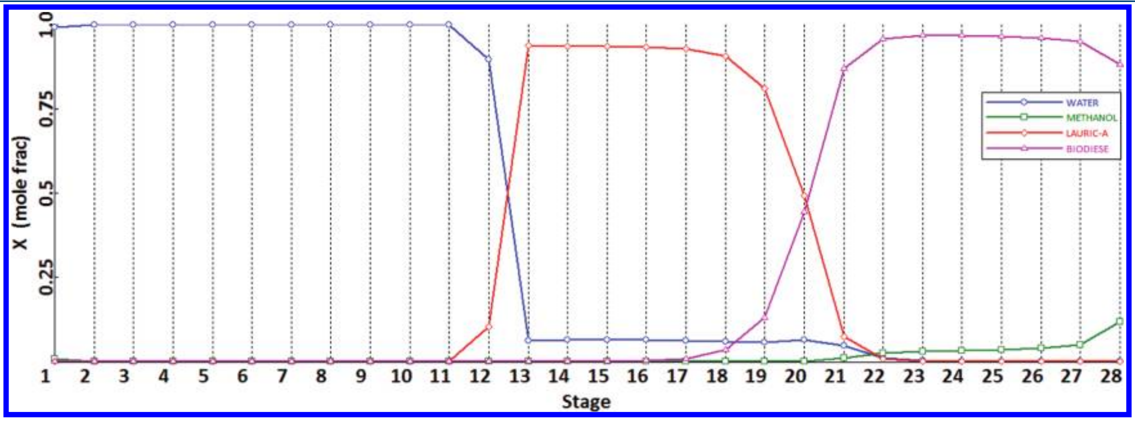


Figure 4. Composition profiles for the distillation column CI in TCRDS-SR.

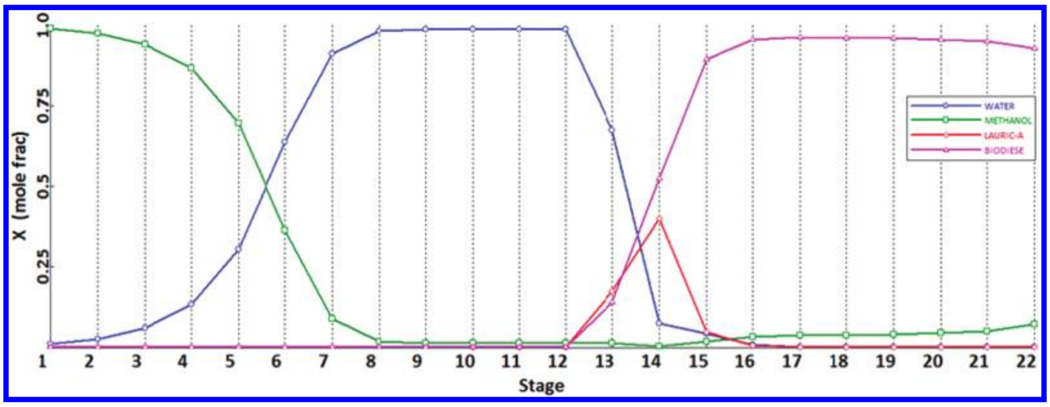


Figure 5. Composition profiles for the distillation column C1 in TCRDS-SS.

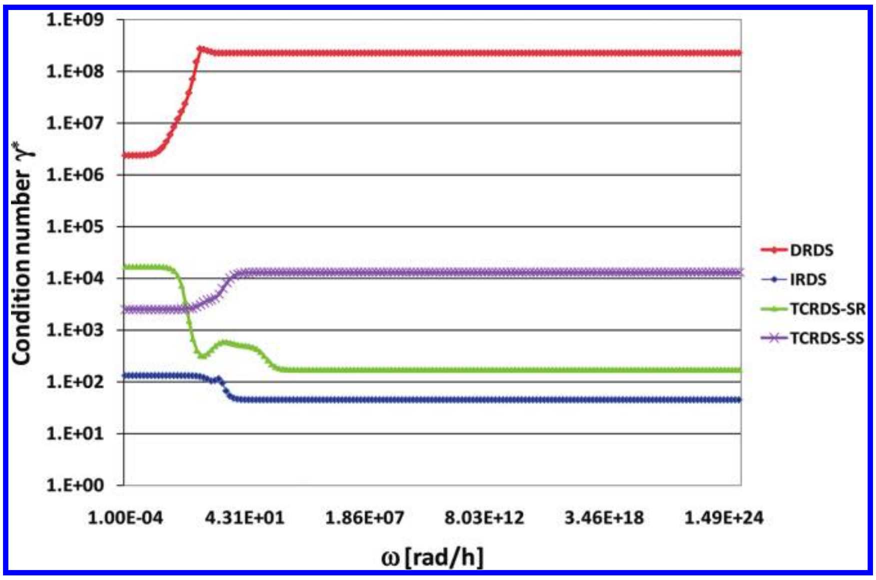


Figure 6. Condition number of the configurations of conventional schemes and thermally coupled distillation schemes with a minimum number of reboilers.

arranged into transfer function matrices. It can be noted that the dynamic responses can be adjusted to first or second order transfer functions with or without dead times.

Figure 6 presents the condition number in the frequency domain of interest, and a clear trend is observed. For this reaction-separation task, the IRDS arrangement shows the lowest values of γ^*, and according to Figure 7, the highest values of σ_*. These results indicate that the IRDS system has better theoretical control properties than the other three sequences. From a physical point of view, low values of the minimum singular value and high values of the condition number imply large movements in the control valves for changes in the set points and load rejection. However, the TCRDS-SR system shows similar values of γ^* and σ_* to those of the IRDS system. It can be expected that the system using a thermally coupled reactive distillation with a minimum number of reboilers will present similar closed-loop dynamic behavior for both set point tracking and load rejection to the indirect conventional reactive distillation arrangement. In the case of the DRDS, it can be seen that it shows the worst control properties because it has the highest values of condition number and the lowest values of minimum singular value. Regarding control properties, the complex distillation sequences exhibit theoretical control properties between the IRDS and DRDS schemes.

At this point it is important to note that according to the results obtained in steady state, it can be concluded that the best design option is the system TCDS-SS as it shows the lowest total annual cost. However, its control properties are not good in comparison with the system using an indirect conventional distillation column (which is the one that shows the highest total annual cost). When the comparison is made only between the coupled arrangements, it is observed that TCRDS-SR shows a total annual cost 22.92% higher and 19 stages more than TCRDS-SS arrangement. However, TCRDS-SR presents significant savings in equipment cost, service consumption, and total cost of operation compared to conventional systems and similar control properties to the indirect conventional reactive distillation arrangement (the best option in the controllability analysis). Thus making a comparative study a feasible best design, for this case of production of fatty ester, is TCRDS-SR with a minimum number of reboilers.

7. CONCLUSIONS

A design methodology for thermally coupled reactive distillation sequences with a minimum number of reboilers has

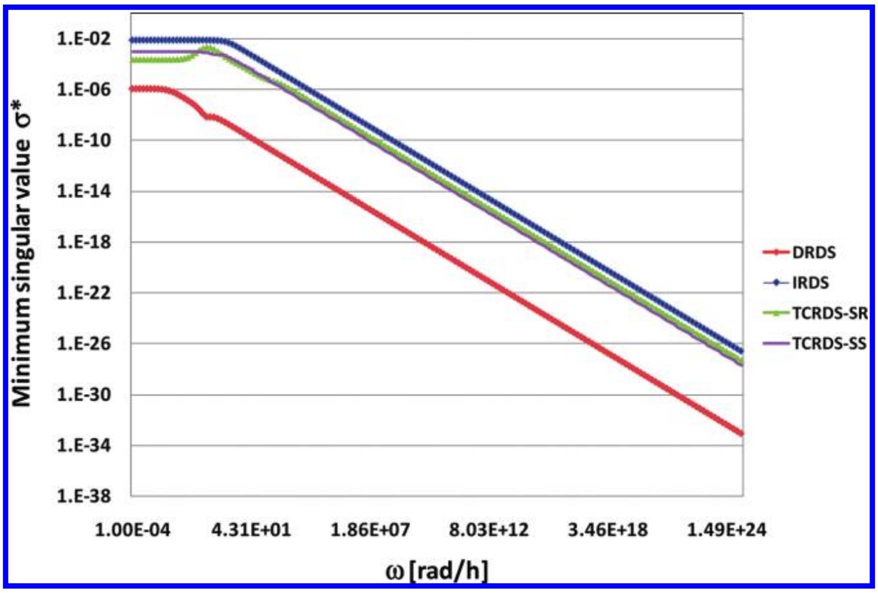


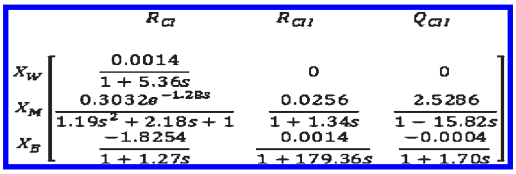
Figure 7. The minimum singular value of the configurations of conventional schemes and thermally coupled distillation schemes with a minimum number of reboilers.

been presented. This methodology is based on stochastic optimization techniques, namely differential evolution. The results indicate that energy requirements of the complex reactive distillation sequences with a side column with a minimum number of reboilers can be reduced significantly over conventional reactive distillation sequences. Particularly, a feasible best design, for this case of production of fatty ester, is TCRDS-SR with a minimum number of reboilers because it presents significant savings in equipment cost, utilities, and total cost of operation compared to conventional systems and similar control properties to the best option in the controllability analysis. The results also indicate that a lack of interconnections (as in case of conventional reactive distillation arrangements) does not necessarily provide the operational advantages originally expected given the resulting, simpler, structural design. It is apparent that the presence of recycle streams, instead of deteriorating the dynamic behavior of separation sequences, may contribute positively to their dynamic properties. In general, our results show that a stochastic optimization approach, using differential evolution with restrictions coupled to AspenONE Aspen Plus, is robust and suitable for the design of thermally coupled reactive distillation systems with a minimum number of reboilers.

APPENDIX

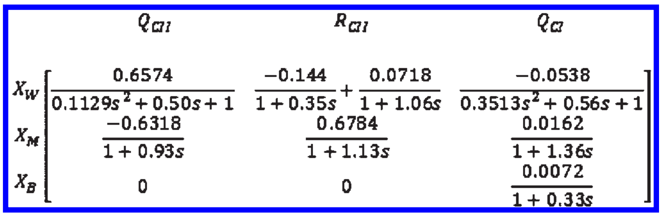
Tables 6−9 show the transfer function matrices generated in Aspen Dynamics, for the four sequences by implementing step changes in each manipulated variable and registering the open loop dynamic response of the product compositions (water, methanol, and biodiesel).

Table 6. Transfer Function Matrix for DRDS



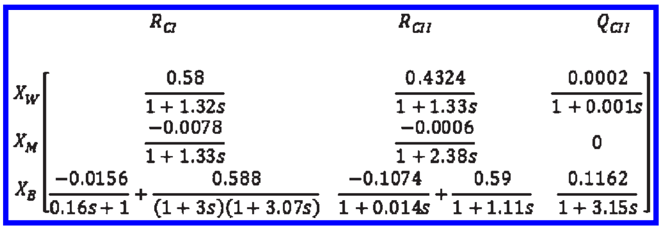
$$\begin{array}{cccc} & R_{CI} & R_{CII} & Q_{CII} \\ X_W & \frac{0.0014}{1+5.36s} & 0 & 0 \\ X_M & \frac{0.3032e^{-1.28s}}{1.19s^2+2.18s+1} & \frac{0.0256}{1+1.34s} & \frac{2.5286}{1-15.82s} \\ X_B & \frac{-1.8254}{1+1.27s} & \frac{0.0014}{1+179.36s} & \frac{-0.0004}{1+1.70s} \end{array}$$

Table 7. Transfer Function Matrix for IRDS



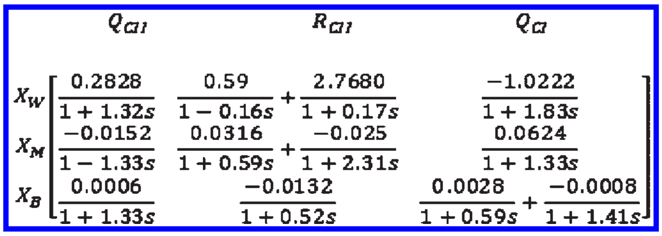
$$\begin{array}{cccc} & Q_{CII} & R_{CII} & Q_{CI} \\ X_W & \frac{0.6574}{0.1129s^2+0.50s+1} & \frac{-0.144}{1+0.35s}+\frac{0.0718}{1+1.06s} & \frac{-0.0538}{0.3513s^2+0.56s+1} \\ X_M & \frac{-0.6318}{1+0.93s} & \frac{0.6784}{1+1.13s} & \frac{0.0162}{1+1.36s} \\ X_B & 0 & 0 & \frac{0.0072}{1+0.33s} \end{array}$$

Table 8. Transfer Function Matrix for TCRDS-SR



$$\begin{array}{cccc} & R_{CI} & R_{CII} & Q_{CII} \\ X_W & \frac{0.58}{1+1.32s} & \frac{0.4324}{1+1.33s} & \frac{0.0002}{1+0.001s} \\ X_M & \frac{-0.0078}{1+1.33s} & \frac{-0.0006}{1+2.38s} & 0 \\ X_B & \frac{-0.0156}{0.16s+1}+\frac{0.588}{(1+3s)(1+3.07s)} & \frac{-0.1074}{1+0.014s}+\frac{0.59}{1+1.11s} & \frac{0.1162}{1+3.15s} \end{array}$$

Table 9. Transfer Function Matrix for TCRDS-SS



$$\begin{array}{cccc} & Q_{CII} & R_{CII} & Q_{CI} \\ X_W & \frac{0.2828}{1+1.32s} & \frac{0.59}{1-0.16s}+\frac{2.7680}{1+0.17s} & \frac{-1.0222}{1+1.83s} \\ X_M & \frac{-0.0152}{1-1.33s} & \frac{0.0316}{1+0.59s}+\frac{-0.025}{1+2.31s} & \frac{0.0624}{1+1.33s} \\ X_B & \frac{0.0006}{1+1.33s} & \frac{-0.0132}{1+0.52s} & \frac{0.0028}{1+0.59s}+\frac{-0.0008}{1+1.41s} \end{array}$$

AUTHOR INFORMATION

Corresponding Author

*Phone: +52 (473) 732-0006 ext. 8142. E-mail: gsegovia@quijote.ugto.mx.

■ ACKNOWLEDGMENT

We acknowledge the financial support provided by Universidad de Guanajuato and CONACyT (Mexico).

■ 8. NOMENCLATURE

ER≡energy requirements
F_{FA}≡flow of fatty acid
F_{M}≡flow of methanol
F_{FV}≡interconnection flow of vapor phase
F_{LV}≡interconnection flow of liquid phase
P≡top pressure
P_{B}≡bottom pressure
Q_{C}≡condenser duty
Q_{B}≡reboiler duty
R_{D}≡distillate rate
R_{B}≡bottoms rate
RR≡reflux ratio
S≡number of stages
S_{FA}≡feed stage of fatty acid
S_{M}≡feed stage of methanol
S_{IN}≡feed stage of column II
S_{SR}≡starting of reactive section
S_{ER}≡ending of reactive section
S_{FV}≡interconnection stage of vapor phase
S_{FL}≡interconnection stage of liquid phase
T_{C}≡condenser temperature
T_{B}≡reboiler temperature

■ REFERENCES

(1) Johansson, T.; McCarthy, S. Global Warming Post-Kyoto: Continuing Impasse or Prospects for Progress? *Energy Dev. Rep. Energy* **1999**, 69.

(2) Kesse, D. G. Global Warming—Facts, Assessment, Countermeasures. *J. Pet. Sci. Eng.* **2000**, *26*, 157.

(3) Cao, X. Climate Change and Energy Development: Implications for Developing Countries. *Resour. Policy* **2003**, *29*, 61.

(4) Murphy, J. D.; McCarthy, K. The Optimal Production of Biogas for Use as a Transport Fuel in Ireland. *Renewable Energy* **2005**, *30*, 2111.

(5) Agarwal, A. K. Biofuels (Alcohols and Biodiesel) Applications as Fuels for Internal Combustion Engines. *Prog. Energy Combust. Sci.* **2007**, *33*, 233.

(6) Di Felice, R.; De Faveri, D.; De Andreis, P.; Ottonello, P. Component Distribution between Light and Heavy Phases in Biodiesel Processes. *Ind. Eng. Chem. Res.* **2008**, *47*, 7862.

(7) Wang, S. J.; Wong, D. S. H.; Yu, S. W. Design and Control of Transesterification Reactive Distillation with Thermal Coupling. *Comput. Chem. Eng.* **2008**, *32*, 3030.

(8) Zhang, L.; Guo, W.; Liu, D.; Yao, J.; Ji, L.; Xu, N.; Min, E. Low Boiling Point Organic Amine-Catalyzed Transesterification for Biodiesel Production. *Energy Fuels* **2008**, *22*, 1353.

(9) Lu, H.; Liu, Y.; Zhou, H.; Yang, Y.; Chen, M.; Liang, B. Production of Biodiesel from Jatropha Curcas L. Oil. *Comput. Chem. Eng.* **2009**, *33*, 1091.

(10) Peña, R.; Romero, R.; Martínez, S. L.; Ramos, M. J.; Martínez, A.; Natividad, R. Transesterification of Castor Oil: Effect of Catalyst and Co-Solvent. *Ind. Eng. Chem. Res.* **2009**, *48*, 1186.

(11) Stiefel, S.; Dassori, G. Simulation of Biodiesel Production through Transesterification of Vegetable Oils. *Ind. Eng. Chem. Res.* **2009**, *48*, 1068.

(12) Kiss, A. A.; Omota, F.; Dimian, A. C.; Rothenberg, G. The Heterogeneous Advantage: Biodiesel by Catalytic Reactive Distillation. *Top. Catal.* **2006**, *40*, 141.

(13) He, B. B.; Singh, A. P.; Thompson, J. C. A Novel Continuous-Flow Reactor Using Reactive Distillation for Biodiesel Production. *Trans. ASAE* **2006**, *49*, 107.

(14) Kiss, A. A.; Dimian, A.; Rothenberg, G. Biodiesel by Catalytic Reactive Distillation Powered by Metal Oxides. *Energy Fuels* **2008**, *22*, 598.

(15) da Silva, N.; de, L.; Santander, C. M.; Batistela, C. B.; Filho, R. M.; Maciel, M. R. Biodiesel Production from Integration Between Reaction and Separation System: Reactive distillation Process. *Appl. Biochem. Biotechnol.* **2010**, *161*, 245.

(16) Kiss, A. A. Separative reactors for integrated production of bioethanol and biodiesel. *Comput. Chem. Eng.* **2010**, *34*, 812.

(17) Kiss, A. A. Heat-integrated reactive distillation process for synthesis of fatty esters. *Fuel Process. Technol.* **2011**, *92*, 1288.

(18) kiss, A. A. Novel process for biodiesel by reactive absorption. *Sep. Purif. Technol.* **2009**, *69*, 280.

(19) Kiss, A. A.; Bildea, C. S. Integrated reactive absorption process for synthesis of fatty esters. *Bioresour. Technol.* **2011**, *102*, 490.

(20) Bildea, C. S.; Kiss, A. A. Dynamics and control of a biodiesel process by reactive absorption. *Chem. Eng. Res. Des.* **2011**, *98*, 187.

(21) Ciric, A. R.; Gu, D. Synthesis of Nonequilibrium Reactive Distillation Processes by MINLP Optimization. *AIChE J.* **1994**, *40*, 1479.

(22) Doherty, M. F.; Buzad, G. Reactive Distillation by Design. *Chem. Eng. Res. Des.* **1992**, *70*, 448.

(23) Viswanathan, J.; Grossmann, I. E. Combined-Penalty Function and Outer-Approximation Method for MINLP Optimization. *Comput. Chem. Eng.* **1990**, *14*, 769.

(24) Viswanathan, J.; Grossmann, I. E. Optimal Feed Locations and Number of Trays for Distillation Columns with Multiple Feeds. *Ind. Eng. Chem. Res.* **1993**, *32*, 2942.

(25) Jackson, J. R.; Grossmann, I. E. A Disjunctive Programming Approach for the Optimal Design of Reactive Distillation Columns. *Comput. Chem. Eng.* **2001**, *25*, 1661.

(26) Yeomans, H.; Grossmann, I. E. Disjunctive Programming Models for the Optimal Design of Distillation Columns and Separation Sequences. *Ind. Eng. Chem. Res.* **2000**, *39*, 1637.

(27) Wang, F. S.; Chiou, J. P. Optimal Control and Optimal Time Location Problems of Differential-Algebraic Systems by Differential Evolution. *Ind. Eng. Chem. Res.* **1997**, *36*, 5348.

(28) Wang, F. S.; Su, T. L.; Jang, H. J. Hybrid Differential Evolution for Problems of Kinetic Parameter Estimation and Dynamic Optimization of Ethanol Fermentation Process. *Ind. Eng. Chem. Res.* **2001**, *40*, 2876.

(29) Srinivas, M.; Rangaiah, G. P. Differential Evolution with Tabu List for Global Optimization and Its Application to Phase Equilibrium and Parameter Estimation Problems. *Ind. Eng. Chem. Res.* **2007**, *46*, 3410.

(30) Gujarathi, A. M.; Babu, B. V. Optimization of Adiabatic Styrene Reactor: Hybrid Multiobjective Differential Evolution (H-MODE) Approach. *Ind. Eng. Chem. Res.* **2009**, *48*, 11115.

(31) Henderson, H.; Wagner, F. S.; Barufatti, N. E.; Ali, M. M. Calculation of Critical Points of Thermodynamic Mixtures with Differential Evolution Algorithms. *Ind. Eng. Chem. Res.* **2010**, *49*, 1872.

(32) Omota, F.; Dimian, A. C.; Bliek, A. Fatty Acid Esterification by Reactive Distillation. *Ind. Eng. Chem. Res.* **2003**, *58*, 3159.

(33) Steinigeweg, S.; Gmehling, J. Esterification of a Fatty Acid by Reactive Distillation. *Ind. Eng. Chem. Res.* **2003**, *42*, 3612.

(34) Price, K. V.; Storn, R. M.; Lampinen, J. A. *Differential Evolution: A Practical Approach to Global Optimization*; Springer: USA, 2005.

(35) Gabor, M.; Mizsey, P. A Methodology to Determine Controllability Indices in the Frequency Domain. *Ind. Eng. Chem. Res.* **2008**, *47*, 4807.

(36) Jantes − Jaramillo, D.; Segovia - Hernández, J. G.; Hernández, S. Reduction of Energy Consumption and Greenhouse Gas Emissions in a Plant of Separation of Amines. *Chem. Eng. Technol.* **2008**, *31*, 1462.

(37) Gómez − Castro, F. I.; Segovia - Hernández, J. G.; Hernández, S.; Gutiérrez − Antonio, C.; Briones - Ramírez, A. Dividing Wall Distillation Columns: Optimization and Control Properties. *Chem. Eng. Technol.* **2008**, *31*, 1246.

(38) Ibarra − Sánchez, J. J.; Segovia - Hernández, J. G. Reducing Energy Consumption and CO_2 Emissions in Extractive Distillation, Part II: Dynamic Behavior. *Chem. Eng. Res. Des.* **2010**, *88*, 135.

(39) Turton, R.; Bailie, R. C.; Whiting, W. B.; Shaeiwitz, J. A. *Analysis, Synthesis and Design of Chemical Process*; Prentice Hall: USA, 2004.