UNCERTAINTIES IN PARAMETER ESTIMATION & 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 nonlinear 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 local and global parameters 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 global parameters versus local parameters results in a better product yield and the minimum error between the specified purity and the purity that is achieved.

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 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 et al. (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 et al., 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 and Diwekar, 2003(a)). 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 and Diwekar, 2003(a); Ulas and Diwekar2003(b)). 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 nonlinear 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 nonlinear parameter estimation problems is non-convex and may have multiple local optima. Therefore local optimization techniques cannot be employed since they do not guarantee to converge to a global optimum. Gau et al. (2000), presented an alternative method for nonlinear 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 and

Onken, 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 global and local parameter values for Wilson model. These profiles are statistically analyzed and represented by Ito processes. Finally, batch distillation optimal control problem is solved for three cases: the stochastic global case (relative volatility is represented by an Ito process, obtained from global parameters), the stochastic local case (relative volatility is represented by an Ito process, obtained from local parameters) and the deterministic case (relative volatility is taken as constant). 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.

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:

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

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

The equations for binary parameters Λ_{12} and Λ_{21} are:

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

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

where v_1 and v_2 are the pure component liquid volumes, T is the system temperature and θ_1 and θ_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:

$$J(\theta) = \left(\frac{\gamma_{i,\exp} - \gamma_{i,calc}}{\gamma_{i,\exp}} \right)^2 \quad (5)$$

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 Table 1 and 2, for the binary systems of tert-butanol(1)-n-butanol(2) and benzene(1)-hexafluorobenzene(2), respectively.

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		
			1	2	Objective function , J( )	1	2	Objective function, J( )
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**

Table 2: Results of parameter estimation for benzene(1)-hexafluorobanzene(2)
(Gau et al. (2000)

DECHEMA Volume: page	No. of data points	P(mmHg)	DECHEMA			Gau et al. (2000) – IN/GB		
			1	2	Objective function , J( )	1	2	Objective function, J( )
7:234	17	300	344	-347	0.0566	**-432**	**993**	**0.0149**

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:

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

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

where the experimental activity coefficients can be calculated from:

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

The probability density estimate of the uncertainty factors for tert-butanol (1)-n-butanol (2) and benzene (1)-hexafluorobenzene (2) are given in Figures 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 energy parameter values reported by Gau et al. (2000).
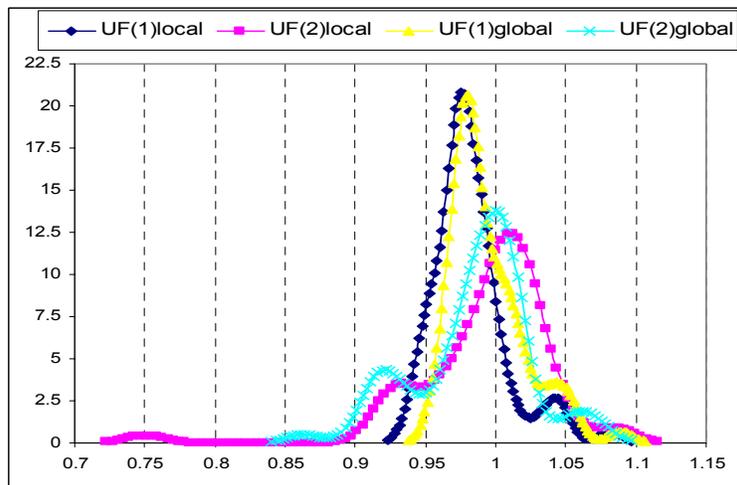
Figure 1: Probability density estimate of uncertainty factors for six experimental data sets of tert-butanol(1)-n-butanol(2) system for globally optimal energy parameters predicted by Gau et al.(2000) using IN/GB method and locally optimal energy parameter values published in DECHEMA VLE Data Collection.
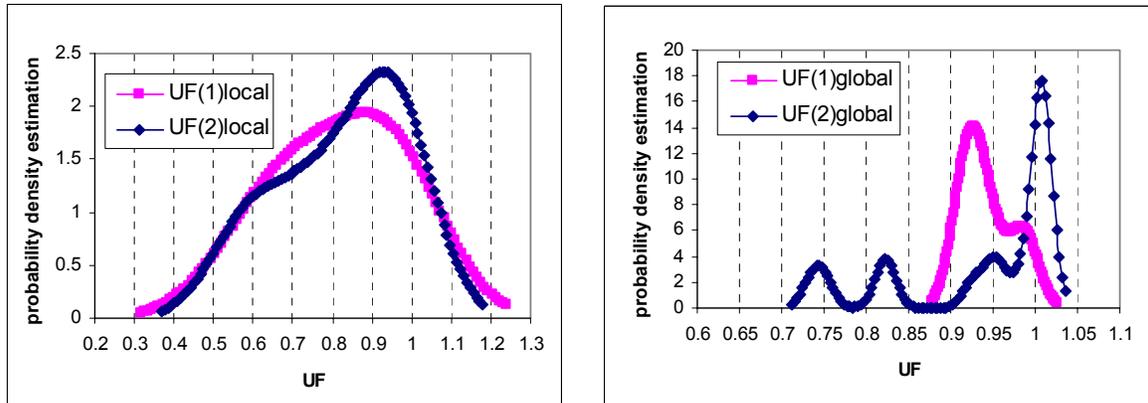
Figure 2: Probability density estimate of uncertainty factors for benzene(1)-hexafluorobenzene(2) system for globally optimal energy parameters predicted by Gau et al.(2000) using IN/GB method and locally optimal energy parameter values published in DECHEMA VLE Data Collection.

2.2 Time-Dependent Uncertainties

After establishing statistically that the Wilson model with the global parameters 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 and Diwekar, 2003a,b).

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 global and local parameters, two different time-dependent profiles of relative volatility are obtained which are shown in Figures 3(a) and 4(a). To generate these profiles, the global and local parameters obtained from data set 6, shown in Table 1, were used.

When the local parameters are used in the Wilson model, the relative volatility profile shown in Figure 4(a) is obtained, which is similar 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 (Quitzsch et al., 1969). The effect of these associations is only captured when global parameters are used in

the Wilson model. The relative volatility profile shown in Figure 3(a) is obtained using the global parameters, which is shows behavior between an ideal system like pentane-hexane and a non-ideal system like ethanol water, presented by Ulas and Diwekar (2003a,b).

Figures 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 global and local parameters are used in Wilson model, respectively.
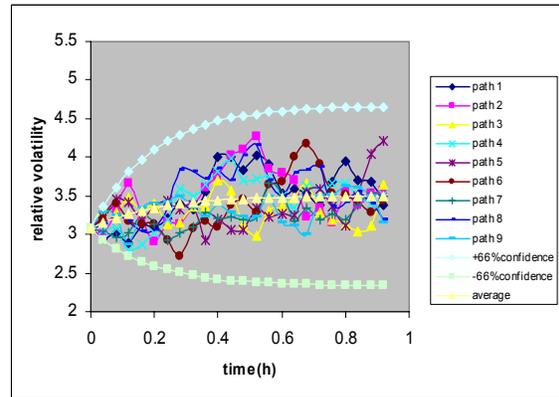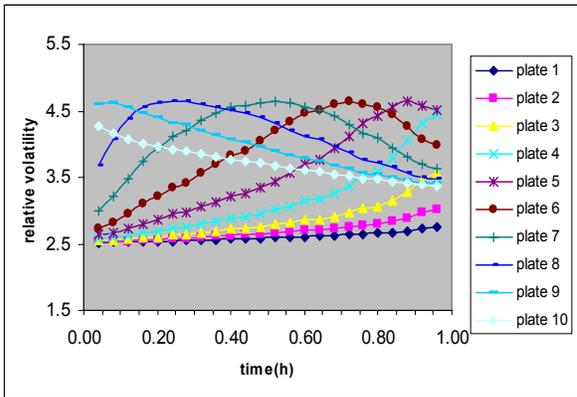
Figure 3(a): The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model global parameters

Figure 3(b): Sample paths of a simple mean reverting process with 66% confidence intervals
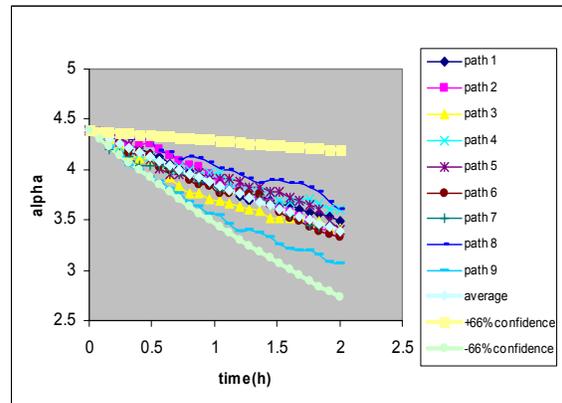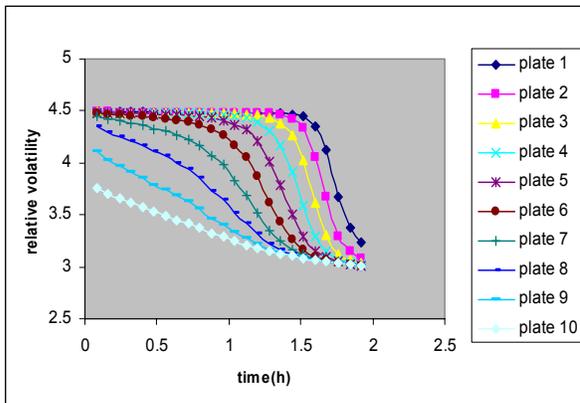
Figure 4(a): The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model local parameters

Figure 4(b): Sample paths of a geometric Brownian motion with 66% confidence intervals

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

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

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

$$dz = \varepsilon_t \sqrt{dt} \qquad (10)$$

In this equation ε_t is a random number drawn from a normal distribution with mean $\mu=0$ and a standard deviation $\sigma =1$. The parameters η, $\bar{\alpha}$ and σ 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 local parameters 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:

$$da = \beta\alpha dt + \sigma\alpha dz \qquad (11)$$

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

System II: benzene(1)-hexafluorobenzene(2)

For the second binary system, benzene(1)-hexafluorobenzene(2), the relative volatility profiles for global and local parameters, obtained using a rigorous model as a proxy for experiments is shown in Figures 5(a) and 6(a). The relative volatilities obtained using locally optimal parameters in Wilson model, are lower that the relative volatilities obtained using globally optimal parameters. Both of these profiles were represented by a simple mean reverting process, shown in Equation 9. For this binary system the use of global versus local parameters in Wilson model affects the constant coefficients of Ito process representation.

When the globally optimal parameters 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 locally optimal parameters are used, the constant coefficients are: $\bar{\alpha} = 1.08$, $\eta = 1.06$, $\sigma = 0.012$ with and R^2 value of 0.95.
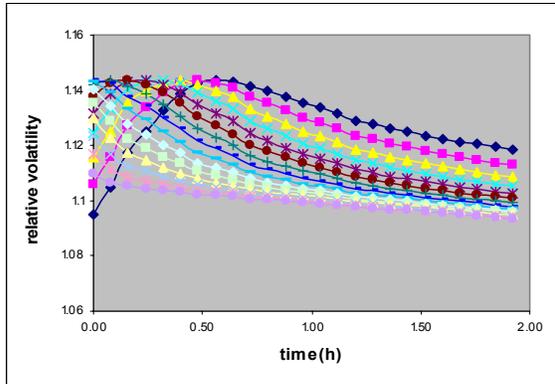
Figure 5(a): The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model global parameters
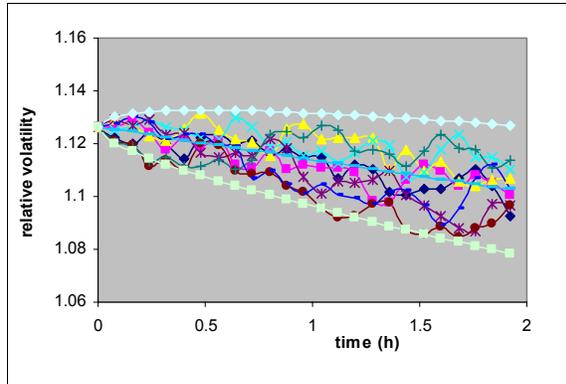
Figure 5(b): Sample paths of a simple mean reverting process with 66% confidence intervals
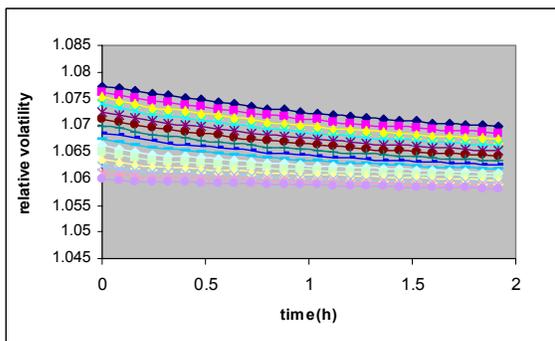
Figure 6(a): The change of relative volatility with respect to time and plate in a batch column from a rigorous simulation using Wilson model local parameters
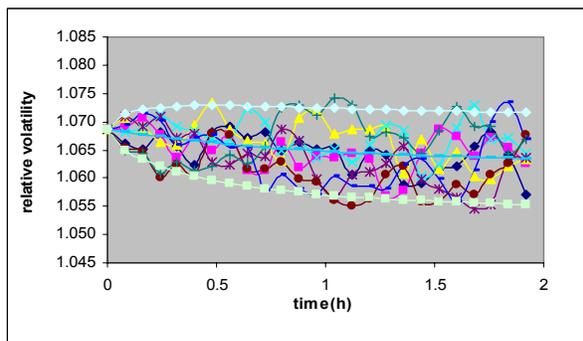
Figure 6(b): Sample paths of a simple mean reverting process with 66% confidence intervals

3. OPTIMAL CONTROL PROFILES FOR LOCAL AND GLOBAL PARAMETERS

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 et al. (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 (2003b) 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 using a mean reverting process, such as the cases for tert-butanol(1)-n-butanol(2) system when the global parameters 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 globally optimal energy parameters are used in Wilson equation. Whereas, when local parameters 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 local parameters for tert-butanol(1)-n-butanol(2). Ulas and Diwekar(2003b) 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 global parameters 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:

Maximize $-x_1(T)$
$\quad R_t$

subject to:

$$\frac{dx_1}{dt} = \frac{dB_t}{dt} = \frac{-V}{R_t + 1}, \qquad\qquad x_1(0) = B_0 = F \qquad\qquad (12)$$

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

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

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

The Hamiltonian function, which should be maximized is:

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

The adjoint equations are:

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

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

If we define:

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

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

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

If we define: $\qquad z = \dfrac{\dfrac{\partial L}{\partial x_2}}{\dfrac{\partial L}{\partial x_1}} = \dfrac{z_2}{z_1}$

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

Also if we define:
$$\xi = \frac{\frac{\partial^2 L}{(\partial x_2)^2}}{\frac{\partial L}{\partial x_1}} = \frac{\omega_t}{z_1}$$

$$\frac{d\xi}{dt} = -\xi\frac{V(1-\frac{\partial x_D^{(1)}}{\partial x_2})}{(R_{tU}+1)x_1} + z\frac{V\frac{\partial^2 x_D^{(1)}}{\partial x_2}}{(R_{tU}+1)x_1} - \xi z\frac{V(x_2-x_D^{(1)})}{(R_{tU}+1)(x_1)^2} \tag{20}$$

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

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 $_2$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 three 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 globally optimal energy parameters 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 local parameters in Wilson model and the maximum distillate problem is solved for the stochastic case using combined maximum principle-NLP technique.

III. *Deterministic case*: relative volatility is taken as constant and the maximum distillate problem is solved for the deterministic case using combined maximum principle-NLP technique.

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 kmol/h
> Pressure: 1 atm
> Batch time: 2 h

For the deterministic case the relative volatility was taken as constant at 3.035, which is corresponds to the initial value of the relative volatility profile from the rigorous model, when the global parameters are used. This algorithm was implemented in MultiBatchDS (Diwekar, 1996). The reflux ratio profiles obtained for the three cases are given in Figure 7.
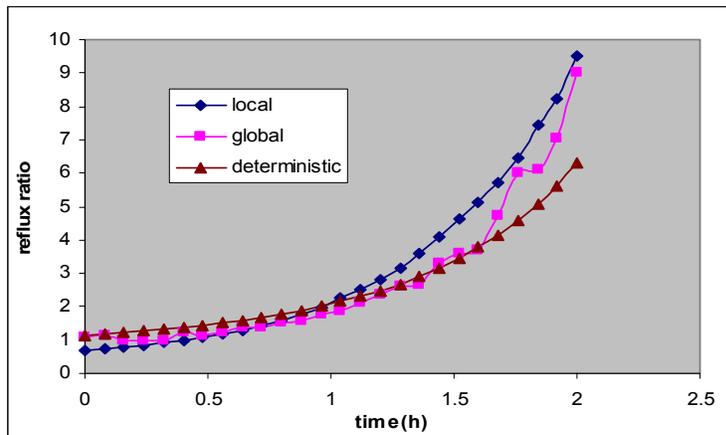
Figure 7: Optimal reflux ratio profiles for the stochastic-global, stochastic-local and deterministic cases

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 (k-mol)
Feed composition: $x_F(1) = 0.55$, $x_F(2) = 0.45$;
Vapor rate: 60 kmol/h
Pressure: 300 mmHg
Batch time: 2 h

For the deterministic case the relative volatility was taken as constant at 1.12. The reflux ratio profiles obtained for the three cases are given in Figure 8.
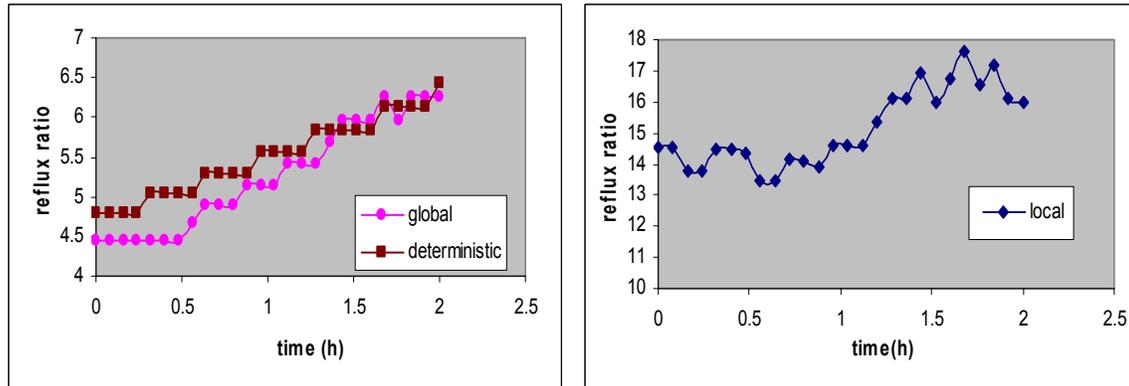
Figure 8: Optimal reflux ratio profiles for the stochastic-global, stochastic-local and deterministic cases

4. RESULTS & DISCUSSION

The reflux ratio profiles obtained for three 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) system. 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 we proceed to stochastic local and deterministic cases, the distillate yield decreases.

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	0.993
% error in global	2.26%
% error in local	4.03%
% error in deterministic	5.65%

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 (k-mol)
Local optimal reflux ratio profile	37.80 (k-mol)
Deterministic reflux ratio profile	36.23 (k-mol)

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	0.769
% error in global	8.96%
% error in local	20.08%
% error in deterministic	9.79%

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

Global optimal reflux ratio profile	18.64 (k-mol)
Local optimal reflux ratio profile	7.18 (k-mol)
Deterministic reflux ratio profile	17.86 (k-mol)

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 three 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.

In Table 6, the results for product yield (distillate) are shown. The highest amount of distillate is obtained when the stochastic global reflux ratio profile 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 to a great extent and a better operating performance is achieved.

5. CONCLUSION

In this paper, the effect of thermodynamic uncertainties due to nonlinear 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 global and local

parameters 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 local parameters 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 local and global parameters. Geometric Brownian motion is used for the profile obtained using local parameters and simple mean reverting process is used for the global parameters. For the benzene(1)-hexafluorobenzene(2) system, the relative volatility profiles are similar for global and local parameters. However, when the local parameters are used in Wilson model, the relative volatility at each plate and time is lower than the profile obtained by using global parameters. The uncertainties in relative volatility are represented by a mean reverting process for both the global and local parameters, with different constant coefficients.

When the optimal control problem is solved for the three cases, stochastic-global case, where the Ito process representation obtained from global parameters is used for relative volatility, stochastic-local case, where the Ito process representation obtained from local parameters is used for relative volatility and deterministic case where the relative volatility is taken as constant, three different reflux ratio profiles are obtained. When these reflux ratio profiles are tested in 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, due to the non-ideal nature of this binary system.

From these results it can be concluded that an optimum operating policy using optimal control in batch distillation can only be obtained if the effect 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.

NOMENCLATURE

F = amount of feed [mol]
H = Hamiltonian
J = objective function for the nonlinear parameter estimation
P_{exp} = total pressure
P_i^{vap} = vapor pressure
R_t = the control variable vector, reflux ratio (function of time)
T = total batch time [h]

UF = uncertainty factor
V = molar boilup rate [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]
$x_{i,exp}$ = composition of the liquid phase
$y_{i,exp}$ = composition of the vapor phase
z_1, z_2 = adjoint variables

Greek symbols

α = relative volatility
$\bar{\alpha}$ = "normal" level of α, the level which α tends to revert
μ = drift parameter
γ_i = activity coefficient
$\gamma_{i,calc}$ = activity coefficient determined from Wilson model
$\gamma_{i,exp}$ = activity coefficient determined from experimental data
η = speed of reversion
λ_{ij} = energy parameters of Wilson model
Λ_{ij} = binary interaction parameters of Wilson model
σ = standard deviation
ν_i = pure component liquid volume

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