



## Uncertainties in parameter estimation and optimal control in batch distillation

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### Abstract

Optimal control problems in batch distillation involve finding a trajectory for the reflux ratio so as to maximize a performance index. Then the controller is asked to follow this trajectory in an open loop fashion. It is important to minimize the effect of uncertainties in thermodynamic models on the optimal control profiles to achieve a better operating performance. The non-linear parameter estimation problem in vapor–liquid equilibrium modeling involves determining the values of model parameters, which provide the best fit to experimental data. It was shown previously by Gau et al. [Fluid Phase Equilibria, 168, 1–8, (2000)] that, using a global optimization procedure based on interval-Newton technique combined with interval-branch-and-bound can significantly reduce the error between the predicted and experimental data. Using this method, it was also shown that for some of the data sets published in DECHEMA, the parameters estimated correspond to local minima. The effect of locally and globally optimal parameter estimates on batch distillation optimal control profiles is demonstrated in this work. Since batch distillation is a dynamic process, the static (parametric) uncertainties are translated into time-dependent uncertainties. The time-dependent changes in relative volatility for the two cases are analyzed and represented by Ito processes. Next, the optimal control problem is solved using the maximum principle and NLP approach. Numerical case studies show that using globally optimal parameter estimates versus locally optimal parameter estimates results in a better product yield and the minimum error between the specified purity and the purity that is achieved.

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**Keywords:** Batch distillation; Optimal control; Ito processes; Time-dependent uncertainties; Thermodynamic models; Wilson model; Interval-Newton method

### 1. Introduction

Batch distillation is an important separation process commonly used in pharmaceutical, specialty chemical and biochemical industries. Because of its unsteady state nature, it is very suitable for high-value, low volume production and it has the flexibility to deal with variations in feed stock and product specifications under different operating conditions. For batch columns, finding an optimum operating policy is a key issue for achieving the most profitable operation.

Optimal reflux policy in batch distillation is a trade-off between constant reflux and variable reflux policies, where a trajectory for reflux ratio is obtained so as to optimize a certain performance index. The trajectory of reflux ratio is then followed by the controller. Diwekar (1992) presented a unified approach to solving optimal control problems in batch distillation using an efficient short-cut method and an algorithm based on the maximum principle and NLP optimization techniques. This article also showed that the different categories of optimal control problems essentially involve the solution of the maximum distillate problem. However, time-dependent uncertainties were not included in this deterministic formulation until recently. For many mixtures encountered in pharmaceutical, specialty chemical and biochemical industries, the thermodynamic models are not exact

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### Nomenclature

$F$	amount of feed (mol)
$H$	Hamiltonian
$J$	objective function for the non-linear parameter estimation
$P_{\text{exp}}$	total pressure
$P_i^{\text{vap}}$	vapor pressure
$R_t$	the control variable vector, reflux ratio (function of time)
$T$	total batch time (h)
UF	uncertainty factor
$V$	molar boil-up rate ( $\text{mol h}^{-1}$ )
$x_1$	state variable representing the quantity of charge remaining in still B (mol)
$x_2$	state variable representing the composition of the key component in the still at the time $t$ , $x_B^{(1)}$ (mole fraction)
$x_D^{(1)}$	composition of the key component in distillate (mole fraction)
$x_F^{(1)}$	composition of the key component in feed (mole fraction)
$x_{i,\text{exp}}$	composition of the liquid phase
$y_{i,\text{exp}}$	composition of the vapor phase
$z_1, z_2$	adjoint variables

### Greek symbols

$\alpha$	relative volatility
$\bar{\alpha}$	“normal” level of $\alpha$ , the level which $\alpha$ tends to revert
$\beta$	drift parameter
$\gamma_I$	activity coefficient
$\gamma_{i,\text{calc}}$	activity coefficient determined from Wilson model
$\gamma_{i,\text{exp}}$	activity coefficient determined from experimental data
$\eta$	speed of reversion
$\theta_{ij}$	energy parameters of Wilson model
$\Lambda_{ij}$	binary interaction parameters of Wilson model
$\sigma$	standard deviation
$v_i$	pure component liquid volume

or there is not enough data to predict the behavior caused by non-idealities. These thermodynamic uncertainties are translated into time-dependent uncertainties due to the dynamic nature of batch distillation. For the first time, Rico-Ramirez, Diwekar, and Morel (2003) and Diwekar (2003) presented a new approach to include time-dependent uncertainties in mathematical formulations of optimal control. The uncertainties in relative volatility for ideal and non-ideal mixtures were represented by Ito processes and the maximum distillate problem was solved for deterministic and stochastic cases (Ulas, Diwekar, & Rico-Ramirez,

2003). It was shown that the stochastic reflux ratio profile improves the process performance indices significantly as compared to the reflux ratio profile computed by deterministic approaches (Ulas & Diwekar, 2003). For example, one case study for a non-ideal system such as ethanol–water showed a 69% improvement in product yield, with using this stochastic approach (Ulas & Diwekar, 2003, 2004). This method also allowed including uncertainties in binary interaction parameters such as UNIFAC and it has been found that the inclusion of binary interaction parameter uncertainties increases the discrepancy between the stochastic and deterministic solution. Therefore, it is important to minimize the effect of thermodynamic uncertainties to obtain optimal reflux ratio profiles and to maintain optimal operation.

Thermodynamic uncertainties are also due to non-linear parameter estimation in vapor–liquid equilibrium modeling, when a set of experimental vapor–liquid equilibrium data is represented by a correlative model and the model parameters are estimated based on a least squares or maximum likelihood analysis. In most of the cases, the objective function in non-linear parameter estimation problems is non-convex and may have multiple local optima. Therefore local optimization techniques cannot be employed since they do not guarantee convergence to a global optimum. Gau, Brennecke, and Stadtherr (2000), presented an alternative method for non-linear parameter estimation problem based on an interval-Newton technique and interval-branch-and-bound, which provides the guarantee of global optimality in parameter estimation. It was shown that for some data sets published in DECHEMA VLE Data Collection (Gmehling, Onken, & Arlt, 1977–1990), the parameters predicted for an activity coefficient model such as Wilson model correspond to local optima and globally optimal parameter values were reliably determined by the interval-Newton generalized bisection algorithm (IN/GB).

In this paper, we demonstrate how the batch distillation optimal control profiles are affected by using the globally optimal parameter values predicted by IN/GB, versus the locally optimal parameters published in DECHEMA. Since batch distillation is a dynamic process, the uncertainties in model parameters are translated into time-dependent uncertainties. Two different time-dependent relative volatility profiles are obtained using globally and locally optimal parameter estimates for Wilson model. These profiles are statistically analyzed and represented by Ito processes. Finally, batch distillation optimal control problem is solved for four cases: the stochastic global case (relative volatility is represented by an Ito process, obtained from globally optimal parameters), the stochastic local case (relative volatility is represented by an Ito process, obtained from locally optimal parameters) and two deterministic cases. The result of our case studies show that the stochastic global reflux ratio profile results in the highest product yield and the product purity is significantly closer to the specified purity for optimal control.

Table 1  
Results of parameter estimation for *tert*-butanol(1)–*n*-butanol(2) (Gau et al. (2000))

DECHEMA volume: page	No. of data points	P (mmHg)	DECHEMA			Gau et al. (2000)-IN/GB		
			$\theta_1$	$\theta_2$	Objective function, $J(\theta)$	$\theta_1$	$\theta_2$	Objective function, $J(\theta)$
2b:156	9	100	951	–602	0.0136	–568	745	0.0103
2b:157	9	300	1068	–638	0.0158	–525	626	0.0130
2b:158	9	500	901	–594	0.0097	–718	1265	0.0069
2b:159	9	700	801	–561	0.0174	–734	1318	0.0137
2f:151	14	760	848	–606	0.0333	–865	2420	0.0111
2f:152	17	760	153	–203	0.1300	–793	1757	0.1164

## 2. Uncertainty quantification

For the case studies presented in this paper, Wilson model is used to predict the vapor–liquid equilibrium in rigorous simulations of batch distillation operation. The expressions for the estimation of liquid phase activity coefficients in Wilson model for a binary system are:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (1)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (2)$$

The equations for binary parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  are:

$$\Lambda_{12} = \frac{v_2}{v_1} \exp \left[ -\frac{\theta_1}{RT} \right] \quad (3)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp \left[ -\frac{\theta_2}{RT} \right] \quad (4)$$

where  $v_1$  and  $v_2$  are the pure component liquid volumes,  $T$  the system temperature and  $\theta_1$  and  $\theta_2$  are the energy parameters that need to be estimated.

These energy parameters are estimated by minimizing the relative squares of error between the activity coefficients determined from experimental data and activity coefficients predicted by Wilson method. The objective function is given below:

$$J(\theta) = \sum_{j=1}^n \sum_{i=1}^2 \left( \frac{\gamma_{ji,\text{exp}} - \gamma_{ji,\text{calc}}(\theta)}{\gamma_{ji,\text{exp}}} \right)^2 \quad (5)$$

Gau et al. (2000) showed that the energy parameters published in DECHEMA for some data sets were in fact local solutions to this problem and new set of globally optimum energy parameters were presented for binary systems of

(a)water(1)–formic acid(2), (b)*tert*-butanol(1)–*n*-butanol(2), (c)water(1)–1,2,-ethanediol(2) and (d)benzene(1)–hexafluorobenzene(2).

In this paper, we consider the binary systems of *tert*-butanol(1)–*n*-butanol(2) and benzene(1)-hexafluorobenzene(2) for our case studies to demonstrate the effect of globally and locally optimum energy parameters, on optimum control profiles in batch distillation. The results of parameter estimation presented by Gau et al. (2000) are summarized below in Tables 1 and 2, for the binary systems of *tert*-butanol(1)–*n*-butanol(2) and benzene(1)–hexafluorobenzene(2), respectively.

### 2.1. Static uncertainties (uncertainty factors)

A statistical analysis was performed on these six data sets to quantify the uncertainties associated with globally and locally optimum energy parameters. For uncertainty quantification, we can define uncertainty factors as the ratio of experimental activity coefficients to activity coefficients computed from Wilson model:

$$\text{UF}(1) = \frac{\gamma_{1,\text{calc}}}{\gamma_{1,\text{exp}}} \quad (6)$$

$$\text{UF}(2) = \frac{\gamma_{2,\text{calc}}}{\gamma_{2,\text{exp}}} \quad (7)$$

where the experimental activity coefficients can be calculated from:

$$\gamma_{\text{exp}} = \frac{y_{i,\text{exp}} P_{\text{exp}}}{x_{i,\text{exp}} P_i^{\text{vap}}} \quad (8)$$

The probability density estimate of the uncertainty factors for *tert*-butanol(1)–*n*-butanol(2) and benzene(1)–hexafluorobenzene(2) are given in Figs. 1 and 2. From the figure, it can be seen that the expected values of uncertainty factors are closer to 1 and the variance is decreased, when the activity coefficients are predicted using the globally optimal parameter estimates reported by Gau et al. (2000). We will refer to

Table 2  
Results of parameter estimation for benzene(1)–hexafluorobenzene(2) (Gau et al. (2000))

DECHEMA volume:page	No. of data points	P (mmHg)	DECHEMA			Gau et al. (2000)-IN/GB		
			$\theta_1$	$\theta_2$	Objective function, $J(\theta)$	$\theta_1$	$\theta_2$	Objective function, $J(\theta)$
7:234	17	300	344	–347	0.0566	–432	993	0.0149

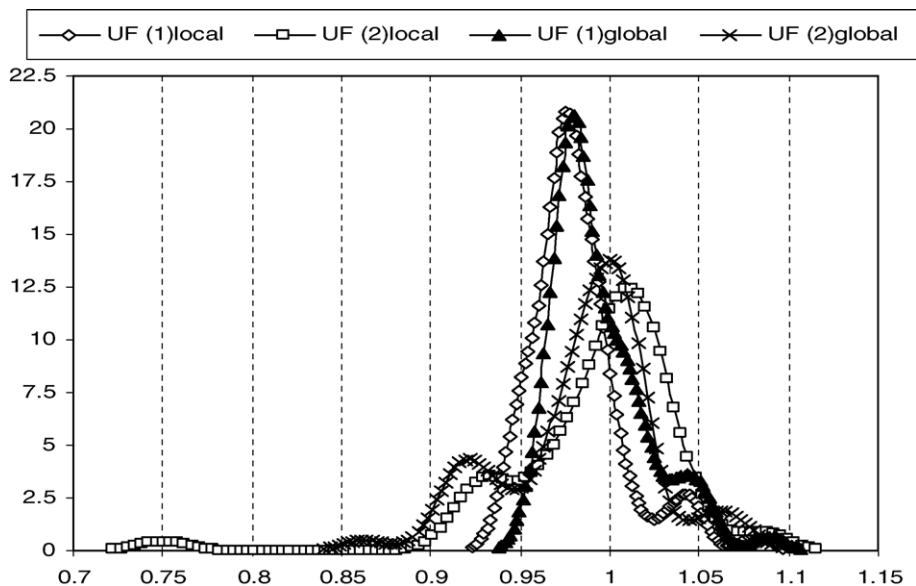


Fig. 1. Probability density estimate of uncertainty factors for six experimental data sets of *tert*-butanol(1)–*n*-butanol(2) system for globally optimal energy parameters predicted by Gau et al.(2000) using IN/GB method and locally optimal energy parameter values published in DECHEMA VLE data collection.

globally optimal parameter estimates as GOPE and locally optimal parameter estimates as LOPE from this point on for simplicity.

## 2.2. Time-dependent uncertainties

After establishing statistically that the Wilson model with the GOPE show less deviation from experimental data, the next step is to determine the time-dependent uncertainties. During batch distillation operation, the relative volatility of the key component changes with respect to time and each plate in the column. This dynamic behavior of relative volatility can be represented by Ito processes. This was shown previously for systems of pentane–hexane (ideal) and

ethanol–water (non-ideal) (Rico-Ramirez et al., 2003; Ulas & Diwekar, 2003, 2004).

### 2.2.1. System I: *tert*-butanol(1)–*n*-butanol(2)

If we take the rigorous model in batch distillation as a proxy for real experiments and simulate the system *tert*-butanol(1)–*n*-butanol(2) using the Wilson model with the GOPE and LOPE, two different time-dependent profiles of relative volatility are obtained which are shown in Figs. 3(a) and 4(a). To generate these profiles, the parameter estimates obtained from data set 6, shown in Table 1, were used, with a constant reflux ratio profile.

When the LOPE are used in the Wilson model, the relative volatility profile shown in Fig. 4(a) is obtained, which is simi-

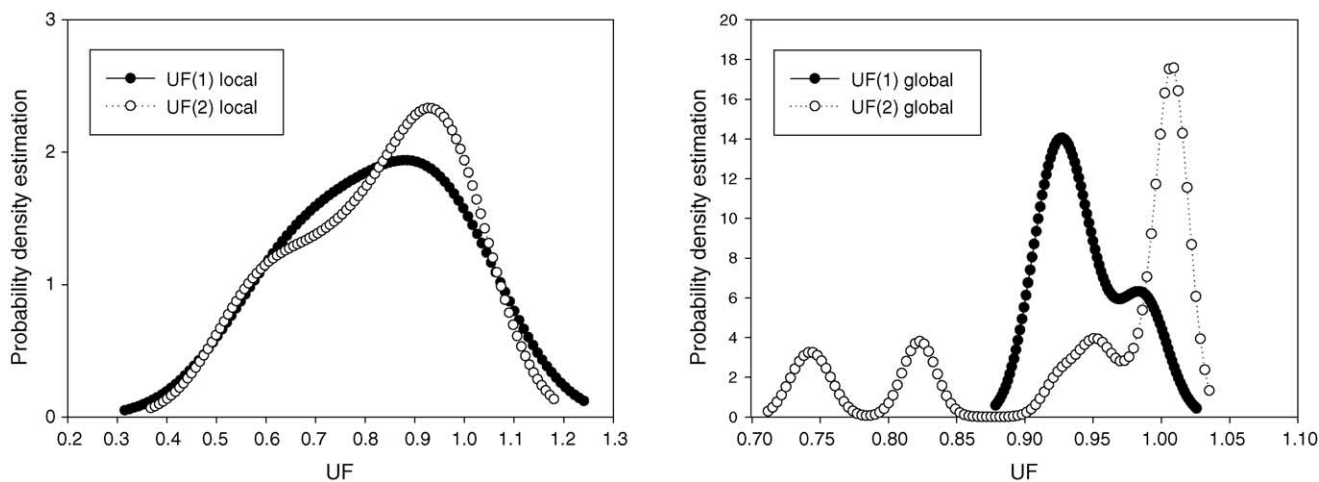


Fig. 2. Probability density estimate of uncertainty factors for benzene(1)–hexafluorobenzene(2) system for globally optimal energy parameters predicted by Gau et al. (2000) using IN/GB method and locally optimal energy parameter values published in DECHEMA VLE data collection.

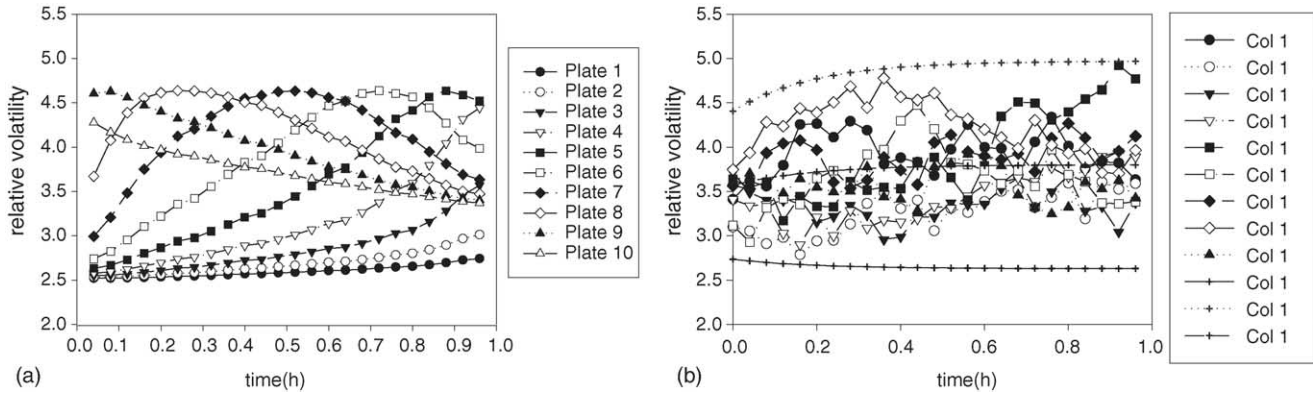


Fig. 3. (a) The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model with GOPE; (b) sample paths of a simple mean reverting process with 66% confidence intervals.

lar to the behavior of an ideal system, such as pentane–hexane (Rico-Ramirez et al., 2003; Ulas et al., 2003).

However, experimental vapor–liquid equilibrium studies show that *tert*-butanol(1)–*n*-butanol(2) system shows negative deviations from an ideal mixture and there are associations present in the mixture (Quitzsich & Koehler, 1969). The effect of these associations is only captured when global parameters are used in the Wilson model. The relative volatility profile shown in Fig. 3(a) is obtained using the GOPE, which shows a behavior between an ideal system like pentane–hexane and a non-ideal system like ethanol–water, presented by Ulas and Diwekar (2003, 2004).

Figs. 3(b) and 4(b), show the sample paths of Ito processes that are used to represent the time dependent changes in relative volatility for the *tert*-butanol(1)–*n*-butanol(2) system when the GOPE and LOPE are used in Wilson model, respectively. To generate these sample paths, equilibration times are also considered, which are not shown in figures.

When the GOPE are used, the time-dependent uncertainties for this system can best be described using a simple mean reverting process, which is given in Eq. (9):

$$d\alpha = \eta(\bar{\alpha} - \alpha) dt + \sigma dz \tag{9}$$

where  $dz$  is the increment of a Wiener process. This increment can be represented in terms of time as:

$$dz = \varepsilon_t \sqrt{dt} \tag{10}$$

In this equation  $\varepsilon_t$  is a random number drawn from a normal distribution with mean  $\mu = 0$  and a standard deviation  $\sigma = 1$ . The parameters  $\eta$ ,  $\bar{\alpha}$  and  $\sigma$  can be found using statistical analysis of the rigorous simulation data for relative volatility. The parameters were found as  $\eta = 4.7$ ,  $\bar{\alpha} = 3.5$  and  $\sigma = 1.1$  with a  $R^2$  value of 0.95.

When the LOPE are used, statistical analysis shows that this system can be best represented by a geometric Brownian motion, which was also used for the ideal system of pentane–hexane (Rico-Ramirez et al., 2003; Diwekar, 2003). The general equation for the geometric Brownian motion is given below:

$$d\alpha = \beta\alpha dt + \sigma\alpha dz \tag{11}$$

As a result of statistical analysis, the constants  $\beta$  and  $\sigma$  were found as  $\beta = -0.128$  and  $\sigma = 0.03$  with an  $R^2 = 0.90$ .

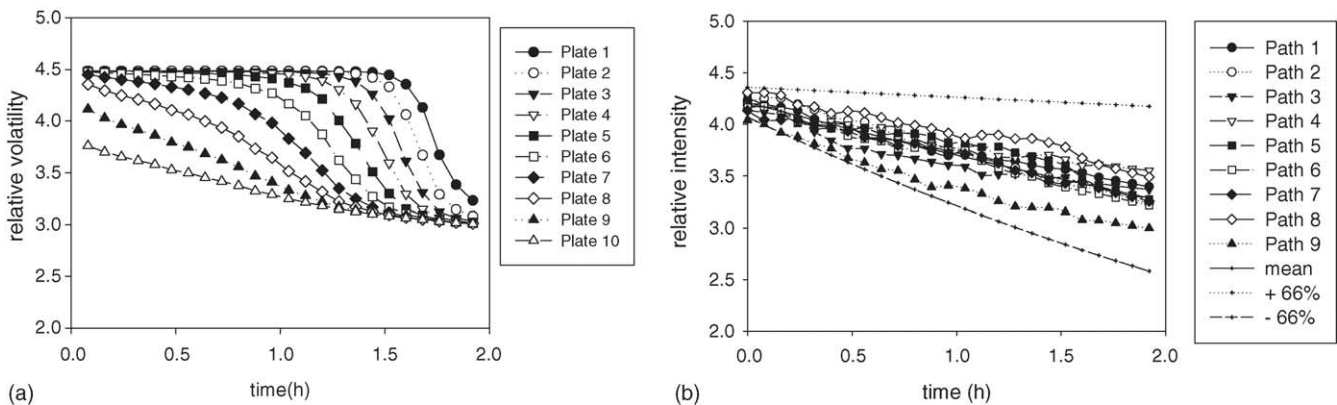


Fig. 4. (a) The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model with LOPE; (b) sample paths of a geometric Brownian motion with 66% confidence intervals.

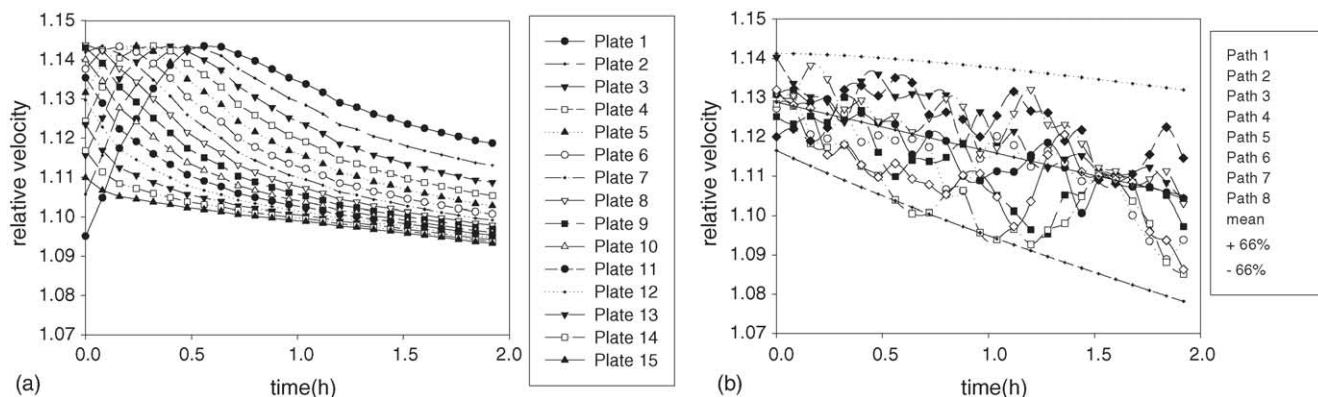


Fig. 5. (a) The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model with GOPE; (b) sample paths of a simple mean reverting process with 66% confidence intervals.

### 2.2.2. System II: benzene(1)–hexafluorobenzene(2)

For the second binary system, benzene(1)–hexafluorobenzene(2), the relative volatility profiles for GOPE and LOPE, obtained using a rigorous model with constant reflux as a proxy for experiments is shown in Figs. 5(a) and 6(a), respectively. The relative volatilities obtained using locally optimal parameters in Wilson model, are lower than the relative volatilities obtained using GOPE. Both of these profiles were represented by a simple mean reverting process, shown in Eq. (9). For this binary system the use of GOPE versus LOPE in Wilson model affects the constant coefficients of Ito process representation.

When the GOPE are used in Wilson model, the constant coefficients of the mean reverting process are:  $\bar{\alpha} = 0.71$ ,  $\eta = 0.03$ ,  $\sigma = 0.018$  with an  $R^2$  value of 0.91. When the LOPE are used, the constant coefficients are:  $\bar{\alpha} = 1.08$ ,  $\eta = 1.06$ ,  $\sigma = 0.012$  with an  $R^2$  value of 0.95. To generate both of the profiles in Fig. 6(a) and (b), the equilibration times are also considered, which are not shown in figures.

### 3. Optimal control profiles for locally and globally optimal parameter estimates

After quantification of uncertainties for the thermodynamic system that is being separated by batch distillation, the next step is to find an optimum operating policy. Maximum distillate problem in batch distillation is an optimum control problem where the optimal reflux ratio profile that maximizes the distillate for a specified purity and time is computed. Rico-Ramirez et al. (2003) and Diwekar (2003) presented a stochastic formulation of the maximum distillate problem, where the time-dependent uncertainties in relative volatility are included in the formulation. It was shown that the uncertainties in relative volatility affect one of the state variables and this state variable can also be represented by an Ito process of the same form. Ulas and Diwekar (2004) solved the maximum distillate problem for the stochastic case, where the time-dependent uncertainties in relative volatility were described using geometric Brownian motion and geometric mean reverting process. The next subsection analyzes the stochastic case where the state variables are described

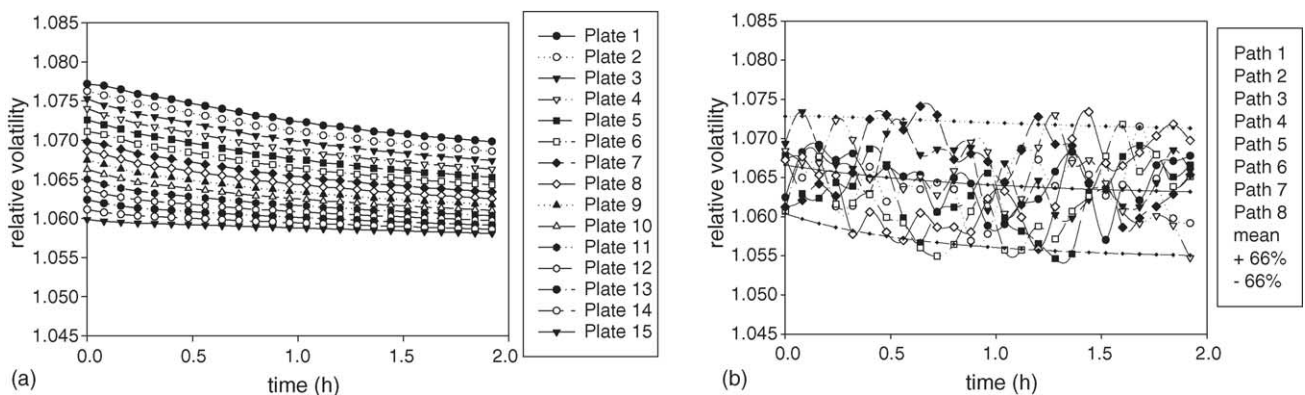


Fig. 6. (a) The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model with LOPE; (b) sample paths of a simple mean reverting process with 66% confidence intervals.

using a mean reverting process, such as the cases for *tert*-butanol(1)–*n*-butanol(2) system when the GOPE are used in the Wilson model and the benzene(1)–hexafluorobenzene(2) system.

### 3.1. Derivation of stochastic optimal reflux ratio profile for a mean reverting process

It was shown in Section 2.2 that the time-dependent uncertainties in relative volatility can be represented by a mean reverting process for benzene(1)–hexafluorobenzene(2) system and for the *tert*-butanol(1)–*n*-butanol(2) system, when the GOPE are used in Wilson equation. Whereas, when LOPE are used, geometric Brownian motion best represents the time-dependent uncertainties in relative volatility for *tert*-butanol(1)–*n*-butanol(2). Using Hengestebeck–Geddes equation and Ito's Lemma, Rico-Ramirez et al. (2003) showed that when the time-dependent uncertainties in relative volatility are represented by a geometric Brownian motion, this affects one of the state variables and this state variable also takes the form of geometric Brownian motion. This formulation is used here for the case of LOPE for *tert*-butanol(1)–*n*-butanol(2). Ulas and Diwekar (2004) showed that this is true for a general case which means that the state variable takes the form of the same Ito process that is used to represent relative volatility.

However, for GOPE we need to derive the optimality conditions for the reflux ratio profile, when the state variables are represented by a mean reverting process. This formulation is given below:

The maximum distillate problem is formulated in batch distillation as:

$$\begin{aligned} & \text{Maximize } -x_1(T) \\ & \text{subject to : } \frac{dx_1}{dt} = \frac{dB_t}{dt} = \frac{-V}{R_t + 1}, x_1(0) = B_0 = F \end{aligned} \quad (12)$$

$$\frac{dx_2}{dt} = \frac{V}{R_t + 1} \frac{(x_2 - x_D^{(1)})}{x_1}, \quad x_2(0) = x_F^{(1)} \quad (13)$$

As mentioned above when the relative volatility is a mean reverting process as shown in Eq. (9), the behavior of relative volatility affects the state variable  $x_2$ . The equation for the state variable  $x_2$  becomes:

$$dx_2 = \frac{V}{R_t + 1} \frac{(x_2 - x_D^{(1)})}{x_1} dt + \sigma_2 dz, \quad x_2(0) = x_F^{(1)} \quad (14)$$

The Hamiltonian function, which should be maximized is:

$$H = \frac{-V}{R_t + 1} \frac{\partial L}{\partial x_1} + \frac{V}{R_t + 1} \frac{(x_2 - x_D^{(1)})}{x_1} \frac{\partial L}{\partial x_2} + \frac{\sigma_2^2}{2} \frac{\partial^2 L}{\partial (x_2)^2} \quad (15)$$

The adjoint equations are:

$$\frac{dz_1}{dt} = z_2 \frac{V(x_2 - x_D^{(1)})}{(R_{tU} + 1)(x_1)^2}, \quad z_1(T) = -1 \quad (16)$$

$$\frac{dz_2}{dt} = -z_2 \frac{V \left( 1 - \frac{\partial x_D^{(1)}}{\partial x_2} \right)}{(R_{tU} + 1)x_1}, \quad z_2(T) = 0 \quad (17)$$

If we define:

$$\frac{\partial L}{\partial x_1} = z_1, \quad \frac{\partial L}{\partial x_2} = z_2 \quad \text{and} \quad \frac{\partial^2 L}{(\partial x_2)^2} = \omega_t$$

Since  $\partial H / \partial R_{tU} = 0$ ;

$$R_{tU} = \frac{\frac{\partial L}{\partial x_1} - \frac{\partial L}{\partial x_2} \frac{(x_2 - x_D^{(1)})}{x_1}}{\frac{\partial x_D^{(1)}}{\partial R_{tU}} \frac{1}{x_1} \frac{\partial L}{\partial x_2}} + \frac{\left[ \sigma_2 \frac{\partial \sigma_2}{\partial R_{tU}} \frac{\partial^2 L}{(\partial x_2)^2} \right] \left[ \frac{(R_{tU} + 1)^2}{V} \right]}{\frac{\partial x_D^{(1)}}{\partial R_{tU}} \frac{1}{x_1} \frac{\partial L}{\partial x_2}} - 1 \quad (18)$$

If we define:

$$z = \frac{\frac{\partial L}{\partial x_2}}{\frac{\partial L}{\partial x_1}} = \frac{z_2}{z_1}$$

$$\frac{dz}{dt} = -z \frac{V \left( 1 - \frac{\partial x_D^{(1)}}{\partial x_2} \right)}{(R_{tU} + 1)x_1} - z^2 \frac{V(x_2 - x_D^{(1)})}{(R_{tU} + 1)(x_1)^2} \quad (19)$$

Also if we define:

$$\xi = \frac{\frac{\partial^2 L}{(\partial x_2)^2}}{\frac{\partial L}{\partial x_1}} = \frac{\omega_t}{z_1}$$

$$\begin{aligned} \frac{d\xi}{dt} = & -\xi \frac{V \left( 1 - \frac{\partial x_D^{(1)}}{\partial x_2} \right)}{(R_{tU} + 1)x_1} + z \frac{V \frac{\partial^2 x_D^{(1)}}{\partial x_2}}{(R_{tU} + 1)x_1} \\ & - \xi z \frac{V(x_2 - x_D^{(1)})}{(R_{tU} + 1)(x_1)^2} \end{aligned} \quad (20)$$

$$R_{tU} = \frac{x_1 - z(x_2 - x_D^{(1)})}{\frac{\partial x_D^{(1)}}{\partial R_{tU}} z} + \frac{x_1 \left[ \sigma_2 \frac{\partial \sigma_2}{\partial R_{tU}} \xi \right] \left[ \frac{(R_{tU} + 1)^2}{V} \right]}{\frac{\partial x_D^{(1)}}{\partial R_{tU}} z} - 1 \quad (21)$$

In this analytical solution it can be seen that the adjoint equations are not affected by the behavior of state variable  $x_2$ , since the additional term  $\sigma_2 dt$  is not dependent on  $x_2$ , which is different from the solution obtained when the state variable is represented by a geometric Brownian motion. The solution algorithm proposed by Diwekar (1992) can be used to solve this problem with this representation. The column model used in this algorithm is the short-cut model, which introduces quasi-steady state approximation to some of the state variables, thereby reducing the dimensionality of the problem. This algorithm combines the maximum principle

and non-linear programming (NLP) techniques. It is an efficient technique which avoids the solution of the two-point boundary value problem for the pure maximum principle formulation or and the solution of partial differential equations for the pure dynamic programming formulation. Numerical results are given in the following subsection.

### 3.2. Global and local solution for optimal reflux profile

Optimal reflux ratio profiles were computed for four cases for *tert*-butanol(1)–*n*-butanol(2) and benzene(1)–hexafluorobenzene(2) systems:

- I. *Stochastic-global case*: uncertainties in relative volatility are represented by the Ito process obtained by using GOPE in Wilson model and the maximum distillate problem is solved for the stochastic case using combined maximum principle-NLP technique.
- II. *Stochastic-local case*: uncertainties in relative volatility are represented by the Ito process obtained by using LOPE in Wilson model and the maximum distillate problem is solved for the stochastic case using combined maximum principle-NLP technique.
- III. *Deterministic case I*: relative volatility is taken as constant and the maximum distillate problem is solved for the deterministic case using combined maximum principle-NLP technique.
- IV. *Deterministic case II*: relative volatility is computed at the top and bottom of the batch column for each integration interval using the Wilson model and the geometric mean of these two values is taken as the constant relative volatility for the next interval, the maximum distillate problem is solved for the deterministic case using the combined maximum principle-NLP technique

#### 3.2.1. Case study I: *tert*-butanol(1)–*n*-butanol(2) system

In this numerical case study a system of *tert*-butanol(1)–*n*-butanol(2) was separated in a batch column where the operation and design related parameters were chosen as: Specified purity:  $x_D(1)=0.94$ ; number of plates: 10; amount of feed: 100 kmol; feed composition:  $x_F(1)=0.4$ ,  $x_F(2)=0.6$ ; vapor rate:  $60 \text{ kmol h}^{-1}$ ; pressure: 1 atm; batch time: 2 h.

This algorithm was implemented in MultiBatchDS (Diwekar, 1996). The reflux ratio profiles obtained for the four cases are given in Fig. 7.

We compared the stochastic local and stochastic global cases to two deterministic cases. For both of the deterministic cases, the shortcut method was used inside the optimal control problem similar to the stochastic cases. For the first deterministic case, the relative volatility was taken as constant at 3.035, which corresponds to the initial value of the relative volatility profile from the rigorous model, when the GOPE are used. For the second deterministic case, the top and bottom relative volatility was computed using the Wilson model with GOPE and the geometric mean of these two values were taken as the constant relative volatility value for

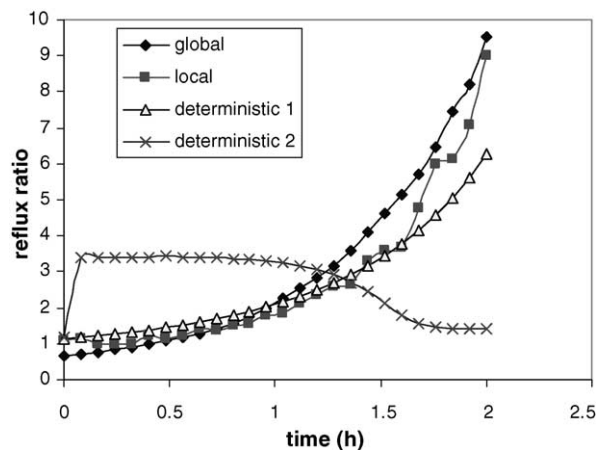


Fig. 7. Optimal reflux ratio profiles for the stochastic-global, stochastic-local and deterministic cases.

the next time interval as mentioned above. From the figure it can be seen that, the reflux ratio profile obtained from the second deterministic approach is quite different than the other profiles. Also there is a jump in the value of reflux ratio since the initial value of relative volatility is calculated using only the bottoms composition, but after the initial point the relative volatility is calculated from the geometric mean of top and bottom. The reflux ratio profiles obtained for the four cases are given in Fig. 7.

#### 3.2.2. Case study II: benzene(1)–hexafluorobenzene(2) system

For this case study a system of benzene(1)–hexafluorobenzene(2) was separated in a batch column where the operation and design related parameters were chosen as: Specified purity:  $x_D(1)=0.70$ ; number of plates: 15; amount of feed: 100 (kmol); feed composition:  $x_F(1)=0.55$ ,  $x_F(2)=0.45$ ; vapor rate:  $60 \text{ kmol h}^{-1}$ ; pressure: 300 mmHg; batch time: 2 h.

For deterministic case (1), the relative volatility was taken as constant at 1.12. From Fig. 8, it can be seen that the deterministic profiles are in between the global and local stochastic profiles.

## 4. Results and discussion

The reflux ratio profiles obtained for four cases in Section 3 for the *tert*-butanol(1)–*n*-butanol(2) and benzene(1)–hexafluorobenzene(2) systems need to be tested by a rigorous model in batch distillation in order to compare the results and determine which reflux ratio profile yields the maximum performance for the batch column. The rigorous model includes the hold-up effects for the batch column and involves the solution of several differential equations, representing the column dynamics.

The results obtained from the rigorous model are shown in Tables 3 and 4 for the *tert*-butanol(1)–*n*-butanol(2) sys-



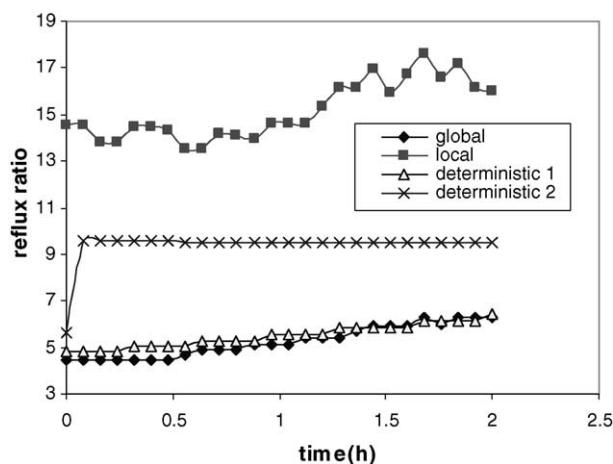


Fig. 8. Optimal reflux ratio profiles for the stochastic-global, stochastic-local and deterministic cases.

tem. The same operation and design related parameters specified in optimal reflux computations were used for the batch column. In Table 3, the results for distillate purity from the rigorous model are presented. Recall that the optimal control problem was solved for a purity constraint of 94%. This means that a purity of 94% should be obtained, when we use a reflux ratio profile that is obtained by a thermodynamic model where the effects of uncertainties are minimized. As it can be seen from the results in Table 3, the reflux ratio profile obtained for the stochastic global case results in a purity of 96.13%, which is closest to 94%. The % error between the specified purity and the purity obtained increases as we proceed to stochastic-local and deterministic cases due to the effect of thermodynamic uncertainties: both static (parametric) and time-dependent.

Furthermore, for the stochastic global case, the highest yield is obtained as compared to stochastic-local and deterministic cases, which can be seen in Table 3. Similarly, as

Table 3  
Results for distillate purity from the rigorous model for *tert*-butanol(1)–*n*-butanol(2) system

Specified purity for optimal control	0.94
Stochastic-global optimal reflux ratio profile	0.961
Stochastic-local optimal reflux ratio profile	0.978
Deterministic reflux ratio profile (1)	0.993
Deterministic reflux ratio profile (2)	0.997
% Error in global	2.26%
% Error in local	4.03%
% Error in deterministic (1)	5.65%
% Error in deterministic (2)	6.06%

Table 4  
Results for amount of distillate from the rigorous model for *tert*-butanol(1)–*n*-butanol(2) system

Global optimal reflux ratio profile	38.73 (kmol)
Local optimal reflux ratio profile	37.80 (kmol)
Deterministic reflux ratio profile (1)	36.23 (kmol)
Deterministic reflux ratio profile (2)	31.6023

Table 5  
Results for distillate purity from the rigorous model for benzene(1)–hexafluorobenzene(2) system

Specified purity for optimal control	0.70
Stochastic-global optimal reflux ratio profile	0.763
Stochastic-local optimal reflux ratio profile	0.841
Deterministic reflux ratio profile (1)	0.769
Deterministic reflux ratio profile (2)	0.767
% Error in global	8.96%
% Error in local	20.08%
% Error in deterministic (1)	9.79%
% Error in deterministic (2)	9.57%

we proceed to stochastic local and deterministic cases, the distillate yield decreases. Using a geometric mean of relative volatility at the top and bottom of the column and updating at every time step using the Wilson model with GOPE when solving the optimal control problem, instead of a constant relative volatility throughout the batch time did not improve the results for the deterministic case. This can be attributed to the fact that the relative volatility profile obtained from taking the geometric mean of the top and bottom of the column is different to some extent than both the stochastic profile and deterministic profile (1). Due to the associations and non-ideal behavior of this mixture, the stochastic profile gave the optimal results.

In Tables 5 and 6, the results obtained from the rigorous model for the benzene(1)–hexafluorobenzene(2) systems are presented. Table 5 shows the results for distillate purity for the four cases. We can see that the purity that is closest to the specified purity of 70% is obtained when the stochastic global reflux ratio profile is used. The stochastic local reflux profile gives the highest error in purity about 20%. This is due to the fact that the local reflux ratio profile is obtained using a relative volatility profile that is lower than both the stochastic global and deterministic profiles. The second deterministic profile slightly improved the results for purity as compared to the first deterministic profile.

In Table 6, the results for product yield (distillate) are shown. The highest amount of distillate is obtained when the stochastic global reflux ratio is used. The local profile gives a product yield that is significantly lower (61%) than the global profile.

The results from this case study validate the fact that if a global optimization method such as interval-Newton-interval-branch-and-bound is used in parameter estimation step, for cases where the local optimizer fails to find the global minimum, the effect of uncertainties on the optimal reflux ratio profiles may be reduced

Table 6  
Results for amount of distillate from the rigorous model for benzene(1)–hexafluorobenzene(2) system

Global optimal reflux ratio profile	18.64 (kmol)
Local optimal reflux ratio profile	7.18 (kmol)
Deterministic reflux ratio profile (1)	17.86 (kmol)
Deterministic reflux ratio profile (2)	11.172 (kmol)

to a great extent and a better operating performance is achieved.

## 5. Conclusion

In this paper, the effect of thermodynamic uncertainties due to non-linear parameter estimation problem in vapor–liquid equilibrium modeling, on the batch distillation optimal control profiles are presented. When a global optimization method such as IN/GB method is used for parameter estimation, the thermodynamic uncertainties (static) are significantly reduced relative to the case in which only a local minimum is found in the parameter estimation problem. The uncertainties were quantified in terms of uncertainty factors which are defined as the ratio between the experimental and predicted activity coefficients for a system of *tert*-butanol(1)–*n*-butanol(2) and benzene(1)–hexafluorobenzene(2). The variance of uncertainty factors is reduced significantly and the expected values are closer to 1.

The dynamic nature of batch distillation translates the static uncertainties to time-dependent uncertainties. Two different relative volatility profiles are obtained for when a rigorous model of batch distillation with GOPE and LOPE is used to simulate the two binary systems mentioned above. For *tert*-butanol(1)–*n*-butanol(2) it can be concluded from the results that when the LOPE are used, the relative volatility profile cannot capture the effect of associations in this mixture and deviations from non-ideality and it is similar to the relative volatility profile for an ideal system (pentane–hexane). Two different Ito processes are used to represent the time-dependent uncertainties in relative volatility for LOPE and GOPE. Geometric Brownian motion is used for the profile obtained using LOPE and simple mean reverting process is used for the GOPE. For the benzene(1)–hexafluorobenzene(2) system, the relative volatility profiles are similar for GOPE and LOPE. However, when the LOPE are used in Wilson model, the relative volatility at each plate and time is lower than the profile obtained by using GOPE. The uncertainties in relative volatility are represented by a mean reverting process for both the GOPE and LOPE, with different constant coefficients.

Then the optimal control problem is solved for the four cases, stochastic-global case, where the Ito process representation obtained from GOPE is used for relative volatility, stochastic-local case, where the Ito process representation obtained from LOPE is used for relative volatility and two deterministic cases where the relative volatility is taken as constant for deterministic case (1) and relative volatility is computed at the top and bottom of the batch column for each integration interval using the Wilson model and the geometric mean of these two values is taken as the constant relative

volatility for the next interval for deterministic case (2). Using these four cases, four different reflux ratio profiles are obtained. When these reflux ratio profiles are tested by a rigorous model, the stochastic-global profile gives the highest yield and a purity that is closest to the purity constraint on the distillate for the optimal control problem. Especially, the yield obtained from the stochastic-global reflux profile for benzene(1)–hexafluorobenzene(2) is significantly higher.

From these results it can be concluded that an optimum operating policy using optimal control in batch distillation can only be obtained if the effects of thermodynamic uncertainties are minimized. The effect of uncertainties due to the usage of local methods during the parameter estimation step in VLE modeling is propagated in time during batch operation and the optimal reflux profile obtained results in a lower product yield and a purity that is significantly different from the specified purity on the distillate.

## Acknowledgement

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