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RBDOPT: a general-purpose object-oriented module for distributed campaign optimization of reactive batch distillation

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Abstract

Reactive batch distillation optimization (RBDOPT) provides a general framework for the simulation and the optimization of multicomponent batch distillation with or without chemical reactions. It models the distillation process as a differential algebraic equation (DAE) system and can handle various modes of operation such as continuous flow of one of the reactants, intermediate feed and inverted distillation. Physical property estimates are obtained from Physical Property Data Service (PPDS) that supports a large number of species and routes to model non-ideal behaviour. RBDOPT is designed specifically for determining optical campaign policies for reactive batch distillation systems with minimal input from a user. Coded in an object-oriented environment (C++), it uses distributed computing techniques to achieve a speedup nearly equal to the number of control variables while solving the optimal control problem.

This paper highlights the main features of RBDOPT and demonstrates its application to the optimization of reactive batch distillation operation.

Keywords: Batch distillation; Reactive distillation; Campaign optimization

1. Introduction

Batch distillation simulation has been an area of extensive research over the past few decades [1–4]. The numerical issues associated with the simulation of this dynamic process have been understood reasonably well for both continuous and staged column models [5,6]. The design of optimal operation policies, on the other hand, has been the focus of only a few recent studies [7,8] in spite of the increasing emphasis on the use of existing distillation units (rather than designing new ones) for the separation of new mixtures, a feature for which a batch facility is particularly useful. To supplement this effort, there is a strong need for a module that has the following features:

1. general applicability and extendibility of distillation simulation to a wide variety of chemical systems,
2. computationally efficient, robust and portable optimization framework, and
3. focus on the optimization of the entire *campaign* of batches, thus assisting in the choice of desirable trade-off among overall production rate, waste generation rate and utilization ratios (this feature is particularly important in the case of reactive distillation [9,10]).

Contemporary understanding of simulation and dynamic optimization issues, and advances on the computer science front in distributed computing techniques and object-oriented programming can be exploited to accomplish these features. Reactive batch distillation optimisation (RBDOPT) (Fig. 1) has been developed with this objective in mind. It is a general-purpose object-oriented module for performing distributed campaign optimization of reactive batch distillation. Some of the important features of RBDOPT are discussed in the following section.

2. General features

2.1. Object-oriented environment

Easy reusability and extendibility of different sections of the code are very important in order to avoid major efforts in the broadening of the scope of chemical engineering software. The object-oriented environment provided through C++ is useful in this regard. RBDOPT defines a distillation column as an object. It then partitions the procedures and data into *public* and *private* categories, depending on

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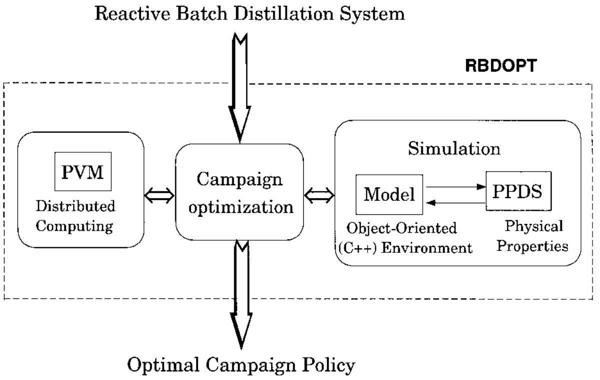

Fig. 1. General structure of RBDOPT.

whether that level of detail is of any importance to a user or not. For example, total reflux conditions, intermediate enthalpy values etc. are not required by a user, therefore, they can be classified as private data, whereas accumulated compositions of different distillation cuts and instantaneous composition of distillate are relevant to a user, hence they constitute public data. For optimizing the integrated performance of an operation consisting of several distillation units, the main module can easily define multiple columns as different *objects* of the distillation *class* and keep the simulation details of those columns active simultaneously for the eventual processing by an optimizer. Through properties like *inheritance*, the object-oriented environment also allows easy adaptation of the distillation column model for simulating other separation processes such as absorption. If needed, the built-in thermodynamic properties interface (PPDS) can be conveniently overwritten by other property data banks or routines either by creating a new object or by *functional overloading*. Though most of the current scientific programs (like PPDS and the Sequential Quadratic Program (SQP) code in the present case) are still in FORTRAN, this should not be looked upon as a major concern since communication can be facilitated easily through special classes developed within RBDOPT. For instance, since FORTRAN and C++ have different ways of storing multidimensional arrays, a special class is developed to ensure correct transfer of these arrays between FORTRAN and C++.

2.2. Model equations

A rigorous model for staged batch distillation can be represented as a differential algebraic equation (DAE) system as shown in Eq. (1)[1,5]. It consists of differential equations representing total and component mass balances and total energy balances. The algebraic equations are due to VLE, stage efficiencies and physical property estimation. In the conventional mode of operation, the bottom product flow rate (B) will be zero while for the inverted distillation column, where feed is introduced into the condenser and the product is collected from the bottom, the distillate flow rate (D) will be zero. The model assumes negligible vapor holdup compared to liquid holdup and hence chemical reactions in the vapor phase are not considered. Both the constant molar holdup case and constant volume holdup cases are accommodated by the model.

Component c: $1 \le c \le J$

Condenser:

$$\frac{\mathrm{d}(A_0X_{0,c})}{\mathrm{d}t} = V_1Y_{1,c} - (L_0 + D)X_{0,c} + r_{0,c}A_0$$

$$\frac{\mathrm{d}A_0}{\mathrm{d}t} = V_1 - (L_0 + D) + \Delta g_0 A_0$$

$$\frac{\mathrm{d}(A_0H_0^L)}{\mathrm{d}t} = V_1H_1^V - (L_0 + D)H_0^L + Q_0$$

$$Y_{o,c} = K_{o,c}X_{o,c}$$

Plate p : $1 \le p \le N$:

$$\frac{\mathrm{d}(A_pX_{p,c})}{\mathrm{d}t} = V_{p+1}Y_{p+1,c} + L_{p-1}X_{p-1,c} - V_pY_{p,c} - L_pX_{p,c} + r_{p,c}A_p$$

$$\frac{\mathrm{d}A_p}{\mathrm{d}t} = V_{p+1} + L_{p-1} - V_p - L_p + \Delta g_p A_p$$

$$\frac{\mathrm{d}(A_pH_p^L)}{\mathrm{d}t} = V_{p+1}H_{p+1}^V + L_{p-1}H_{p-1}^L - V_pH_p^V - L_pH_p^L + Q_p$$

$$Y_{p,c} = Y_{p+1,c}(1 - e_{p,c}) + e_{p,c}K_{p,c}X_{p,c}$$

Reboiler:

$$\frac{\mathrm{d}(A_bX_{b,c})}{\mathrm{d}t} = L_NX_{N,c} - (V_b + B)Y_{b,c} + r_{b,c}A_b + FX_{f,c}$$

$$\frac{\mathrm{d}A_b}{\mathrm{d}t} = L_N - (V_b + B) + \Delta g_b A_b + F$$

$$\frac{(\mathrm{d}A_bH_b^L)}{\mathrm{d}t} = L_NH_N^L - V_bH_b^V + Q_b$$

$$Y_{b,c} = K_{b,c}X_{b,c}$$

$(1 \le n \le N)$ or $(n = o)$ or $(n = b)$:

$$\rho_n = \rho_n(X_{n,c}, T_n, P_n)$$

$$A_n = A_n(X_{n,c}, T_n, P_n, \tau_n)$$

$$K_{n,c} = K_{n,c}(P_n, T_n)$$

$$H_n^L = H_n^L(X_{n,c}, P_n, T_n)$$

$$H_n^V = H_n^V(Y_{n,c}, P_n, T_n)$$

$$\sum_{c=1}^{C} Y_{n,c} = 1$$

$$\Delta g_n = \sum_{c=1}^{J} r_{n,c}$$

For conventional distillation:

$$B = 0.$$

For inverted distillation:

$$D = 0$$

For constant volume holdup case:

$$A_n = \frac{\tau_n \rho_n}{M_n} \qquad (n \neq b) \tag{1}$$

2.3. Physical property estimation

Accurate estimation of physical properties is important in the simulation of a chemical process. A robust physical properties estimates system with associated constant data banks, an extensive collection of data to support a large number of species, a wide variety of physical properties routes for modeling non-ideal behavior, and which is easy to access and requires minimal information from a user is essential for routine use of batch column simulation. RBDOPT uses the PPDS system developed at National Engineering Laboratory, UK. It supports over 900 components and 36 physical property routes including SRK, UNIFAC, UNIQUAC, NRTL and Wilson's equation. If needed, a user can overwrite this interface with his own data at any stage of simulation.

2.4. Numerical solution and the total reflux conditions

It is well known that solving a DAE system is, in general, more complex than solving an ordinary differential equation (ODE) system, particularly due to the difficulty in estimating derivatives for the algebraic variables [11–13]. To alleviate this problem, the common practice is to exploit the particular structure of a DAE system to convert it into an ODE system. This, however, may not always be possible. Moreover, in some cases, a user may find it convenient to modify the model by either providing new algebraic equations or by manipulating the existing ones, hence a DAE representation is maintained within RBDOPT. It should, however, be noted that if the index of a DAE system [14] is greater than one, there may arise severe numerical difficulties in achieving a converged solution. In some cases, the index of a DAE system can simply be reduced by a proper rearrangement of the model equations, therefore, before any qualitative modification of the model, a structural analysis of the system to reduce the index of the system is beneficial. For the model we considered, the index of the system has been shown to be one, if at least the top pressure is specified [11]. We considered a pre-defined pressure profile for our model and hence the index of the DAE system will remain one provided that the reaction kinetics does not involve a pressure term.

LSODI [15], DASSL [16] and DASPK [17] are commonly used DAE solvers. The merits of these solvers are discussed in the references and hence are not reproduced here. RBDOPT uses DASPK to integrate the DAE system on account of its robustness in handling stiffness (without any need for user-supplied derivatives) and an efficient calculation procedure to compute a consistent set of initial derivatives. However, obtaining a consistent set of initial conditions is important in getting an accurate DAE solution. RBDOPT uses total reflux conditions to initialize the DAE system Eq. (1). Since in the case of non-reactive distillation, iterative schemes have been used successfully [5,8], RBDOPT uses the following scheme to obtain total reflux conditions:

1. Set $A_b =$ initial charge, $X_{b,c} =$ initial charge composition and $A_p^0 = 0$.
2. Estimate the bubble point of the mixture from $X_{b,c}$ and P_p, and find the corresponding vapor phase composition $Y_{b,c}$ from VLE.
3. Mass balance at total reflux gives $X_{n,c} = Y_{b,c}$.
4. For $p = N$ through 0 ($p = 0$ means condenser), repeat steps (2) and (3) while ensuring $\sum_{c=1}^{C} Y_{(p,c)} = 1$ is satisfied at the plate temperature T_p. If not, update T_p by

   $$T_p = T_{p\,\mathrm{old}} + \frac{\mathrm{error}(T_{p\,\mathrm{old}})}{\mathrm{error}(T_{p\,\mathrm{old}}) - \mathrm{error}(T_{p\,\mathrm{old}} + 1)}$$

   where

   $$\mathrm{error}(T_{p\,\mathrm{old}}) = \log\left(\sum_{c=1}^{C} Y_{(p,c)}\right).$$
5. Compute molar holdup A_p at the conditions determined previously.
6. If composition profiles between the successive iterations are sufficiently close (within an acceptable cumulative error), go to step (9).
7. Set

   $$A_p^s = A_p^{s-1} + (A_p^s - A_p^{s-1})\lambda.$$
8. Perform overall mass-balance to update A_b and $X_{b,c}$ and go to step (2).
9. Calculate liquid and vapor flow rates using stage energy balances

   $$V_{p+1} = \frac{(H_p^V - H_{p-1}^L)V_p}{(H_{p+1}^V - H_p^L)}.$$

This scheme converges rapidly provided that the reboiler holdup is large compared to the plate holdup and the relaxation parameter λ ($0 \leq \lambda \leq 1$) is adjusted properly. A high value of λ tends to give a solution in few iterations but may occasionally lead to divergence or oscillations, whereas a small value may take high CPU times. For most applications, $\lambda = 0.5$ was found to give a good trade-off between computational speed and the reliability of convergence to the solution.

In many applications, total reflux conditions are straightforward either due to the actual startup procedure used e.g. the entire column is filled up with one of the species (usually the most volatile component in the mixture), and therefore, only the reboiler content is multicomponent in nature; or due to a numerical simplification that assumes this type of practice. However, in the case of reactive distillation, such simplifying assumptions may be detrimental since they may lead to significant miscalculations of the conversion of the reaction. For instance, if a simplified set of total reflux conditions predicts premature evaporation of one of the reactants, not only the separation efficiency but also the extent of the reaction computed by the model would be incorrect. In fact, depending on the chemical reaction involved, the total reflux operation needs to be designed and controlled properly to obtain a satisfactory purity of the product [19].

In the case of a reversible reaction case where reactive distillation is used essentially to overcome the chemical equilibrium constraint, it is important that the product withdrawal begins only after chemical equilibrium is established throughout the column since chemical equilibrium represents the maximum concentration of the product. These conditions of chemical equilibrium are coupled with phase equilibrium conditions and are additional constraints on the total reflux conditions. One simplified approach is to assume chemical equilibrium in the feed and then to follow a sequential scheme (as shown previously) to attain the column conditions. This is a good approach if column hold-up is small compared to the reboiler hold-up. If this is not true, a set of algebraic equations (the DAE model with derivative and product withdrawal as zero) must be solved simultaneously. For this purpose, an IMSL routine DNEQBF that uses a factored secant update method to solve non-linear algebraic equations is linked to RBDOPT. Numerically, this is a challenging problem due to the possibility of multiple solutions, a phenomenon similar to the multiple steady states observed in continuous distillation simulations. A good initial estimate of the solution of the algebraic equations may need to be provided based either on the experimental data or from a detailed hydraulic model that simulates the detail flow pattern in the column to identify if the phase or chemical or both equilibriums exist in different sections of a column at the total reflux conditions. In the case of an irreversible reaction, reactive distillation may be used to withdraw the product as soon as it is formed to arrest further side reactions, and hence the duration of the total reflux period should be designed accordingly.

The DAE system is generally stiff around the point at which the total reflux operation is disrupted by the sudden withdrawal of the products. In order to handle numerical difficulties at this point, the *forcing function* approach has been used successfully [5]. In RBDOPT, we overcame this problem by relaxing the limit on the step size in DASPK, and thus the local accuracy requirement, without any significant effect on the overall composition of distillation cuts. For example, for the acetic anhydride case discussed in Section 4.2, the normal step size was constrained to 0.001 h but the initial step size (used for the first few steps) was constrained only to 0.01 h. If needed, the same approach can be adopted to relax the accuracy requirement over a small region around points of discontinuity such as at the addition of intermediate feed. As a heuristic, we found that if this region is less than 1% of the total production period, the overall accuracy is not affected significantly.

2.5. *Dynamic optimization*

A batch distillation optimization problem typically involves terms corresponding to the production rate, the purity of the product, waste generation and/or the energy requirement either in the objective functions or in the constraints. Since the control variable, usually the reflux level or boilup rate, is a function of time, a dynamic optimization or *optimal control* problem must be solved. There are two approaches to solve this problem viz. Pontryagin's maximum principle [20] and discretization techniques. The former solves a two point split boundary value problem involving simulation and adjoint variable equations to yield a continuous control profile, whereas the latter discretizes the dynamic profile of a control variable into different time periods (control vector parameterization (CVP) approach) and fits a basis function, either a step or a ramp function. Thus, the dynamic optimization problem transforms into a non-linear programming problem (NLP) with the durations and the level or slope of these functions as the new control variables. If the number of periods is increased, this new set of control variables would approach the original continuous control profile. As an extension of this approach, the model equations can be solved as a part of the optimization constraint set (*collocation technique*) instead of the sequential solutions of the model equations and the optimization problem, as in the case of CVP. The relative merits of these techniques are well discussed [7,12] and are not repeated here. CVP is widely used due to its simplicity and robustness in handling non-linearities and stiff systems by isolating the simulation and optimization complexities. Moreover, unlike the collocation technique, CVP does not require any special-purpose NLP code for computational efficiency and can provide feasible intermediate solutions that may be of interest to a user. RBDOPT uses CVP for the optimal control problem and an SQP method [21] for solving the resultant NLP.

2.5.1. *Gradient estimation and distributed computing*

Providing the analytical expressions of the gradients required for an optimization algorithm is not always convenient, if not impossible, for a user. Numerical computation of these gradients often presents a major computational burden. Symbolic differentiation, divided differences and automatic differentiation are three established techniques used for this purpose [22]. Symbolic differentiation, which relies on the term by term exact differentiation of the function, tends to fail with an increase in the complexity in function description (to avoid this, restructuring of the model equations may be needed). The divided differences method is probably the most commonly used technique. Under the divided differences method, the control variables are perturbed and the gradients are computed by carrying out a series of simulation runs (which is equal to the number of control variables for the forward or the backward difference formula, and is twice the number of control variables for the central difference formula) and using the classical finite difference formulae Eq. (2). One can also use a polynomial fit to obtain further accuracy, if needed, at the expense of additional simulation runs.

$$\left.\frac{\partial f(x)}{\partial x}\right|_{x_0} \approx \frac{f(x_0 \pm \delta) - f(x_0)}{\delta}$$

or

$$\left.\frac{\partial f(x)}{\partial x}\right|_{x_0} \approx \frac{f(x_0 + \delta) - f(x_0 - \delta)}{2\delta} \tag{2}$$

By proper selection of the perturbation step size, good accuracy can be obtained in the gradient estimation. While the step size should be as small as possible to get a good estimate of the local gradients, it should not be so small that the computer truncation error in the function evaluation becomes significant, leading to an erroneous gradient estimation.

Automatic differentiation relies on the fact that every function, no matter how complicated, is executed on a computer as a sequence of elementary operations (such as additions and multiplications) and elementary functions (such as sin and cos) and therefore, by applying the chain rule repeatedly, exact function derivatives can be obtained. This method is shown to yield as high as 60% CPU saving over the divided differences method [22]. However, in RBDOPT, a speedup as high as the number of control variables is obtained by exploiting the fact that the simulation runs with the perturbed control variables are strictly independent of each other, and hence can easily be parallelized. These simulation runs can then be carried out using distributed computing techniques on either a multiprocessor or a network of computers. In order to have the portability of using RBDOPT in different computer environments, the latter option was employed in this work.

Parallel Virtual Machine (PVM) [23] is a software package that allows the exploitation of a network of heterogeneous computers so that it can function as a single high-performance parallel machine. RBDOPT interacts with the network of computers through the functions provided by PVM. The main program (*master*) runs on a master machine and at the gradient estimation point different simulation runs are spawned on different computers either arbitrarily or in a pre-specified manner (e.g. computers with less load can be used preferentially). Since the overheads associated with the communication among these computers are very small due to the fact that the simulation runs are fully independent of each other (communication is required only for providing data to slave computers and transferring results to the master computer), the maximum speedup obtained is almost equal to the number of control variables (or the number of computers, whichever is less). This leads to an efficient utilization of the computing facility as well. A supplementary tool XPVM provides a visual picture of the status of the program and the load distribution within the network of computers.

3. Simulation validation

In order to verify the accuracy of RBDOPT and its robustness in handling varied degrees of stiffness and discontinuities, a number of distillation applications were simulated. Some of these runs are presented below and are compared with the results reported in the literature.

3.1. Cyclohexane–toluene separation

Domenech and Enjalbert [24], and Mujtaba [18] considered the binary distillation of cyclohexane and toluene. The conditions for the separation and the numerical parameters are given in Table 1. The column was initialized by considering binary feed in the reboiler and following the scheme discussed earlier. The simulation is fairly straightforward and does not encounter any stiffness problem. As can be seen in Table 2, our results match well with the experimental results of Domenech and Enjalbert and the simulation results of Mujtaba. In case 1 in Table 2, our simulation results show some deviation from the experimental results obtained by Domenech and Enjalbert towards the end of the operation but a similar trend was observed in the simulation plots presented by Domenech and Enjalbert [24]. We modeled VLE using the Soave–Redlich–Kwong (SRK) route, however, the use of ideal VLE models also produced similar results (less than 1% deviation). Both simulation runs required about 4 s on an HP 9000 (model 755/99).

Table 1
Cyclohexane–toluene separation conditions and numerical parameters

No. of plates	4
Initial charge	200 lb mol
Initial mole fraction (Cyclohexane, toluene)	Case 1: (0.62, 0.38); Case 2: (0.55, 0.45)
Reflux ratio	Case 1: 3 Case 2: 4
Stage efficiency	75%
Pressure	1 atm
Simulation grid size	0.01 h
Relaxation parameter	0.5
Total reflux conditions tolerance level	0.001
DAE tolerance level	0.1
DAE maximum step-size allowed	0.1

Table 2
Cyclohexane–toluene results

Case	Cyclohexane mole fraction in accumulated distillate			
	Distillate (lb mol)	Domenech and Enjalbert experimental results [23]	Mujtaba simulation results [18]	Our simulation results
1	21	0.94	0.95	0.93
	50	0.92	0.87	0.91
	110	0.83	0.81	0.76
	140	0.55	0.5	0.46
2	10	0.93	0.94	0.92
	40	0.90	0.92	0.89
	60	0.89	0.90	0.86
	131	0.37	0.38	0.38

3.2. Quaternary hydrocarbon separation

A complex separation of a hydrocarbon mixture of propane, butane, pentane and hexane was considered by Boston et al. [25] and Mujtaba [18]. From the numerical perspective, this is a challenging simulation problem due to the discontinuities introduced by five changes in the reflux ratio and the boilup rate, and due to the addition of intermediate feed (Table 3). These discontinuities create additional problem in the case of the DAE system since a consistent set of derivative values for the algebraic variables need to be recalculated. The stiffness and the discontinuities were handled by constraining the step size within DASPK to 0.01 h. This prevents DASPK from passing over a larger region by using a larger step size (and thus overlooking the local stiffness) that often leads to the convergence problem.

Comparison of our results with those in the literature [25,18] (Table 4) shows good agreement (less than 2% deviation). The simulation took 5.3 min on an HP 9000 (model 755/99), significant portion of the CPU time being spent in integrating the DAE system around the time of the addition of intermediate feed and the changes in boilup rate.

Table 3
Quaternary hydrocarbon separation conditions and numerical parameters

No. of plates	8
Initial charge	100 lb mol
Initial mole fraction (Propane, *n*-Butane, *n*-Pentane, *n*-Hexane)	(0.1, 0.3, 0.1, 0.5)
Intermediate charge	20 lb mol (at 5.88 h)
Intermediate mole fraction	(0, 0.4, 0, 0.6)
Holdup	0.00493 lb mol (for each plate) 0.0493 lb mol (for condenser)
Pressure	1 atm
Simulation grid size	0.01 h
Relaxation parameter	0.5
Total reflux conditions tolerance level	0.001
DAE tolerance level	0.1
DAE maximum step-size allowed	0.01

3.3. Methanol esterification by reactive distillation

Production of methyl acetate by esterification of methanol Eq. (3) can be carried out in a reactive distillation unit since one of the products, methyl acetate, is the most volatile component in the mixture. The conditions for the separation (Table 5) are the same as those used by Mujtaba [18] except that both the reactants are taken in the initial charge itself (Mujtaba [18] introduced methanol at the end of the total reflux conditions). We assumed that at the total reflux conditions, the reboiler charge reaches chemical equilibrium and this equilibrium mixture then satisfies the phase equilibrium conditions in the column.

$$\text{methanol} + \text{acetic acid} \rightleftharpoons \text{methyl acetate} + \text{water}$$

$$r_{\text{methanol}} = -X_{\text{acetic acid}} X_{\text{methanol}} + X_{\text{methyl acetate}} X_{\text{water}} \quad \text{(per hour)} \tag{3}$$

The reaction term, in general, adds stiffness to the system, therefore, as in the case of the hydrocarbon separation example, the DASPK step size was constrained to 0.01 h. Our results (Table 6) match reasonably well with the result reported by Mujtaba [18]. Some deviations in the present and final distillate composition are probably due to the different feed policies. The first run (period I and II) took 1.3 min while the second run (period I and III) took 1.5 min of CPU on an HP 9000 model 755/99.

These different simulations verified the accuracy and the numerical robustness of RBDOPT in handling multicomponent distillation with or without chemical reactions. From an optimization perspective, robustness in the presence of the discontinuities is a critical issue since, usually, an optimal reflux profile consisting of a series of step changes or ramps is sought from an NLP solver and the simulations are prone to run into convergence problem around the points of reflux changes, especially if the change is substantial. In the case of reactive distillation with reversible reactions, the issue is even more important since, in general, after every product cut, the distillation mixture is driven to chemical equilibrium (which typically repre-

Table 4
Quaternary hydrocarbon separation results

Period		Boston et al. [25]		Mujtaba [18]		Our results	
		(lb mol)	Composition[a]	(lb mol)	Composition[a]	(lb mol)	Composition[a]
I: 4.07 h	PD[d]	–	(0.8, 0.2, 0, 0)	–	(0.75, 0.25, 0, 0)	–	(0.76, 0.24, 0, 0)
$R^b = 5$	AD[e]	8.13	(0.99, 0.01, 0, 0)	8.14	(0.98, 0.02, 0, 0)	8.14	(0.98, 0.02, 0, 0)
$VF^c = 12$	SP[f]	91.74	(0.02, 0.33, 0.1, 0.55)	91.86	(0.02, 0.33, 0.1, 0.55)	91.77	(0.02, 0.033, 0.1, 0.55)
II: 1.81 h	PD	–	(0.02, 0.98, 0, 0)	–	(0.031, 0.969, 0, 0)	–	(0.03, 0.97, 0, 0)
$R = 20$	AD	11.76	(0.85, 0.15, 0, 0)	11.76	(0.85, 0.15, 0, 0)	11.74	(0.85, 0.15, 0, 0)
VF = 42	SP	88.12	(0, 0.32, 0.11, 0.57)	88.24	(0, 0.32, 0.11, 0.57)	88.17	(0, 0.32, 0.11, 0.57)
III: 18.27 h	PD	–	(0, 0.16, 0.84, 0)	–	(0, 0.25, 0.75, 0)	–	(0, 0.25, 0.75, 0)
$R = 25$	AD	36.54	(0, 0.99, 0.01, 0)	36.55	(0, 0.99, 0.01, 0)	36.5	(0, 0.99, 0.01, 0)
VF = 52	SP	71.6	(0, 0, 0.13, 0.87)	71.68	(0, 0, 0.13, 0.87)	71.6	(0, 0.00, 0.13, 0.87)
IV: 4.31 h	PD	–	(0, 0, 0.8, 0.2)	–	(0, 0, 0.61, 0.39)	–	(0, 0, 0.61, 0.39)
$R = 15$	AD	8.6	(0, 0, 0.99, 0.01)	8.62	(0, 0.02, 0.94, 0.04)	8.62	(0, 0.02, 0.94, 0.04)
VF = 32	SP	63	(0, 0, 0.02, 0.98)	63.06	(0, 0, 0.02, 0.98)	63.01	(0, 0, 0.02, 0.98)
V: 1.78 h	PD	–	(0, 0, 0.02, 0.98)	–	(0, 0, 0.09, 0.91)	–	(0, 0, 0.09, 0.91)
$R = 25$	AD	12.17	(0, 0, 0.79, 0.21)	12.18	(0, 0.01, 0.78, 0.21)	12.26	(0, 0.01, 0.78, 0.21)
VF = 52	SP	59.4	(0, 0, 0, 1)	59.38	(0, 0, 0, 1)	59.45	(0, 0, 0, 1)

[a] Composition in mole fraction of propane, butane, pentane and hexane.
[b] R: Reflux ratio.
[c] VF: Vapor flow rate from the top plate (V_1) in lb mol/h.
[d] PD: Present distillate.
[e] AD: Accumulated distillate.
[f] SP: Still pot content.

sents the highest concentration of the product) by employing a high reflux ratio.

4. Optimization of reactive batch distillation operation

Conversion of the reactants is an additional objective/issue in reactive distillation. The sensitivity of conversion to the control variables must be studied properly before designing a suitable operation policy. While a low reflux ratio may lead to an excessive withdrawal of the reactant(s), thereby adversely affecting the conversion, a high reflux ratio may result in an undesirable side reaction. Thus, in general, the performance of a reactive distillation operation is more intricately related to the operation policy than that of ordinary distillation.

Table 5
Methanol esterification conditions

No. of plates	8
Initial charge	5 kmol
Initial mole fraction (methanol, acetic acid, methyl acetate, water)	(0.45, 0.45, 0, 0.1)
Holdup	0.001 kmol (for each plate) 0.01 kmol (for condenser)
Pressure	1 atm
Condenser vapor load	2.5 kmol/h
Simulation grid size	0.01 h
Relaxation parameter	0.5
Total reflux conditions tolerance level	0.001
DAE tolerance level	0.1
DAE maximum step-size allowed	0.01

In addition to its suitability in the production of fine chemicals, the batch mode of operation is an attractive choice in reactive distillation in the following two cases:

1. when the reaction is slow and a large resident time is required to attain high conversion and,
2. when the chemical reaction is so fast that a significant reaction may occur before the continuous column reaches steady state (this may even post difficulty in attaining steady state or may lead to oscillations).

4.1. Production of ethyl acetate

A number of esterification reactions are suitable for the reactive distillation operation in which continuous withdrawal of a product shifts chemical equilibrium in the favorable direction, thus leading to a higher conversion than that obtained in a conventional reactor. We considered the esterification of ethanol with acetic acid Eq. (4).

$$\text{ethanol} + \text{acetic acid} \rightleftharpoons \text{ethyl acetate} + \text{water}$$

$$r_{\text{ethanol}} = 4.76e^{-4} C_{\text{acetic acid}}\, C_{\text{ethanol}} - 1.63e^{-4} C_{\text{ethyl acetate}}\, C_{\text{water}} \quad (\text{in gmol/l/min}) \qquad (4)$$

Table 6
Methanol esterification separation results

Period		Mujtaba [18]		Our results	
		(lb mol)	Composition[a]	(lb mol)	Composition[a]
I: 5.0 h	PD[c]	–	(0, 0.07, 0.93, 0)	–	(0, 0.06, 0.94, 0)
R^b = Total	SP[d]	5.0	(0.21, 0.20, 0.24, 0.35)	5.0	(0.2, 0.21, 0.24, 0.35)
II: 9.0 h	PD	–	(0, 0.18, 0.11, 0.71)	–	(0, 0.27, 0.14, 0.59)
$R = 9$	AD[e]	2.25	(0, 0.29, 0.68, 0.03)	2.25	(0, 0.29, 0.69, 0.02)
	SP	2.75	(0.27, 0, 0, 0.73)	2.75	(0.25, 0, 0, 0.75)
III: 18.0 h	PD	–	(0, 0.14, 0.06, 0.8)	–	(0, 0.29, 0.1, 0.61)
$R = 19$	AD	2.25	(0, 0.24, 0.74, 0.02)	2.25	(0, 0.24, 0.75, 0.01)
	SP	2.75	(0.22, 0, 0, 0.78)	2.75	(0.21, 0, 0, 0.79)

[a] Composition in mole fractions of acetic acid, methanol, methyl acetate and water.
[b] R: Reflux ratio.
[c] PD: Present distillate.
[d] SP: Still pot content.
[e] AD: Accumulated distillate.

We solved the *maximum conversion problem* [18] formulated as shown in Eq. (5).

$$\max_{R} \text{ (conversion of ethanol)} \tag{5}$$

subject to

1. model equations and
2. purity constraint on the product cut.

Due to the close boiling points between ethanol and ethyl acetate, (351.7 and 350.2 K, respectively), the reflux policy needs to be designed carefully so as to withdraw ethyl acetate selectively over ethanol. The conditions for the separation are given in Table 7.

The main module of RBDOPT defined the distillation column (an object) and was allowed to access only the data pertaining to the optimization problem (viz. purity of the distillation cuts and amount of the product) keeping the column details (e.g. composition and temperature profiles) inaccessible. This sort of data abstraction becomes useful when the operation of multiple distillation columns is to be optimized in an integrated fashion (as required in the case of campaign optimization). The object-oriented environment allows the information pertaining to each column to be partitioned conveniently and in a memory-efficient manner. The objective function and the constraint set were supplied through the main module which then invoked the distributed computing architecture to spawn different simulation runs on different slave computers in order to compute the gradients. Reflux level (constant for the entire product cut) and its duration are the two control variables in the optimization problem.

The results are shown in Figs. 2 and 3 and Table 8. Due to the specific initialization scheme used (discussed earlier) in this work, the total reflux conditions are established in the beginning of the operation, hence maximum ethyl acetate purity is observed at time = 0. The purity (55%) and the conversion (42.53%) obtained are significantly lesser than

Table 7
Ethanol esterification conditions and numerical parameters

No. of plates	8
Initial charge	5 kmol
Initial mole fraction (ethanol, acetic acid, ethyl acetate, water)	(0.45, 0.45, 0, 0.1)
Holdup	0.0125 kmol (for each plate) 0.1 kmol (for condenser)
Pressure	1 atm
Condenser vapor load	2.5 kmol/h
Simulation grid size	0.01 h
Relaxation parameter	0.5
Total reflux conditions tolerance level	0.001
DAE tolerance level	0.1
DAE maximum step-size allowed	0.01

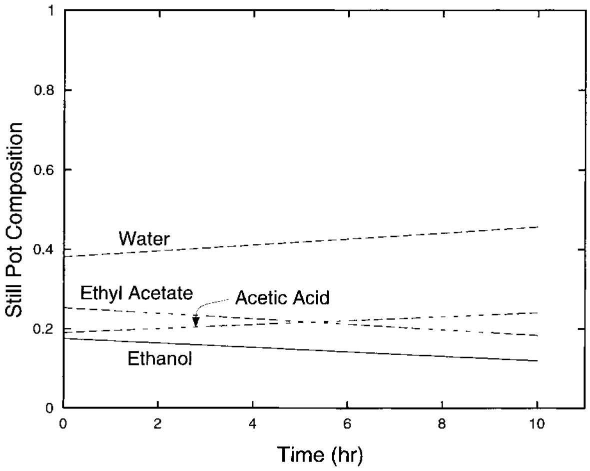

Fig. 2. Still pot composition profiles at optimal conditions.

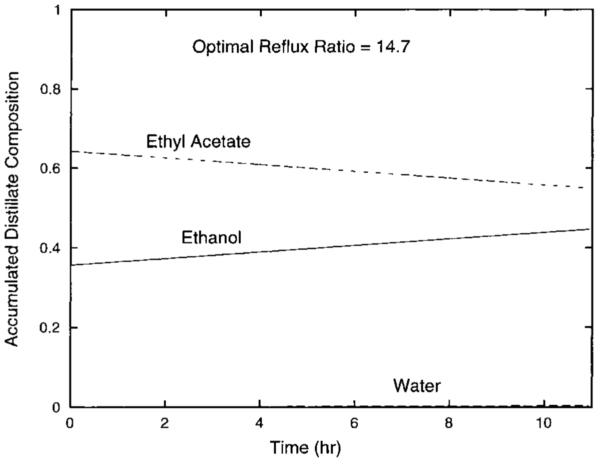

Fig. 3. Accumulated distillate composition profiles at optimal conditions.

those obtained by Mujtaba [18] (80% and 71%, respectively) but similar low values of these quantities are reported by Savkovic-Stevanovic et al. [26] and Wajge et al. [6]. The optimal results for this chemical system are relatively insensitive to the operation policy (for the same amount of product collected, a 10% increase in the reflux level reduces the purity by only 3%) due to the slow rate of reaction. The small conversion obtained (42.53%) despite the use of a reactive distillation column suggests the necessity of a suitable policy for the further reprocessing of the off-cuts.

The optimization run was taken on a suite of HP 9000 model 715/50 machines. Three of these computers were used, one master and two *slaves*. The master required 4.09 min of CPU while the slave computers used 4.08 and 4.07 min. The run took 12.22 min when only one computer was used. Thus, a speedup of around three was achieved using a network of three computers.

4.2. Hydrolysis of acetic anhydride

Acetic anhydride is manufactured by dehydration of acetic acid via the Scrubber or Wacker process [27]. The side product is a mixture consisting of acetic anhydride, water and acetic acid (boiling points are 138.7°C, 100°C and 118°C, respectively). Acetic anhydride and water in the mixture may undergo undesirable hydrolysis, a fast reaction, to produce back acetic acid. Alejski [28] considered the separation of this mixture with the objective of recovering the maximum amount of acetic anhydride with the minimal hydrolysis of acetic anhydride. The chemical reaction and the kinetic data are shown in Eq. (6)[29] and the conditions for the separations are shown in Table 9.

Table 8
Ethanol esterification optimal conditions

Batch time	10.93 h
Reflux ratio	14.7 kmol
Product quantity	1.74 kmol
Product mole fraction (ethanol, acetic acid, ethyl acetate, water)	(0.45, 0.55, 0, 0)
Conversion obtained	42.53%
Kuhn–Tucker error tolerance	0.001
Perturbation size for computing gradients	1.0
No. of optimization iterations	4

Table 9
Acetic anhydride hydrolysis conditions

No. of plates	10
Initial charge	2 kmol
Initial mole fraction (acetic anhydride, water, acetic acid)	(0.2, 0.2, 0.6)
Holdup	0.01 kmol (for each plate) 0.03 kmol (for condenser)
Pressure	0.52 atm
Condenser vapor load	20 kmol/h
Simulation grid size	0.001 h
Relaxation parameter	0.5
Total reflux conditions tolerance level	0.001
DAE tolerance level	0.1
DAE maximum step-size allowed	0.001

$$\text{acetic anhydride} + \text{water} \rightarrow \text{acetic acid}$$

$$r_{\text{acetic anhydride}} = 1.05e^5 C_{\text{acetic anhydride}} C_{\text{water}} \quad (\text{in gmol/l/s}) \tag{6}$$

Logically, the first cut should remove most of the water rapidly to prevent hydrolysis of acetic anhydride while the second cut then should recover acid, leaving behind acetic anhydride in the residue. The optimization problem we considered is defined by Eq. (7)

$$\max_{R} \ (\text{amount of acetic anhydride} + wt_{\text{end}}) \tag{7}$$

subject to

1. model Eq. (1),
2. purity constraint on acid in cut 2, and
3. purity constraint on acetic anhydride in residue.

The are eight control variables (two reflux levels in each distillate cut and the durations of these cuts). A reflux policy that corresponds qualitatively with this understanding serves as a good initial estimate for the optimization algorithm. The results of the optimization run are shown in Fig. 4 and Table 10. The optimal reflux ratio trend is logical, maintaining a very low reflux (0.3) in the beginning to remove water. If the reflux level is increased by 10% from its optimal value, the purity of acetic anhydride reduces from 92% to 77.4%. This shows the strong relationship between the reflux policy and the performance of reactive distillation.

The lower step size (0.001 h) was used by RBDOPT for integrating the model equations to overcome the conver-

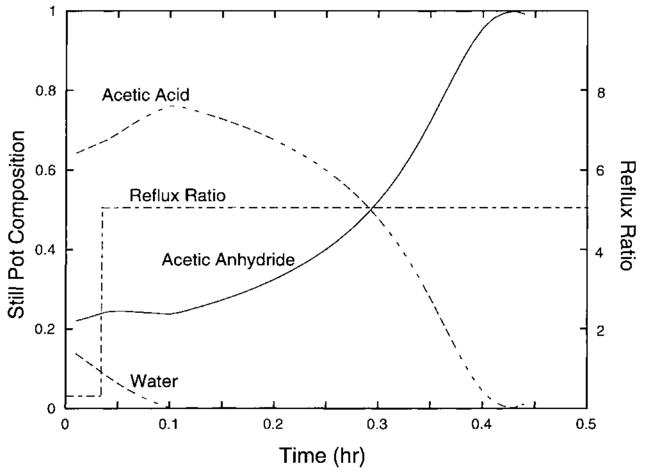

Fig. 4. Instantaneous composition profiles at optimal conditions.

gence problem due to the stiffness caused by the fast rate of reaction. For the optimization run, the master took 30.7 min of CPU and the nine slave computers took 9.52 and 8.86 min on HP 9000 model 715/50. With only one computer, 49 min of CPU were needed. Thus, a speedup of 1.6 was achieved using a network of three computers. The speedup in this case is lower than in the case of ethanol esterification because the number of function evaluations performed by the optimization runs were higher than the gradient evaluations and hence the distributed computing architecture was invoked few times. This is probably due to the stiffness of the system which leads to a series of function calls in a small region (that does not require recalculations for the gradients) in order to satisfy the constraints satisfactorily.

5. RBDOPT for designing campaign strategy

The design of optimal operation policies is important for the overall performance of batch distillation operation, particularly so, in the presence of chemical reactions. This is mainly due to the fact that the conversion obtained becomes an additional objective which increases the interaction between operation policy and performance. Moreover, when resource utilization and/or minimization of waste are comparable in importance to the production rate, the design of the operation policy should encompass an entire campaign of batches rather than a single batch. This notion of campaign optimization is very relevant and rewarding in the optimization of reactive batch distillation operation [9,10]. The object-oriented environment used to support this module helps in simulating multiple distillation operations in a structured and memory efficient manner, and thus, the integrated performance of a campaign of reactive distillation batches can be optimized conveniently.

Table 10
Acetic anhydride hydrolysis optimal conditions

Batch time	0.414 h
Cut 1 amount	0.446 kmol
Cut 1 mole fraction	(0.028, 0.455, 0.517)
Cut 2 amount	1.29 kmol
Cut 2 mole fraction	(0.032, 0.068, 0.9)
(acetic anhydride, water, acetic acid)	
Residue amount	0.2621 kmol
Residue mole fraction	(0.92, 0, 0.08)
Kuhn–Tucker error tolerance	0.001
Perturbation size for computing gradients	0.001
No. of optimization iterations	4

6. Conclusions

RBDOPT is found to be useful in the design of operation policies for reactive batch distillation. The object-oriented environment of RBDOPT makes it easy to extend its scope to a wide variety of distillation systems and is also convenient in simulating multiple distillation operations, as required in campaign optimization. The stiffness and the discontinuities present in the simulation were handled satisfactorily and efficiently by tuning the numerical parameters of the DAE solver. This numerical robustness and efficiency are critical in solving an optimization problem. With the help of a portable distributed computing framework, a speedup which is almost equal to the number of control variables is obtained without any efforts from the user's side for computing numerical gradients (as might be the case with symbolic differentiation).

The RBDOPT distillation model does not consider hydrodynamics on the trays, or chemical reactions in the vapor phase. Also, there is no automatic step size control for getting a converged DAE solution; the user is required to choose the step size based on the numerical understanding of the simulation of the process. The distributed computing framework within RBDOPT comes to a halt even if one of the spawned jobs is interrupted on the slave computer. The efforts to improve RBDOPT in these areas are underway.

7. Source code

For additional information regarding RBDOPT and the source code, please send an e-mail to reklaiti@ecn.purdue.edu.

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Appendix

Nomenclature

A	molar holdup
B	bottom product flow rate
C	molar concentration
D	distillate flow rate
e	Murphree efficiency
F	continuous feed rate
H	molar enthalpy
J	number of components
K	k-value
L	liquid flow rate
M	molecular weight
N	number of plates
P	pressure
Q	rate of heat transfer
R	reflux ratio
r	reaction rate
s	iteration counter
T	temperature in Kelvin
t	time
V	vapor flow rate
w	weightage factor
X	liquid mole fraction
Y	vapor mole fraction

Greek letters

Δg	rate of change in number of moles
λ	relaxation parameter
ρ	density
τ	volume

Subscripts

b	reboiler
c	component c: $1 \leq c \leq J$
d	distillate
f	continuous feed
o	condenser
p	Plate p: $1 \leq p \leq N$

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