Chemical Product and Process Modeling

Volume 3, *Issue* 1 2008 *Article* 6

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Recommended Citation:
Rahman, Imran; Ahmad, Arsalan; Kumar, Prakash; and Kulkarni, Bhaskar D. (2008) "Optimization of a Continuous Process for the Recovery of Lactic Acid Using Differential Evolution Algorithm," *Chemical Product and Process Modeling*: Vol. 3: Iss. 1, Article 6.
DOI: 10.2202/1934-2659.1111

Optimization of a Continuous Process for the Recovery of Lactic Acid Using Differential Evolution Algorithm

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Abstract

Purified lactic acid is used for production of biodegradable polymer. Esterification with methanol and subsequent hydrolysis in distillation column using cation exchange resin as catalyst to produce purified lactic acid has obvious advantages. In this paper, we present a theoretical study on optimization of industrial production (1000 t/year) of pure lactic acid using differential evolution (DE), a robust global optimization technique. The objective function is to minimize the overall cost with a view to obtain the optimized values of the decision variables: esterification reaction temperature, number of stages, feed location, reflux ratio, catalyst weight, number of reactive stages and position of reactive stages for hydrolysis.

KEYWORDS: reactive distillation, differential evolution, lactic acid

1. INTRODUCTION

Use of biodegradable polymers such as polylactic acid as a substitute for petrochemicals-based polymers is desirable to combat the environmental damage. Production of biodegradable polymer is becoming increasingly more important, as a result of rising price and diminishing resources of crude oil (Seo et al., 1999). Use of alternative renewable biomass and its transformation through fermentation to L-lactic acid is therefore looked at with enhanced interest.

High purity lactic acid can be prepared by esterification of crude lactic acid obtained from the fermented broth and subsequent distillation of ester and its hydrolysis to yield the alcohol and pure lactic acid (Vikroy, 1985). However, the purification of dilute lactic acid obtained from bacterial fermentation is difficult due to its low vapor pressure, tendency to undergo self-esterification, and the presence of troublesome impurities (Seo et al., 1999).

Recently reactive distillation has drawn considerable attention because of its striking advantages, especially for equilibrium-limited reactions. Purification of lactic acid through reactive batch distillation was investigated by several investigators (Seo et al., 1999; Kim et al., 2000; Kim et al., 2002). Earlier Schopmeyer et al.(1944) suggested esterification of lactic acid (40-60 % wt) in presence of homogenous catalyst in a jacketed kettle. Li et al. (2005) and Kumar et al. (2006) investigated the esterification of lactic acid with methanol in a reactor followed by hydrolysis of methyl lactate using cation exchange resin as catalyst in continuous column. The use of solid ion exchange resin as catalyst has advantage over sulphuric acid which leads to equipment corrosion. Kumar et al. (2006) also simulated CSTR and hydrolysis column separately and studied the effect of operating parameters one by one to delineate the optimum column configuration. All these parameters have conflicting effects and trade off is difficult.

Several authors have studied the reactive distillation column optimization (Ciric and Gu, 1994; Cardoso et al, 2000; Stichlmair and Frey 2001; Jackson and Grossman 2001; Gangadwal and Kienle 2006; Melles et al. 2000; Dalaouti and Seferlis 2006; Lima et al. 2006; Burri and Manousiouthakis, 2004; Noeres, et al. 2004). These studies mainly focus on optimization of total number of stages, reflux or boilup ratio, feed plate location and liquid-phase volumes on each stage after specification of input feed composition and operating conditions such as temperature, column pressure etc.

Ciric and Gu (1994) applied mixed integer non-linear programming (MINLP) technique to optimize the reactive distillation (RD) column with a view to minimize the total annualized cost. The problem was solved by using a modified form of the generlized Benders decomposition (GBD) algorithm. Stichlmair and Frey (2001) designed RD columns by solving MINLP models of conceptually derived superstructures while Jackson and Grossman (2001) used the generalized disjunctive programming approach. Recently, Gangadwala and Kinele (2007) applied MINLP technique to optimize the RD column. The simple branch and bound (SBB) solver from general algebraic modeling system (GAMS) was employed as a MINLP solver. It is known that the MINLP formalism can get entrapped into a locally optimum solution instead of the desired globally optimum one. Moreover, MINLP methods are complex, computationally intensive and many simplifications become necessary to make them affordable (Wang et al. 1998).

In recent years, the stochastic search algorithms are studied by Cardoso et al. (2000) and Gomez et al. (2006) to solve the reactive distillation optimization problem. A simulated annealing-based algorithm (M-SIMPSA) was used by Cardoso et al.(2000) for the optimization of non-equililibrium reactive distillation column for production of ethylene glycol. Later, Gomez et al. (2006) used a combination of simulated annealing and sequential quadratic programming. Costa and Oliviera (2001) studied seven test problems using GA & Evolution Strategies (ESs) and compared the results with M-SIMPSA algorithm. They found that the performance of M-SIMPSA is comparable to Genetic algorithm (GA).

Previous studies (Storn, 1995; Storn and Price, 1997; Wang and Chiou, 1997; Babu and Sastry, 1999; Babu and Angira, 2002; Chakraborti et al., 2004; Colaco et al., 2004; Babu et al., 2005) have shown that differential evolution (DE) is an efficient, effective and robust evolutionary optimization method. The details on DE algorithm, various strategies of DE and wide range of applications in various engineering, manufacturing and management areas are well documented (Angira and Babu, 2006).

Genetic algorithm and differential evolution are stochastic optimization methods based on population. The main difference between the GA and DE is the mutation scheme that makes DE self adaptive and the selection process. In DE, all solutions have the same chance of being selected as parents without dependence of their fitness value. The better one of new solution and its parent wins the competition providing significant advantage of converging performance over GA (Karaboga and Okdem, 2004). Karaboga and Okem (2004) compared the performance of the DE algorithm to that of some other well known genetic algorithms. From the simulation studies, it was observed that the convergence speed of the DE is significantly better than the GAs. Therefore, the DE algorithm seems to be a promising approach for engineering optimization problems.

In this paper, DE strategy has been evaluated for optimization of reactive distillation column for the hydrolysis of methyl lactate preceded by esterification reactor for seven decision variables simultaneously. To ensure that the CSTR temperature matches with the feed tray temperature of reactive distillation column, CSTR and hydrolysis column are simulated simultaneously. The reactive distillation simulation model is obtained by incorporating the reaction terms in the mass and heat balance equations of the conventional model for distillation. The kinetic data (Appendix I) and vapor-liquid equilibrium data (Appendix II) described by Sanz et al.(2002) and Sanz et al.(2003), respectively, have been used.

2. PROBLEM DEFINITION

The semi commercial CSTR and reactive hydrolysis column shown in Fig. 1 and produces 1000 metric ton/year (1.541 kmol/h) of pure lactic acid. The feed to the CSTR consists of crude lactic acid, methanol and water, and esterification takes place in presence of catalyst and vapor stream from the reactor consisting of methanol, methyl lactate and water is fed to a fractionating column and the following reaction is assumed to take place with and without catalyst.

$$\text{Lactic acid} + \text{Methanol} \Leftrightarrow \text{Methyl Lactate} + \text{Water} \tag{1}$$

At column temperature, the lactic acid ester undergoes hydrolysis. As the equilibrium is disturbed by fractionating out the alcohol, the hydrolysis process progresses in the effort to restore the alcohol to the equilibrium concentration. As fractionation is continued, the hydrolysis becomes practically complete, at a position near the bottom of the column. Methyl alcohol vapors rising in the column pass through condenser and get collected as distillate. The aqueous solution of purified lactic acid travels downward to the reboiler. The lactic acid thus purified is drawn off from the reboiler and sent to an evaporator for concentration to the desired strength.

Li et al. (2005) reported purification of lactic acid based on the esterification of raw lactic acid from fermentation broth with methanol and sulphuric acid as catalyst in a reactor at boiling point and then the vapor mixture fed to catalytic distillation column for hydrolysis of methyl lactate to achieve pure lactic acid. Methyl lactate was also present in the distillate due to incomplete hydrolysis to lactic acid. Similarly, Kumar et al. (2006) studied lactic acid esterfication in CSTR using ion exchange catalyst and hydrolysis in catalytic disitillation column. The conversion of methyl lactate in a column of 20 stages was 100 %.

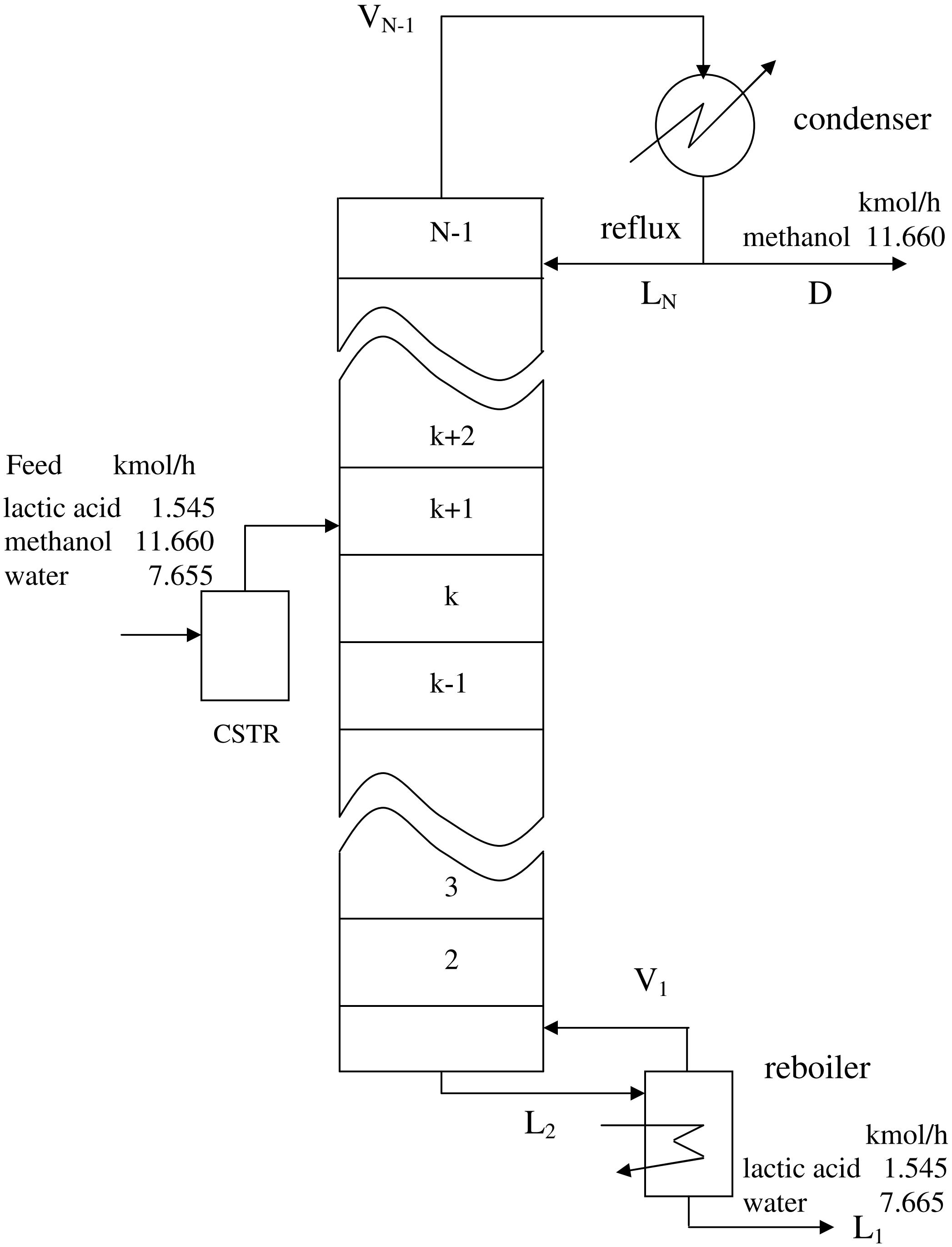

Figure 1. Schematic of reactive distillation column

DOI: 10.2202/1934-2659.1111

The objective is to get the pure lactic acid at the bottom with 100 % conversion of lactic acid in CSTR and methyl lactate in the column so as to get all lactic acid converted to methyl lactate and methanol at the top at minimum cost. The decision variables are the reaction temperature of the CSTR, number of stages, number of reactive stages, feed location, catalyst quantity, reflux ratio and position of reactive stages in a column. The feed to CSTR consists of 50 % crude lactic acid and methanol to lactic mole ratio of 7.55, on esterification of crude lactic acid, and vapor stream of the CSTR is fed to distillation column.

A minimum azeotrope for the binary reactive system water (88%), methyl lactate (12%) has been reported by Sanz et al. (2003). The esterification kinetics of lactic acid with methanol (i) without addition of catalyst and (ii) catalyzed by ion-exchange resins (Appendix I) were presented by Sanz et al. (2002).

3. PROBLEM FORMULATION

The objective function used in this study is representative of the total annual cost (C_T) that is made-up of two components namely, the operating cost (C_1) and the capital cost (C_2). While C_1 accounts for the heating and cooling cost pertaining to the reboiler and condenser, the cost component C_2 accounts for the number of stages, reboiler and condenser. The overall optimization objective is expressed as:

$$\text{Minimize } C_T \qquad (2)$$

where C_T ($) is a function of a M-dimensional decision variable vector, $\mathbf{x}$ ($=[x_1, x_2, ..., x_m, ..., x_M]^T$). The seven decision variables (M = 7) considered for optimization are: (i) CSTR temperature(x_1), (ii) the total number of stages (x_2), (iii) feed location (x_3), (iv) reflux ratio (x_4), (v) catalyst weight (x_5) (vi) number of reactive stages (x_6) and (vii) position of reactive stages (x_7). The evaluation procedure for the cost components C_1 and C_2 is discussed in Appendix IV. The solution to the minimization problem defined in equation (2) should satisfy the following constraints:

- Equality constraints

  As defined by the material balance, equilibrium, summation of mole fraction and heat balance equations (see Appendix III).
- Purity constraints taken into account in convergence criteria (Equation 3)
- The constraint on maximum catalyst loading on a stage is taken as in equation 11.

Simulation of reactive distillation processes involves the simultaneous solution of material and energy balances and stoichiometric relationships. This corresponds to the solution of a considerably large set of non-linear equations combined with the UNIQUAC method for predicting the vapor-liquid equilibrium

(VLE). It is recognized that the chemical reaction may be distributed over several stages.

The assumptions made for modeling the reactive distillation column are: the vapor and liquid phases are in equilibrium on each tray; no reaction occurs in the vapor phase; the liquid phase is always homogenous. The heat of reaction is considered negligible.

Convergence of column model depends on starting guesses for the composition profile and flow rates in the column. The use of the Newton-Raphson method requires a proper starting guess for the composition profile. When the starting point is far from the solution, these methods can converge to impossible physical conditions or may not converge at all (Cardoso et al., 2000). Fig. 2 describes the steps involved in reactive distillation column simulation. The programming language used is Fortran.

The simulation stops with a feasible distillation column when the global material balance of all components is obeyed as described by the equation

$$\sqrt{\sum_{i=1}^{C}\left[\sum_{k=1}^{N}\left(F_{ik}+\sum_{j=1}^{R}\nu_{ij}\varepsilon_{jk}\right)-P_i\right]^2} < \varsigma_c \tag{3}$$

The algorithm ends up when global material balance to the column is verified. A non-plausible column is obtained when Newton-Raphson method exceeds a pre-specified maximum number of iterations failing to satisfy the global material balance. This situation leads to unfeasible column and objective function value is simply penalized with a large constant value.

4. RESULTS AND DISCUSSION

The staged continuous reactive distillation column design is obtained by optimization using the DE algorithm. The performance of DE technique for optimizing the above-stated problem, procedural details and the results obtained thereby are described in the following.

The reaction temperature (x_1) of the CSTR influences the reaction rates and evaporation of methyl lactate and is included as decision variable. Since the total number of stages (N) and number of reactive stages can assume only discrete values, the related decision variables (x_2, x_6) are converted into its integer equivalent. Also, for the procedural convenience, the values of the feed location variable (x_3) and reactive stage position (x_7) are normalized. Accordingly, the following expressions have been used for computing the values of N, NR and the discrete values (f_l ,RPS) of the feed location variable, x_3 and reactive stage position (x_7).

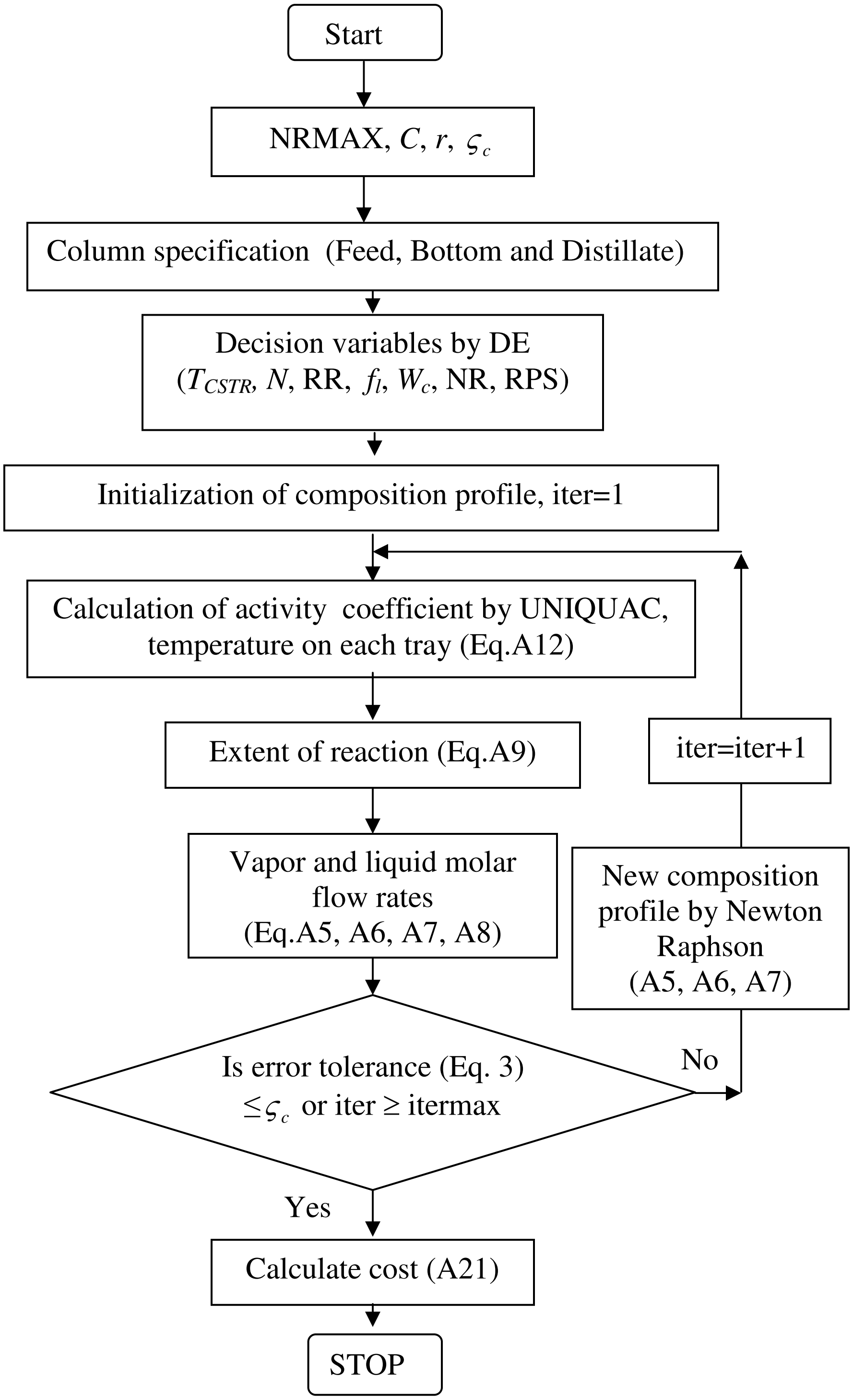

Figure 2. Simulation algorithm

To obtain practical design it is necessary to constrain the decision variables. Based on the earlier studies (Schopmeyer et al., 1944, Li et al., 2005, Kumar et al, 2006), the minimum and maximum values of the decision variables were decided as shown below.

$$CSTR\ \ temperature\ \ T = x_1 \qquad 349 \le x_1 \le 358 \tag{4}$$

$$N = \mathrm{int}(x_2) \qquad 16 \le x_2 \le 22 \tag{5}$$

$$\text{Feed location } (f_l) = \mathrm{int}(1 + x_3 N) \qquad 0.33 \le x_3 \le 0.95 \tag{6}$$

$$\text{Reflux ratio(RR)} = x_4 \qquad 1 \le x_4 \le 1.5 \tag{7}$$

$$\text{Catalyst weight } (\mathrm{W_c}) = x_5 \qquad 4 \le x_5 \le 12 \tag{8}$$

$$\text{Number of reactive stages (NR)} = x_6 \qquad 2 \le x_6 \le 6 \tag{9}$$

$$\text{Position of reactive stages (RPS)} = \mathrm{int}(1 + x_7 N) \qquad 0.05 \le x_7 \le 0.6 \tag{10}$$

where int(**.**) refers to the integer function.

For heterogeneously catalysed reactive distillation processes, one of the hardware choice is to use standard packed column internals such as Raschig rings and make these catalytically active; this is the strategy adopted by Sundmacher and Hoffmann (1994). The commercially available catalytic packing such as Katapack-S uses Amberlyst 15 as catalyst. The packing density of catalyst in Katapack-S is around 0.21 (v/v). Therefore, there is a maximum limit on kg of catalyst that can be loaded on a tray for a given diameter and is given by (Gagadwal and Kienle, 2006)

$$M_{cat} = 150.0\frac{\pi}{4} D_{col}^2 HETP \tag{11}$$

It is assumed the quantity of catalyst is uniform in all the reactive stages.

In this study we have considered catalytic and noncatalytic Raschig ring-shaped packing for reactive and non-reactive sections. The value of packing factor for catalytic packing is assumed to be the same as for the noncatalytic packing. The diameter of the column is calculated from the total vapor load based on the vapor velocity corresponding to the top temperature and capacity factor. The vapor velocity (v) can be derived from flooding velocity. Douglas (1994), reported the simplified flooding velocity correlation for tray column as a function of gas density (ρ_G). On similar lines a simple equation for packed bed with one inch Raschig ring and 80% flooding can be written as

$$v = 0.61/\sqrt{\rho_G} \tag{12}$$

In the DE-based function minimization procedure for reactive distillation the objective function can be the minimization of cost (C_T).

$$\xi(\mathbf{x}) = \min\ C_T \tag{13}$$

subject to a check for the constraint satisfaction. The DE simulation procedure may not converge in some cases requiring the corresponding candidate solution to be penalized by assigning it a higher cost. This way it is ensured that the constraint violating solution does not compete in the subsequent generations.

In the case of problems involving function minimization, locating the deepest local or the global minimum assumes great importance. The stochastic nature of the DE search method assists in achieving this objective. Notwithstanding this observation, a special care was taken during DE implementations so that the search space was thoroughly explored. Using different random number sequences changes the initial candidate solution population in the DE optimization technique. In this way, a different search sub-space is explored each time, thereby, giving the optimization algorithm a fair chance of locating the deepest local or the global minimum on the objective function surface.

The values of DE parameters: i) the population size NP, ii) the weight applied to the random differential (scaling factor) F and iii) the crossover constant CR used in the optimization simulations are chosen such that : (i) the DE simulations do not take long CPU times to converge; and (ii) the DE - searched solutions possess adequate precision. It may be noted that, as the NP value (representing the size solution population) decreases, the CPU time required to manipulate the candidate solutions also goes down proportionately. On the other hand, it is essential that *NP* should be sufficiently large to explore the solution-space as widely as possible. Some general guidelines suggested by Babu et al. (2004) are; i) NP should be about 5 to 10 times the number of parameters in a vector, *F* lies in the range of 0.4 to 1.0 and iii) CR preferred value is 0.1. to 1, but in general CR should be as large as possible.

The DE algorithm is implemented for minimizing an objective cost function describing the CSTR and reactive distillation column design in Fig. 3. The cost function takes into account the column specifications, limits on decision variables, constraints and uses the DE parameters to find global optima. Several runs were performed and the best result obtained by DE parameter described in Table 1. The DE-optimized values of the seven process decision variables namely (i)) CSTR temperature, (ii) feed location, (iii) reflux ratio, (iv) catalyst weight (v) number of reactive stages, (vi) position of reactive stages and the total number of stages (N), and the corresponding minimized value of the total cost is presented in Table 2. The optimal configuration obtained by DE has 18 stages of which 2 are reactive for a total annualized cost of $6,934. The reactive stages are 3th stage and 4th stage having 5.39 kg of catalyst on each stage. The optimal feed location is above the middle of the column at 10th stage. Table 2 shows column specification for the optimal configuration. The composition and temperature profiles as a function of the stage number, pertaining to the DE-based solution are shown in Fig. 3 and 4, respectively, the trends of profiles shown in the figures are in good agreement with those obtained by Kumar et al. (2006).

Table 1. DE optimization parameter

DE variable	value
Number of generation	2
Population size	35
Crossover constant	0.60
Mutation constant	0.5

Table 2. DE-based optimized solutions for distillation column

Column variable	value
Number of Stages	18
Feed location	10
Reflux ratio	1.43
Number of reactive stages	2
Reactive stages position	3
Weight of catalyst per stage (kg)	5.39
CSTR temperature	350
Q_R (kJ/h)	3.015×10^5
Q_C (kJ/h)	1.1085×10^6
Q_{RCSTR} (kJ/h)	8.0956×10^5
Diameter of the column (m)	0.70
Annualized production cost ($)	6,934

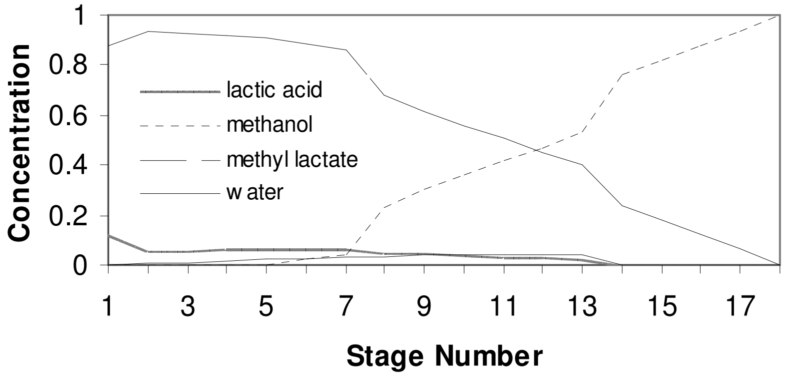

Figure 3. Composition profiles corresponding to the DE-based optimal solution for the methyl lactate hydrolysis

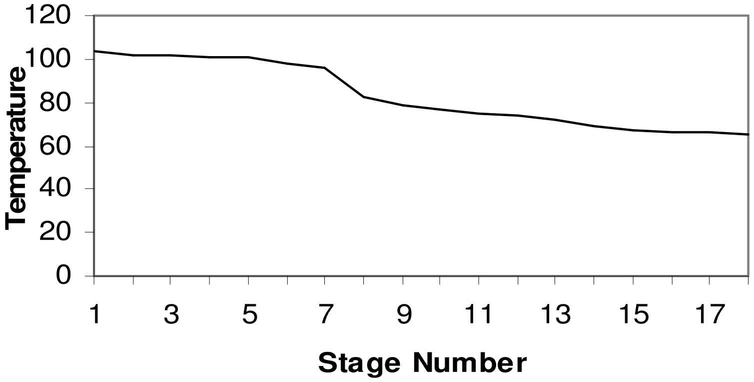

Figure 4. Temperature profile corresponding to the DE-based optimal solution for the methyl lactate hydrolysis

5. CONCLUSIONS

This paper demonstrates a successful application of Differential Evolution algorithm for the optimal design of a semi commercial industrially operated reactive distillation column along with CSTR. The vapor feed obtained from esterification of crude lactic acid in a CSTR is fed continuously to distillation column. The CSTR temperature matches with the feed tray temperature of reactive distillation column. The results demonstrate that the use of a distillation column with CSTR can provide a more-economic process because the distillation column and the CSTR can be operated at their optimum temperatures.

The column parameters optimized are total number of stages, feed location, reflux ratio, catalyst weight, number of reactive stages, position of reactive stages for hydrolysis of methyl lactate to produce pure lactic acid and CSTR temperature. The optimization results obtained suggest that the generalized DE methodology can be successfully employed for optimizing CSTR and reactive distillation column simultaneously.

NOMENCLATURE

a	activity
B_i	bottom flow rate of component i, kmol/h
C	number of component
C_p	heat capacity of water
C^o_{pack}	packing cost per unit volume
C_s	steam cost
C_{steel}	column material (steel) cost
C_w	cooling water cost
CR	crossover constant
D_i	distillate flow rate of component i, kmol/h
d_c	column diameter
$E_{A,1}$	apparent activation energy, kJ/mol
F	scaling factor
f_{ik}	feed flow rate of component i onto tray k, kmol/h
F_{cstr}	feed flow rate to CSTR, kmol/h
fl	feed location
H_{Lk}	liquid enthalpy, kmol/h
H_{Vk}	vapor enthalpy, kmol/h
ΔH_k	heat reaction for reaction, J/kmol
iter	iteration
itermax	maximum iteration
L_k	liquid flow rate off tray k, kmol/h
M_{cat}	total catalyst weight
N	number of stages
N_D	number of yearly working days
N_{gen}	number of generation
N_{gen}^{max}	maximum number of generation
NP	population size

NR	Number of reactive stages
k_1°	exponential factor for the esterification reaction, $\mathrm{mol/g\,min}$
K_{eq}	equilibrium constant
K_{ik}	vapor liquid equilibrium ratio
k_M	adsorption coefficient for methanol
k_W	adsorption coefficient for water
P_c	pressure within the column, kPa
P_i	the production rate of component *i*, kmol/h
P_s	saturation pressure, kPa
Q_B	reboiler duty, kJ/h
Q_C	condenser duty, kJ/h
Q_{cstr}	CSTR duty, kJ/h
r	number of reaction
R	gas constant, kJ/mol.K
r_{ij}	reaction on tray,
RR	reflux ratio
RPS	position of reactive stages
T	temperature, K
ΔT	temperature difference
ΔT_{REB}	log mean temperature for reboiler
ΔT_{COND}	log mean temperature condenser
U_{REB}	overall heat transfer coefficient for reboiler
U_{COND}	overall heat transfer coefficient condenser
V_k	vapor flow rate off tray *k,* kmol/h
ν_{ij}	stoichiometric coefficient of component *i* in the reaction *j*
W_c	catalyst weight, kg
W_s	column wall thickness
x_{ik}	mole fraction of component *i* on liquid phase off tray *k*
x_{di}	distillate mole fraction of component *i*

Greek letters

α_{ik}	activity coefficient for component *i* on tray *k*
λ	enthalpy of vaporization of mixture, J/kmol
λ_{steam}	latent heat of steam vaporization

ε_{jk}	extent of reaction j (j =1,r) on tray k
ρ_s	density of steel
ξ	objective function
ς_c	appropriate value for termination of simulation

Subscripts

LH	lactic acid
M	methanol
ML	methyl lactate
W	water

Appendix I : Reaction and Kinetics

Homogeneous Autocatalyzed Reaction

The lactic acid esterification with methanol without addition of a catalyst is as follows (Sanz et al., 2002):

$$r = n_\circ \frac{dX}{dt} = k_1^\circ \exp(-E_0 / RT) a_{LH} \left(a_{LH} a_M - \frac{a_{ML} a_W}{K_{eq}} \right) \tag{A1}$$

where

$k_1^\circ = 6.024 \times 10^8 \text{ mol g}^{-1} \text{ min}^{-1}$, $E_{A,1} = 56.45$ kJ/mol

Ion-Exchange-Catalyzed Reaction

A general expression given for the L-H model by Sanz et al., 2002 is

$$r = \frac{n}{W} \frac{dX}{dt} = k_1^\circ \exp(-E_{A,1} / RT) \frac{\left(a_{LH} a_M - \dfrac{a_{ML} a_W}{K_{eq}} \right)}{(1 + k_W a_W + k_M a_M)^2} \tag{A2}$$

where

$k_1^\circ = 1.310 \times 10^8 \text{ mol g}^{-1} \text{ min}^{-1}$, $E_{A,1} = 48.67$ kJ/mol, $k_M = 11.38$, $k_W = 8.18$

The temperature dependent of chemical equilibrium constant, K_{eq} can be expressed by the empirical function (Sanz et al, 2003).

$$\ln K_{eq} = (-2.60) - \frac{(-1954.2)}{T} \tag{A3}$$

Appendix II : Vapour Liquid Equilibria (VLE) Data

The UNIQUAC binary parameters for reactive quaternary system lactic acid, methanol, methyl lactate and water at 103.33 kPa given below in Table A1.

Table A1. The UNIQUAC binary parameters for the quaternary system methanol(1), water(2), methyl lactate(3) and lactic acid(4) Sanz et al,2003).

System (i, j)	A_{ij} / K	A_{ji} / K
methanol(1)-water(2)	-192.6	325
methanol(1)-methyl lactate(3)	866.6	-164.4
methanol(1)-lactic acid(4)	322.59	17.14
water(2)-methyl lactate(3)	-20.05	325.31
water(2)-lactic acid(4)	-84.80	-26.1
methyl lactate(3) -lactic acid(4)	367.14	-302.09

Vapor pressure (p_i) is function of temperature only. This dependency can be described by Antoine equation.

$$\text{Antoine equation} \quad : \qquad \log(p_i) = A - \frac{B}{(T + C)} \tag{A4}$$

Table A2. The Antoine equation Parameters, A, B and C (Sanz et. al, 2003).

Compound	Antoine constants			Temp range /K
	A	B	C	
Methanol	7.21274	1588.63	-32.5988	288.00-512.60
Water	7.0436	1636.909	-48.230	373.15-423.15
Methyl lactate	7.24147	2016.46	-32.104	207.15-584.00
Lactic acid	7.51107	1965.70	-91.021	273.15-500.15

Appendix III : Column Model for Reactive Distillation

Component material balance equations:

$$F_{cstr} x_i - F_{cstr} y_i + \sum_{j=1}^{r} v_{ij} \varepsilon_{jcstr} = 0 , \quad i = 1,\ldots,C \tag{A5}$$

$$L_2 x_{i2} - V_1 K_{i,1} x_{i,1} - B_i + \sum_{j=1}^{r} v_{ij} \varepsilon_{j1} = 0 \quad i = 1,\ldots,C \tag{A6}$$

$$f_{ik} + V_{k-1}K_{i,k-1}x_{i,k-1} + L_{k+1}x_{i,k+1} - L_k x_{i,k} - V_k K_{i,k}x_{i,k} + \sum_{j=1}^{R} v_{ij}\varepsilon_{jk} = 0 \qquad \text{(A7)}$$

$$k = 2,\ldots, N-1, \qquad i = 1,\ldots,C$$

$$V_{N-1}K_{N-1,i}x_{i,N-1} - V_N K_{N,i}x_{i,N} - L_N x_{i,N} - D_i + \sum_{j=1}^{r} v_{ij}\varepsilon_{jN} = 0 \quad i = 1,\ldots,C \qquad \text{(A8)}$$

$$\varepsilon_{jk} = W_k r_{jk}\,,\ j = 1,\ldots, r\,,\ k = 1,\ldots, N \qquad \text{(A9)}$$

$$\sum_{i=1}^{C} x_{ik} - 1 = 0 \quad , k = 1,\ldots, N \qquad \text{(A10)}$$

$$\sum_{i=1}^{C} K_{ik}x_{ik} - 1 = 0\,,\ k = 1,\ldots, N \qquad \text{(A11)}$$

$$K_{ik} = \frac{Ps_{ik}\alpha_{ik}}{P} \qquad \text{(A12)}$$

$$F_k H_{Vk} + V_{k-1}H_{Vk-1} + L_{k+1}H_{Lk+1} - L_k H_{Lk} - V_k H_{Vk} + \sum_{j=1}^{r}\varepsilon_{jN}\Delta H_j = 0 \qquad \text{(A13)}$$

$$i = 1,\ldots,C$$

$$P_i = xd_i D + B_i \ , \quad i = 1,\ldots,C \qquad \text{(A14)}$$

Appendix IV : Total Annual Cost for Reactive Distillation Column

The objective function (C_T) for the reactive distillation represents the total annual cost ($) consisting of capital and operating cost. The capital cost comprises of cost of column, packing, reboiler and condenser. The operating cost have two components; steam cost for heating of CSTR and reboiler, and cooling water cost for condenser:

$$\left\{\begin{matrix} Total \\ Cost, \\ C_T \end{matrix}\right\} = \left\{\begin{matrix} Operating \\ Cost, \\ C_1 \end{matrix}\right\} + \left\{\begin{pmatrix} \text{depreciation} + \\ \text{interest} + \\ \text{maintenance} \end{pmatrix} \times \begin{pmatrix} Capital \\ Cost, \\ C_2 \end{pmatrix}\right\} \qquad \text{(A15)}$$

where operating cost, C_1, is calculated according to the equation given below.

$$C_1 = \frac{Q_r \times C_s \times N_D \times 24}{\lambda_{steam}} + \frac{Q_c \times C_w \times N_D \times 24}{C_p\,\Delta T} + \frac{Q_{cstr} \times C_s \times N_D \times 24}{\lambda_{steam}} \qquad \text{(A16)}$$

The capital cost, C_2 ($/yr), consists of packing (C_{pack}), column (C_{col}), reboiler (C_r), and condenser(C_c) costs, where C_{pack} is computed as:

$$C_{pack} = A_c \times N \times HETP \times C^o_{pack} \qquad \text{(A17)}$$

In the above equation, A_c represents the column area and $HETP$ for the packing is taken as 0.46 m (www.cheresources.com), The C_{col} is calculated on the basis of internals from the following correlation.

$$C_{col} = 3.14 \times 1.4 \times d_c \times N_{st} \times HETP \times W_s \times \rho_s \times C_{steel} \qquad \text{(A18)}$$

The cost of reactive packing is taken double of non-reactive packing. The C_{cstr}, C_r and C_c are evaluated on the basis of heat transfer area ($ 500/m^2) calculated for CSTR (A_{cstr}), reboiler (A_r) and condenser (A_c).

$$A_r = \frac{Q_r}{U \times \Delta T_m} \qquad \text{(A19)}$$

$$A_c = \frac{Q_c}{U \times \Delta T_m} \qquad \text{(A20)}$$

Heat transfer area for CSTR (A_{cstr}) is calculated in similar way as it is done for reboiler.

Assuming depreciation, interest, and maintenance costs of 18%, 15% and 2%, respectively, the total annual cost to be minimized is evaluated as:

$$C_T = C_1 + 0.35\ C_2 \qquad \text{(A21)}$$

Specification: C_p = 4.18 kJ/kg, λ_{steam} =2200 kJ/kg, C_s =0.0186 $/kg , C_w = 0.0075 $/kg , N_D =300, C^o_{pack} = 2325.58 $/m^3, W_s = 0.006 m, ρ_s = 8000 kg/m^3 , C_{steel} = $50/kg, U_{REB} = 900 W/m^{2}K, U_{COND} = 500 W/m^{2}K, ΔT_{REB} = 48, ΔT_{COND} =16.

REFERENCES

Angira R., Babu B. V. "Optimization of process synthesis and design problems: A modified differential evolution approach", Chem. Eng. Sci., 61, 4707–4721(2006).

Babu, B.V., Sastry, K.K.N. "Estimation of heat-transfer parameters in a trickle-bed reactor using differential evolution and orthogonal collocation", Computers & Chemical Engineering, 23, 327–339(1999).

Babu, B.V., Angira, R. "A differential evolution approach for global optimization of MINLP problems", Proceedings of Fourth Asia Pacific Conference on Simulated Evolution and Learning (SEAL-2002), Singapore, November 18–22, 2, 880–884 (2002).

Babu, B.V., Rakesh Angira, and Anand Nilekar, "Optimal Design of an Auto-Thermal Ammonia Synthesis Reactor Using Differential Evolution", Proceedings of The Eighth World Multi-Conference on Systemics, Cybernetics and Informatics (SCI-2004), Orlando, Florida, USA, July 18-21, 2004.

Babu, B.V., Pallavi, G., Chakole, Syed Mubeen, J.H. “Multiobjective differential evolution (MODE) for optimization of adiabatic styrene reactor”, Chem. Eng. Sci., 60(17), 4822–4837(2005).

Bastos, J. “Modeling extractive distillation processes”, Ph.D. thesis, Universidade do Porto (in Portuguese). (1987)

Burri J. F. and Manousiouthakis V. I. “Global optimization of reactive distillation networks using IDEAS” , Comput. Chem. Eng., 28(12), 2509-2521 (2004).

Buzad, G., & Doherty, D. F. “New tools for the design of kinetically controlled reactive distillation columns for ternary mixtures”, Comput. Chem. Eng., 19, 395–408(1995).

Chakraborti, N., Mishra, P., Erkoc, S. “A study of the Cu clusters using gray-coded genetic algorithms and differential evolution”, Journal of Phase Equilibria and Diffusion, 25,16(2004).

Cardoso, M.F., Salcedo, R.L., Azevedo, S.F., Barbosa, D. “Optimization of reactive distillation processes with simulated annealing”, Chem. Eng. Sci., 55, 5059-5078(2000).

Ciric, A. R. & Gu, D. “Synthesis of nonequilibrium reactive distillation processes by MINLP optimization”, A.I.Ch.E. J., 40(9), 1479(1994).

Colaco, M.J., Dulikravich, G.S., Martin, T.J. “Optimization of wall electrodes for electro-hydrodynamic control of natural convection during solidification”, Materials and Manufacturing Processes 19 (4), 719–736(2004).

Dalaouti N. and Seferlis P. “A unified modeling framework for the optimal design and dynamic simulation of staged reactive separation processes”, Comput. Chem. Eng., 30 (8), 1264-1277 (2006).

Douglas, J. “Conceptual Design of Chemical Processes”, International edition, McGraw-Hill, Inc.,1988.

DOI: 10.2202/1934-2659.1111

Gangadwal, J., Kienle A. “MINLP optimization of butyl acetate synthesis”, Chem. Eng. Process., 46, 107-118 (2007).

Gómez, J.M., Reneaume, J.-M. Roques, M., Meyer, M. Meyer, X., Mixed integer nonlinear programming formulation for optimal design of a catalytic distillation column based on a generic nonequilibrium model, Ind. Eng. Chem. Res., 45 (4), 1373-1388 (2006)

Henley E.J., Seader J. D. “Equilibrium stage separation in chemical engineering”, John Wiley & Sons, New York, 1981.

Huss, R. S., Chen, F.,Malone M. F., Doherty M. F. “Computer-Aided tools for the design of reactive distillation systems”, paper presented at ESCAPE 9, June 1999.

Jackson J. R., Grossmann I. E. “A disjunctive programming approach for the optimal design of reactive distillation columns”, Comput. Chem. Eng. 25,1661–1673(2001).

Karabo D., Okdem S., “A Simple and Global Optimization Algorithm for Engineering Problems: Differential Evolution Algorithm”, Turk. J. Elec. Engin. 12(1), 53-60, 2004.

Kim, Y.J., Hong, W.H., Wozny, G. “Effect of recycle and feeding method on batch reactive recovery system of lactic acid”, Korean J. Chem. Eng.,19(5), 808-814(2002).

Kim, J.Y., Kim, Y.J., Hong, W.H., Wozny G. “Recovery process of lactic acid using two distillation columns, Biotechnol. Bioprocess Eng.”, 5,196-201(2000).

Kumar, R, Nanavati, H., Noronha S.B., Mahajani, S.M., “A continuous process for the recovery of lactic acid by reactive distillation”, J. Chem. Technol. Biotechnol., 81, 1767-1777(2006).

Li, M.A, Yang, Z., Jichu, Y. “Purification of lactic acid by heterogeneous catalytic distillation using ion-exchange resins”, Chinese J. Chem. Eng,13(1),24-31(2005).

Lima R. M. , Salcedo R.L. and Barbosa D. “SIMOP: Efficient reactive distillation optimization using stochastic optimizers”, Chem. Eng. Sci., 61(5),1718-1739 (2006).

Melles S., Grievink H., and Schrans S. M. “Optimisation of the conceptual design of reactive distillation columns”, Chem. Eng. Sci., 55(11), 2089-2097(2000).

Noeres, C., K. Dadhe, Gesthuisen, R., Engell S. and Górak A. “Model-based design, control and optimisation of catalytic distillation processes” ,Chem. Eng. and Process., 43(3), 421-434(2004).

Price K. “Differential Evolution vs. the Functions of the 2nd ICEO’, Proceedings of 1997 IEEE International Conference on Evolutionary Computation (ICEC_ 97), Indianapolis, USA, pp. 153–157,13–16 April 1997.

Price, K., Storn, R. “Differential Evolution – A simple evolution strategy for fast optimisation” Dr. Dobb's Journal 22(4),18–24 and 78(1997).

Sanz, M.T., Beltran S., Calvo, B., Cabezas, J.L. “Vapor Liquid Equilibria of the Mixtures involved in the esterification of lactic acid with methanol”, J. Chem. Eng. Data, 48, 1446-1452(2003).

Sanz M. T. Muga R. Beltran S., Cabezas J. L. “Autocatalyzed and Ion-exchange-resin-catalyzed esterification kinetics of lactic acid with methanol”, Ind. Eng. Chem. Res., 41,512-517(2002)

Schopmeyer H. H., Arnold C. R. “Lactic acid purification”, US patent No. 235370, 1944.

Seo, Y., Hong, W.H., Hong, H.H. “Effects of operation variables on the recovery of lactic acid in a batch distillation process with chemical reactions”, 16(5), 556-561(1999).
Stichlmair, J. Frey T. “Mixed-integer nonlinear programming optimization of reactive distillation processes”, Ind. Eng. Chem. Res. 40, 5978–5982 (2001).

Storn, R., 1995. “Differential evolution design of an IIR-filter with requirements for magnitude and group delay”, Technical Report, International Computer Science Institute. Available via Internet:_ftp.icsi.berkeley.edu/pub/techreports/1995/tr-95-026.pdf.

Storn, R., Price, K. “DE-a simple and efficient heuristic for global optimization over continuous space”, Journal of Global Optimization 11(4), 341–359(1997).

Storn R, Price K. “Differential evolution—A simple and efficient adaptive scheme for global optimization over continuous spaces”, Technical Report TR-95-012, International Computer Science Instititute, Berkely, California, 1995.

Sun, J., Zhang Q. Tsang, E.P.K. “DE/EDA: A new evolutionary algorithm for global optimization”, Information Sciences,169, 249–262(2005).

Sundmacher, K., Hoffmann, U. “Multicomponent mass transfer and energy transport on different length scales in a packed reactive distillation column for heterogeneously catalysed fuel ether production”, Chem. Eng. Sci., 49, 4443-4464(1994).

Wang, K. Qian Y., Yuan Y. and Yao, P. “Syntheses and optimization of heat integrated distillation systems using an improved genetic algorithms”, Comput. Chem. Eng., 23 ,125-136(1998).

Wang, F.S., Chiou, J.P. “Optimal control and optimal time location problems of differential-algebraic systems by differential evolution”, Ind. Eng. Chem. Res., 36, 5348–5357(1997).

Vikroy, T. B. “Lactic Acid’, Comprehensive Biotechnolgy, Murray Moo-Young, eds. Permagon Press, Oxford(1985)