On the Dynamics of Batch Distillation : A Study of Parametric Sensitivity in Ideal Binary Columns

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Abstract

The paper addresses parametric sensitivity in batch distillation processes. By considering the effect of small changes in the operating parameters, e.g., initial conditions, we show that even ideal binary columns may display highly sensitive regions of operation. Through analysis of a general model we determine operating conditions that favor parametric sensitivity and show that parametric sensitivity in general will be most severe in columns operated with reflux or internal reflux ratio as a manipulated input. The analytical results are verified through numerical computations for several case studies.

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1 Introduction

Batch distillation has become of increasing importance in industry during the last decades. In academia, this is reflected in the large number of articles that have appeared on optimization of batch distillation operations. Somewhat surprisingly, however, the fundamental dynamic behavior of batch distillation columns has received little attention in the literature. In this paper we consider one important aspect of batch distillation dynamics, namely the sensitivity of key output variables to small changes in operating conditions. Such sensitivity is termed *parametric sensitivity*.

The study of parametric sensitivity in batch distillation is important not the least because the output of most optimization schemes is an optimal profile for a so-called control variable, e.g., reflux ratio, which is implemented in an *open-loop* fashion (e.g., Macchietto and Mujtaba [10]). This implies that there is no feedback correction if key outputs diverge from the desired trajectories and an "optimal operating policy", when implemented, may yield highly unexpected results if the column displays parametric sensitivity. Thus, it is crucial to understand whether parametric sensitivity may occur and, if so, what operating conditions that favor such sensitivity. In this work we aim at providing some preliminary insight into this important problem.

Outline of Paper: In Section 2 we introduce the reader to batch distillation and typical ways of operating batch columns. In Section 3 we discuss the analysis of parametric sensitivity for general systems and discuss the validity of frequently employed criteria for parametric sensitivity in batch reactors. In section 4 we analyze a general model of a binary batch distillation column and provide analytical conditions that identify under which operating conditions parametric sensitivity is likely to occur. The analytical results are verified through numerical computations of several case studies. Finally, in Section 5, we discuss the practical implications of parametric sensitivity for operation of batch columns and provide a complete example for illustration.

2 Batch Distillation

Conventional batch distillation columns are usually operated as either a batch rectifier or a batch stripper, although other designs are also proposed (see e.g. Davidyan [3]). In this work, however, we limit ourselves to rectifying columns consisting of the different sections demonstrated in the schematic in figure 1.

The different sections are a heated vessel (reboiler) where the liquid is vaporized, the column section with trays or packed material, the condenser (total or partial) where the vapor leaving the column is condensed, a reflux drum which collects the condensed vapor and one or more receivers (accumulators) where the distillate is collected. Some of the distillate is normally returned to the column (reflux) in order to improve the separation.

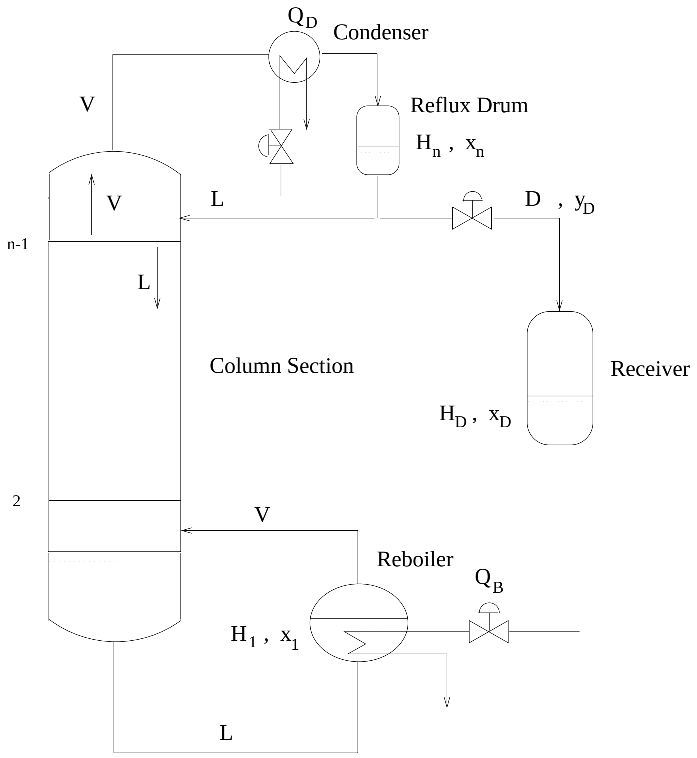


Figure 1: Multistage batch distillation column

Operating policies. During startup batch columns are usually operated under total reflux until steady state or to a state when the distillate composition reaches a desired purity. During the production period operation is usually performed according to one of the following policies

(1) Constant reflux ratio

(2) Constant distillate composition

(3) Optimal reflux ratio

For the latter case, there exists a vast literature on determining the optimal policy in which operation is optimized based on some criteria, e.g. maximum amount of distillate or minimum distillation time (see e.g. Sørenson [18], Mujtaba and Macchietto [12] or Kerkhof and Vissers [9]).

The results presented in this paper are for open-loop operating policies and are therefore of relevance mainly for case (1) and (3).

Control Configurations. With a control configuration we understand the manipulated inputs that are available for composition control. For instance, the LV-configuration implies that reflux L and boilup V are available for composition control. Note that a configuration results from configuring the level control system, e.g., the LV-configuration results when the distillate flow D is used for condenser level control. For batch distillation columns, the most common configurations are probably the LV-, $(L/V)V$ and $(L/D)V$-configurations.

In models of continuous as well as batch distillation columns it is usually assumed that the control inputs, e.g., reflux L, may be manipulated on a molar rate basis, i.e., in $[kmol/min]$. This is mainly due to the fact that it is the molar flows that naturally enters the material balances in a model and thus determine the separation. However, as pointed out by Jacobsen and Skogestad (1991), in operating columns the liquid flows reflux L and distillate flow D are more likely to be manipulated on a mass or volume rate basis. This may seem like a trivial difference. However, as shown by Jacobsen and Skogestad (1991), the use of mass or volume flows may introduce multiple steady states and unstable operating points in the case of continuous distillation. The reason is that the transformation between molar and mass/volume flows is nonlinear, due to the composition dependence, and may become singular under certain conditions. Based on these results we might expect that the use of mass or volume flows will have a profound influence also on the behavior of batch distillation columns. Thus, having first analyzed the case with molar inputs in Section 4.1, we go on to analyze the case with mass inputs in Section 4.2.

3 Analysis of Parametric Sensitivity

The concept of *parametric sensitivity* was introduced in the chemical engineering literature by Bilous and Amundson [2]. They considered a tubular reactor in which a first order irreversible chemical reaction occurred, and showed that small changes in the heat transfer coefficient may produce large changes in the effluent. Sensitivity was predicted analytically by the first order derivatives of the states to some operating parameters, and the system was said to exhibit parametric sensitivity when these derivatives increased to very large values. Nonlinear simulations of the reactor showed that formation of a considerable hot spot, also referred to as temperature runaway, may occur in certain operating regions if care is not taken when choosing the operating conditions, e.g., the ambient temperature.

Since the pioneering work of Bilous and Amundson [2], there has been a moderately increasing literature on parametric sensitivity in chemical engineering processes. Essentially all this work has been directed towards different types of chemical reactors. A number of different criteria have been proposed for identification of regions of parametric sensitivity. Most of the early works were concerned with developing criteria based on the geometry of the temperature profiles in chemical reactors. Criteria based on the occurrence of a positive second order derivative of the temperature before the *hot spot*, i.e. the maximum temperature, was proposed by Adler end Enig [1]. Such criteria have an advantage in that they are based on intrinsic properties of the system, such that it is not required to a priori fix the critical value of the parameter, as opposed to the criteria presented by Bilous and Amundson. Some authors also paid attention to the close relation between parametric sensitivity and thermal explosion, or runaway theory (see e.g. articles by Morbidelli and Varma [11] or Vajda and Rabitz [19]). Most of these works are yet again based on the early results of Semenov [16].

We will in this work consider systems of nonlinear ordinary differential equations on the form

$$\dot{\mathbf{x}} = f\left(\mathbf{x}, \xi(t), t\right), \quad \mathbf{x}\left(0\right) = \mathbf{x}_0 \tag{1}$$

$$\mathbf{x} \in \mathcal{R}^n, \xi \in \mathcal{R}^p, f : \mathcal{R}^n \times \mathcal{R}^p \mapsto \mathcal{R}^n$$

where $\mathbf{x}$ denotes the vector of state variables and ξ are the parameters, e.g., control inputs. The solution of (1) is conveniently denoted by

$$\mathbf{x}(t) = \phi(t, \xi(t), \mathbf{x_0}) \tag{2}$$

From the theory of non–linear ordinary differential equations (see e.g Sansone and Conti [15]) we know that a sufficient condition for the uniqueness of $\phi(t, \xi(t), \mathbf{x}_0)$ is that (1) be a Lipschitzian or a Carathéodory system. The Lipschitz conditions ensure that integral curves never intersects, thus ruling out the possibility of multiplicities along the state trajectory. These conditions are met for most models of batch distillation columns.

In studying parametric sensitivity we are interested in the sensitivity of a nominal trajectory $x^*(t)$ to *small* changes $\delta\xi$ and δx_0 in the system parameters ξ and the initial state x_0, respectively. In the linear approximation, the perturbation $\delta x(t)$ of the nominal trajectory is given by the solution of the linear nonstationary differential equation

$$\dot{\delta\mathbf{x}} = A(t)\delta\mathbf{x} + B(t)\delta\xi; \quad \delta\mathbf{x}(0) = \delta\mathbf{x}_0 \tag{3}$$

with $A(t) = \partial f/\partial x$ and $B(t) = \partial f/\partial\xi$ evaluated along the nominal trajectory $x^*(t)$. The state $\delta\mathbf{x}(t)$ then trace out the trajectory for the difference between the nominal state $x^*(t)$ and the perturbed state $x^*(t) + \delta\mathbf{x}(t)$. Typically, if $||\delta x(t)||$ in some sense becomes large for some t and small perturbations $||\delta\xi||$ and $||\delta x_0||$, then the system is said to exhibit parametric sensitivity (e.g., Bilous and Amundson, 1956; Vajda and Rabitz, 1992, 1993). Thus, the definition of parametric sensitivity is qualitative rather than quantitative. In general, to determine the extent of parametric sensitivity one has to evaluate the sensitivity functions $|\delta x_i(t)|/|\delta\xi_j|$ and $|\delta x_i(t)/|\delta x_{0j}|$ by solving (3). Since, in the general case, an analytical solution does not exist for (3), the sensitivity functions has to be computed numerically for specific examples.

In this work we would like to determine under which operating conditions parametric sensitivity is likely to occur in batch distillation. This information may be difficult to extract from studies of specific examples. Thus, we look for simple indicators of parametric sensitivity which may be evaluated analytically. By considering equation (3) it is easily recognized that one particular situation in which to expect large parametric sensitivity is when the trajectory is unstable, i.e., when the perturbation $\delta x(t)$ grows exponentially for small perturbations δx_0 or $\delta\xi$. If the Jacobian $A(t)$ in (3) is constant, then instability of (3) (and thereby of (1)) occurs when some eigenvalue of A is in the RHP, i.e., has positive real part. However, for nonstationary systems, which always results when linearizing around a nominal trajectory, $A(t)$ varies with t and the situation is not that simple. In fact, in this case neither necessary nor sufficient conditions for instability are available based on an eigenvalue analysis of $A(t)$. Sufficient conditions are, however, available if one instead consider the eigenvalues of $A(t) + A^T(t)$ (see e.g., Willems, 1970). Such conditions are on the other hand considered highly conservative and hence not very useful. Other conditions based on the boundedness of the time variation of the elements a_{ij} of $A(t)$ or the use of Liapunov methods have also been proposed (see e.g. Sansone and Conti [15] or Jordan and Smith [8]), but are not considered very useful as either due to their complexity and potential conservativeness.

Given the conservative nature of most conditions proposed in the literature for stability, we will in this work assume that the occurrence of RHP eigenvalues usually implies exponential growth of $\delta x(t)$ locally. This is a reasonable assumption for most systems, although rare examples of the opposite are found in the literature. An eigenvalue analysis of $A(t)$ is thus used to find candidates among "systems" (in the sense of oprating regimes) that may display parametric sensitivity. For low–order systems we show that simple analytical conditions may be derived for occurrence of RHP eigenvalues. In order to illustrate the implications of the eigenvalue analysis we will, however, compute the *sensitivity* for perturbations in the initial conditions x_0 for specific examples.

Computing the Sensitivity Functions. If we consider the homogeneous linear system

$$\dot{\delta\mathbf{x}} = A(t)\delta\mathbf{x}; \quad \delta\mathbf{x}(0) = \delta\mathbf{x}_0 \tag{4}$$

a solution in terms of its trajectory in state space may be given by

$$\delta\mathbf{x}(t) = \mathbf{F}(t,t_0)\mathbf{F}(t_0,t_0)^{-1}\delta\mathbf{x}_0 \tag{5}$$

where $\mathbf{F}(t,t_0)$ is called a *fundamental matrix* defined as a solution of the matrix differential equation

$$\dot{\mathbf{F}}(t) = A(t)\mathbf{F}(t,t_0) \tag{6}$$

The *transition matrix* $\phi(t_0,t_0)$ is the fundamental matrix for which the initial solution is $\phi(t_0,t_0) = I$, the identity matrix.

In the work by Bilous and Amundson [2] it is suggested that the transition matrix may be computed by evaluating the matrix exponential of the *integral* of A, i.e.

$$\phi(t,t_0) = e^{\int_{t_0}^{t} A(t)dt} \tag{7}$$

However, in order for the *integral solution* (7) to be correct it is required that the Jacobian matrices $A(\tau)$ and $A(t)$ commute, i.e. $A(t)A(\tau) = A(\tau)A(t)\ \forall t,\tau$. This is a severe requirement and rarely satisfied for time–varying systems (see e.g. Wiberg [20]). We found by comparing various ways of computing the transition matrix that the integral solution (also suggested in a textbook by Douglas [4]) may produce large errors, and thus contradictive results for the sensitivity functions.

4 Parametric Sensitivity in Batch Distillation

In this section we analyze a general dynamic model of a binary batch distillation column. The following common assumptions are made for the batch columns considered

- Ideal VLE.
- Ideal trays
- Total condenser

- Constant molar flows
- Negligible holdup on the plates and in the condenser.

With these assumptions we obtain a model with only two states, one for reboiler composition and one for reboiler holdup, and this permits us to develop analytical expressions for the eigenvalues of the Jacobian $A(t)$, which we use for prediction of parametric sensitivity.

The dynamics, and hence the parametric sensitivity, will in general depend on which configuration the column is operated with. We thus need to analyze different configurations separately. We start by considering the LV-, $(L/D)V$- and $(L/V)V$-configurations which all have the same properties with respect to stability of the trajectory (under the modelling assumptions given above). With these configurations we make the common assumption that all flows are given on a molar rate basis, i.e., in $[kmol/min]$. However, as mentioned previously, in practice, the liquid flows are usually given on a mass or volume rate basis. In section 4.2 we therefore consider reflux L_w and distillate flow D_w given on a mass basis (subscript w) and consider the parametric sensitivity of columns operated with the L_wV-, $(L_w/D_w)V$- and $(L_w/V)V$-configurations.

4.1 LV-, $(L/D)V$- and $(L/V)V$-configurations

The LV, $(L/D)V$ and $(L/V)V$-configurations are all common configurations in industrial operation of batch distillation columns. However, we here make the common assumption that all flows are given on a molar rate basis, which usually is not the case in industrial operation. In order to understand the difference of academic models with molar flows and real columns with mass or volume flows, however, we study this case first and address the case with mass flows in the next section.

Dynamic Model. The following equations apply for the reboiler

$$\frac{dH_B}{dt} = L - V \tag{8}$$

$$\frac{dx_B}{dt} = \frac{1}{H_B}\left[L\left(x_2 - x_B\right) - V\left(y_B - x_B\right)\right] \tag{9}$$

where H_B is the reboiler holdup whereas x_B and y_B denote the compositions of the liquid and vapor phase respectively. Based on the asumption of negligible holdup on the trays, the compositions for these are computed from algebraic equations, i.e.,

$$L(x_{i+1} - x_i) + V(y_{i-1} - y_i) = 0 \tag{10}$$

For the case of constant relative volatility, α, the vapor composition is given by the VLE equation

$$y_i = \frac{\alpha x_i}{1 + (\alpha - 1)x_i} \tag{11}$$

Analytical Treatment We now want to consider the eigenvalues of the linear model obtained from linearization of the nonlinear model along a nominal trajectory. The eigenvalues are computed from the Jacobian

$$A(t) = \begin{pmatrix} 0 & 0 \\ \frac{1}{H_B^2}V(y_B - x_B) - L(x_2 - x_B) & \frac{1}{H_B}[L(\frac{\delta x_2}{\delta x_B} - 1) - V(\frac{\delta y_B}{\delta x_B} - 1)] \end{pmatrix} \tag{12}$$

and the eigenvalues become

$$\lambda_1 = 0 \quad \lambda_2 = \frac{L(\frac{\partial x_2}{\partial x_B} - 1) - V(\frac{\partial y_B}{\partial x_B} - 1)}{H_B} \tag{13}$$

We see that one eigenvalue always is 0 and this is explained by the integrating nature of the reboiler holdup. By considering the second eigenvalue λ_2 we determine the necessary and sufficient condition for a RHP eigenvalue

$$L\left(\frac{\partial x_2}{\partial x_B} - 1\right) - V\left(\frac{\partial y_B}{\partial x_B}\right) > 0 \tag{14}$$

It is not straightforward to determine under which conditions (14) is satisfied. We may however simplify (14) by a few algebraic manipulations of the model equations. Since condenser dynamics are neglected we have that $y_{n-1} = y_D$. The overall material balance for the light component is then written

$$Vy_B + Ly_D = Lx_2 + Vy_D \tag{15}$$

or

$$y_B = \frac{L}{V}x_2 + \frac{V-L}{V}y_D \tag{16}$$

Differentiating equation (16) with respect to x_B yields

$$\frac{\partial y_B}{\partial x_B} = \frac{V}{L}\frac{\partial x_2}{\partial x_B} + \frac{V-L}{V}\frac{\partial y_D}{\partial x_B} \tag{17}$$

and

$$\frac{\partial x_2}{\partial x_B} = \frac{V}{L}\frac{\partial y_B}{\partial x_B} + \frac{L-V}{L}\frac{\partial y_D}{\partial x_B} \tag{18}$$

Inserting (18) in (14) and simplifying yields

$$\lambda_2 = \frac{(V-L)(1 - \frac{\partial y_D}{\partial x_B})}{H_B} \tag{19}$$

which yields the necessary and sufficient condition for a RHP eigenvalue

$$\lambda_2 \; > \; 0 \;\text{ iff }\; \frac{\partial y_D}{\partial x_B} < 1 \tag{20}$$

If we consider one stage columns with a total condenser we have that y_D is in equilibrium with x_B. y_D thus only depends on α and x_B. By differentiation of the VLE equation (11) we may show that a necessary and sufficient condition for a RHP eigenvalue in this case is given by

$$x_B \; > \; \frac{\sqrt{\alpha} - 1}{\alpha - 1} \tag{21}$$

For one stage columns we thus find that sensitivity is favored by separations where the initial composition of light component x_{B0} and the relative volatility α are large.

For multistage columns the case is more complicated, and it is improbable to find analytic conditions for the partial derivative $\partial y_D / \partial x_B$ in (20). However, if we consider *sharp separations*, some important approximate results may be derived. Most batch columns are in practice operated such that the transient behavior (product drawoff) starts from an initial state of total reflux. This leads to a large buildup of light component in the upper section of the column. As product drawoff commences on finds that, close to the point where practically all light component has been withdrawn, the mole fraction of light component drops from $y_D \simeq 1$ to $y_D \simeq 0$ in a short period of time. During this period the *intermediate cut* is withdrawn, which is the fraction of distillate with composition ranging from for example $0.2 \leq y_D \leq 0.8$, as illustrated in figure (2). This off–cut is either recycled to subsequent batches or processed separately. The size of the intermediate cut decreases strongly with

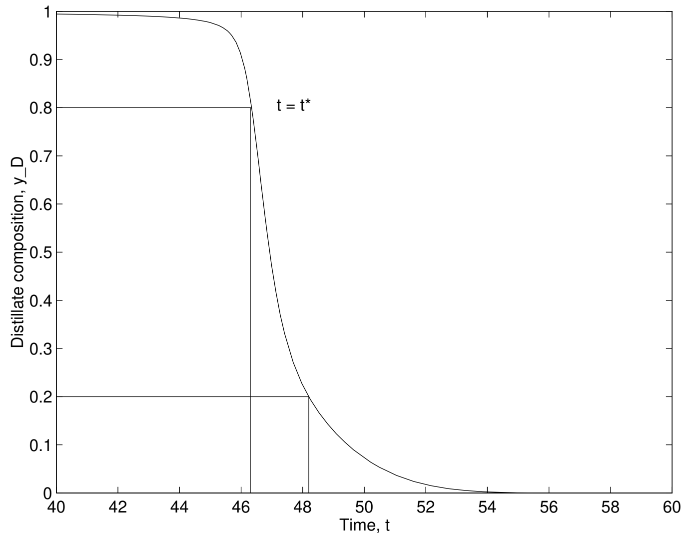


Figure 2: Composition profile for distillate stream, y_D

increasing *Efficiency factor* $E = \alpha^n$, as shown by Rose and Welshans [14], where n denotes number of stages. E is often used in the literature as a measure of the sharpness of separation (see e.g. Rose and Welshans [14] and Pigford *et.al.* [13]). If we denote the time when collection of intermediate cut begins by t^*, we may use the following approximations in the vicinity of t^*

$$\begin{array}{llll} t < t^* & y_D \simeq 1, & \partial y_D/\partial x_B \simeq 0 & \Rightarrow \lambda_{max} \simeq (V-L)/H_B \\ t > t^* & y_D \simeq 0, & \partial y_D/\partial x_B \gg 1 & \Rightarrow \lambda_{max} \simeq 0 \end{array} \tag{22}$$

The approximation is valid for *sharp separations*, and we provide numerical results for some example columns in the next section which illustrates that such is the case.

Numerical Results. In figure we show that the Jacobian matrix displays RHP eigenvalues for a large operating region.

In order to confirm the analytical results derived above, we perform simulations for a few case studies. We consider a *base case* of a column with the data given in Table 1. The effect of changing α and x_{B0} was examined by computing the eigenvalues and sensitivity functions for two additional cases where we changed the values given for the *base case* to $\alpha = 5$ and $x_{B0} = 0.75$ respectively. The composition profiles for the three cases are shown in figure 3, where the solid line illustrates the *base case*. The solid line in figure 4 shows the maximum eigenvalue along the trajectory of the base case, and we see that the eigenvalue is in the RHP for a

Table 1: Process data for *base case*

Number of trays :	$N = 8$ + Total condenser
Molar reflux :	$L = 5$ $[kmole/min]$
Molar Boilup :	$V = 5.5$ $[kmole/min]$
Relative volatility :	$\alpha = 4$
Molar weight of light component :	$M_1 = 20$ $[kg/kmole]$
Molar weight of heavy component :	$M_1 = 40$ $[kg/kmole]$
Initial composition in reboiler :	$x_{B0} = 0.5$
Initial amount in reboiler :	$H_{B0} = 100 kmoles$

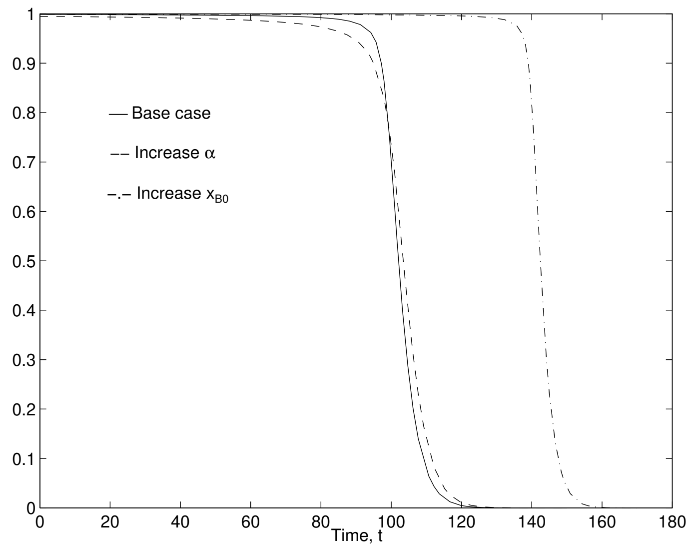


Figure 3: Composition profiles for distillate for LV–configuration

extended period of time. By comparing figures 3 and 4 it is seen that λ_{max} for all cases displays a peak in the region where y_D drops. We also note that the magnitude of λ_{max} increases somewhat with increasing values of α and x_0, in agreement with the analytical results presented above. It should however be emphasized that the magnitude of λ_{max} is small such that large sensitivity is not to be expected. In order to investigate the goodness of our previous assumptions leading to the approximate equations for λ_{max} in (22), we obtained the following results from the simulations

$$\begin{array}{ll} \lambda_{max}(t = 77.8 < t^*) = 0.0078 & (V - L)/H_B = 0.0083 \\ \lambda_{max}(t = 128.6 < t^*) = 0.0131 & (V - L)/H_B = 0.0141 \end{array} \quad (23)$$

We further see that $\lambda_{max} \simeq 0$ for $t > t^*$, and thus conclude that our assumptions are viable for these separations.

Figure 5 shows the sensitivity function $\partial x_B/\partial x_{B0}$. The sensitivity function gives the effect of a small perturbation in the initial composition on the composition of the reboiler. Since the magnitude of the sensitivity function, $\|\delta x_B\|$, grows exponentially when $\lambda_{max} > 0$ we have that parametric sensitivity is exhibited. $\|\delta x_B\|$ however

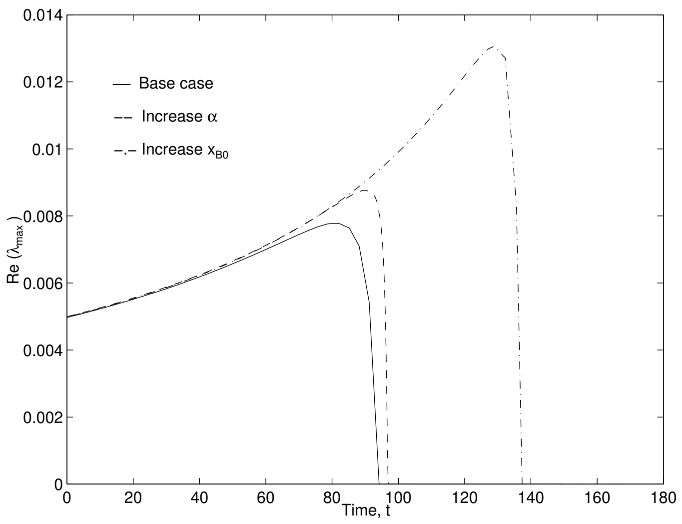


Figure 4: $Re(\lambda_{max})$ for LV–configuration

decays to zero as x_B goes to zero, so that one may argue that the columns are only *locally divergent (unstable)*. The implications are however not restricted to local phenomena as there are large deviations also for y_D. We do not present results for other variables such as y_D in this section. Effects of sensitivity on other variables than the states (x_B) will be considered later in the article in terms of a more complete case study. By comparing with figure 4 we further note that largest sensitivity $\|\delta x_B\|_{max}$ is found close to the peak value of λ_{max}. This clearly shows that there is a close connection between exponential divergence and positive eigenvalues.

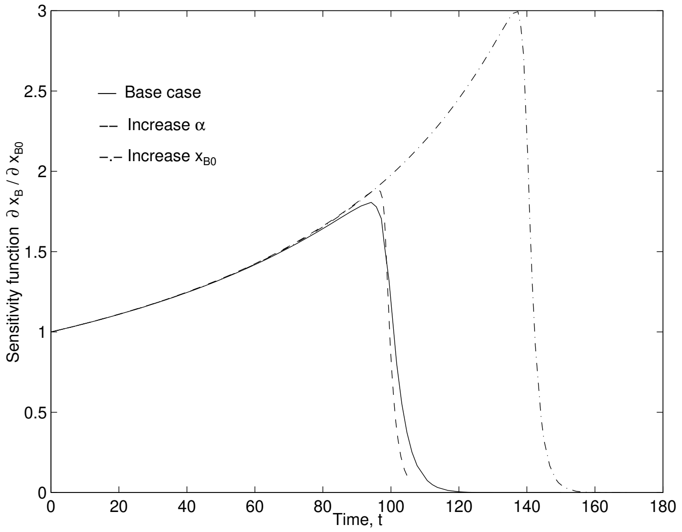


Figure 5: Sensitivity functions $\partial x_B/\partial x_{B0}$ for LV–configuration

4.2 L_wV-, $(L_w/V)V$- and $(L_w/D_w)V$- configurations

We consider here the case where the liquid flows are given on a mass rate basis, i.e., Lw and D_w in $[kg/min]$ (similar results are obtained if we instead consider volumetric flows). As mentioned above this is the typical case in industrial batch columns. For the case of the $(L_w/D_w)V$-configuration, the units for the flows are not important if both reflux and distillate flow are measured in the same units. Thus, the results presented in the previous section will apply also to the $(L_w/D_w)V$-configuration. However, as we shall see, the use of reflux on a mass rate basis has a strong impact on parametric sensitivity for the L_wV- and $(L_w/V)V$-configurations. Note that these two configurations are identical if we assume boilup V fixed.

The transformation between mass and molar reflux is given by

$$L = \frac{L_w}{M}, \quad M = y_D M_1 + (1 - y_D) M_2 \tag{24}$$

Here M_1 and M_2 denote the molar weight of the light and heavy component respectively. Note that the transformation is strongly nonlinear due to the dependence of the distillate composition y_D. For the case of continuous distillation, Jacobsen and Skogestad [6] have shown that the transformation even may become singular causing multiple steady state solutions and instability. Thus, we should expect the transformation (24) to have a significant impact also on the behavior of batch distillation columns.

The dynamic model is in this case the same as the one given in section 4.1 with the addition of equation (24). The Jacobian of the dynamic model linearized around a nominal trajectory now becomes

$$A(t) = \begin{pmatrix} 0 & \frac{L \frac{\partial y_D}{\partial x_B}(M_1 - M2)}{M} \\ \frac{V(y_B - x_B) - L(x_2 - x_B)}{H_B^2} & \frac{L(\frac{\partial x_2}{\partial x_B} - 1) - V(\frac{\partial y_B}{\partial x_B} - 1) + (x_2 - x_B) L \frac{M_2 - M_1}{M} \frac{\partial y_D}{\partial x_B}}{H_B} \end{pmatrix} \tag{25}$$

The analytical expressions for the eigenvalues becomes highly complex in this case and we therefore make use of the matrix properties **trace** and **determinant** of A, denoted tr$\mathbf{A}$ and det$\mathbf{A}$ respectively, in the following analysis. From the characteristic equation for the 2×2 case we may conveniently write the solution for the eigenvalues as

$$\lambda_{1,2} = \frac{\mathrm{tr}A \pm \sqrt{(\mathrm{tr}A)^2 - 4\det A}}{2} \tag{26}$$

We easily deduce from (26) that RHP eigenvalues occur for the cases where $\det A < 0$ or $\mathrm{tr}A > 0$.

Analytical Treatment. From the Jacobian $A(t)$ (25) we derive

$$\det\mathbf{A} = -\frac{[V(y_B - x_B) - L(x_2 - x_B)]\, L \frac{M_2 - M_1}{M} \frac{\partial y_D}{\partial x_B}}{H_B^2} \tag{27}$$

$$\mathrm{tr}\mathbf{A} = \frac{L(\frac{\partial x_2}{\partial x_B} - 1) - V(\frac{\partial y_B}{\partial x_B} - 1) + (x_2 - x_B) L \frac{M_2 - M_1}{M} \frac{\partial y_D}{\partial x_B}}{H_B} \tag{28}$$

The expression for the trace of A may be simplified to

$$\mathrm{tr}\mathbf{A} = \frac{(V - L)(1 - \frac{\partial y_D}{\partial x_B}) + (x_2 - x_B) L \frac{M_2 - M_1}{M} \frac{\partial y_D}{\partial x_B}}{H_B} \tag{29}$$

We first investigate the conditions for which $\det A < 0$. By examing the individual terms in (27) we make the following observations. Due to the second law of thermodynamics it is required that $\partial y_i/\partial x_i > 0$ for homogeneous mixtures (see e.g. Doherty and Perkins [5]), thus $\partial y_D/\partial x_B > 0$. Further we always require that $V - L = D > 0$, since the opposite implies a negative distillate stream or draining of the condenser. Since we also have that $y_B > x_2$, we derive the following necessary and sufficient condition for $\det A < 0$, i.e., the existence of one and only one RHP eigenvalue, from equation (27).

$$M_2 > M_1 \tag{30}$$

The molar weight of the heavy component (M_2) is for most separations carried out in industry larger than the molar weight of the light component. Hence for most industrial separations one should expect RHP eigenvalues, and therefore potentially exponential divergence of nearby trajectories, at all times t! Furthermore, this eigenvalue will in general be significantly larger than the eigenvalues found with molar flows in section 4.1.

We would now like to understand under which operating conditions we get the largest value of the positive eigenvalue. If $\det A$ decreases (becomes more negative) and $\mathrm{tr} A$ simultaneously increases then the RHP eigenvalue increases in magnitude. We find three conditions that has this effect

- Large internal flows L and V.
- Large difference between the molar weights.
- Large values of $\frac{\partial y_D}{\partial x_B}$, i.e., intermediate values of distillate composition y_D.

Given the results from the treatment above, we then turn to the case where $M_1 > M_2$. Separations of water and some organic liquids are examples of such mixtures. In this case we have that $\det A > 0$ for all t and hence either we have two RHP eigenvalues or we have two LHP eigenvalues. To study this closer we now focus on the condition $\mathrm{tr} A > 0$ for RHP eigenvalues. From equation (29) we note that

$$\mathrm{tr} A < \frac{(V-L)(1 - \frac{\partial y_D}{\partial x_B})}{H_B} \tag{31}$$

and thus, if $\mathrm{tr} A > 0$, we have that the maximum eigenvalue must be less than or equal to the maximum eigenvalue for the $(L/V)V$- and LV-configurations given by (20). Thus, in this case the use of mass flows should expectedly reduce the sensitivity compared to the case with molar flows, i.e., the mass flows have a stabilizing effect.

Numerical Results. The process data for the example column is given for the *base case* in table 1. To gain more insight into the conditions that favor sensitivity for operation with the L_wV– and $(L_w/V)V$–configurations, we again consider behaviour in the vicinity of $t \simeq t^*$ in some more detail. If the size of the intermediate cut is small, this implies that the distillate composition (y_D) remains close to one until it abruptly drops to virtually zero in a short period of time. Since the molar weight of the distillate stream is a unique function of the top composition (see equation (24), the size of the reflux (molar) stream will change as follows

$$
\begin{array}{ll}
t_0 \leq t \leq t^* & L \simeq L_1 = \frac{L_w}{M_1} \\
t^* \leq t \leq t^* + \Delta t & L_1 \leq L \leq L_2 = \frac{L_w}{M_2} \\
t^* + \Delta t \leq t \leq t_f & L \simeq L_2
\end{array}
\tag{32}
$$

As Δt decreases operation of the column with $L_w V$ configuration becomes essentially similar to the LV configuration except for the period of time denoted by Δt in Equation (32). L changes quite abruptly from $L \simeq L_1$ to $L \simeq L_2$ on a small interval (Δt) and this interval decreases as n increases. The nonlinear transformation between molar and mass reflux $L = L_w/M_w$ is thus close to singular, such that one might expect sensitivity to increase. On the other hand one must take into account that the effect of the transformation contributes on a decreasing interval such that the integral effect may decrease.

We consider the same case studies as reported for the LV–configuration, and the reflux is in this cas given by $L_w = 100\ [kg/min]$. In figure 6 we illustrate typical profiles for the distillate composition and the molar reflux. The dramatic changes that occur in the vicinity of t^* is quite clearly demonstrated. We see that L drops from $L \simeq 5$ to $L \simeq 2.5$ within a small region of operation such that (32) applies.

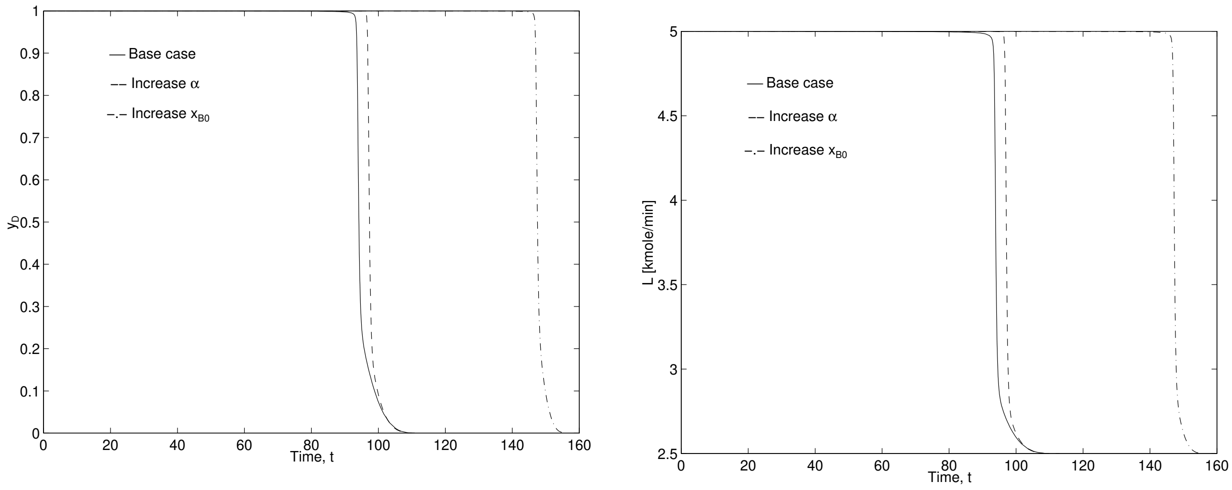


Figure 6: Distillate composition and molar reflux profiles for $L_w V$–configuration

Figure 7 a) shows that λ_{max} exhibits a considerable peak in the region where y_D drops, and we note that λ_{max} is significantly larger than with the (LV)–configuration. The peaks of the sensitivity functions are however not significantly larger. The reason is that we only consider the magnitude of the *absolute sensitivity*. If one alternatively computes the *scaled sensitivity*, which are obtained by introducing appropriate scaling, we demonstrate in our final example that the sensitivities are significantly larger. We also recognize the exponential growth of the sensitivity functions when $\lambda_{max} > 0$. This is taken as a partial confirmation of the connection between parametric sensitivity and occurrence of RHP eigenvalues.

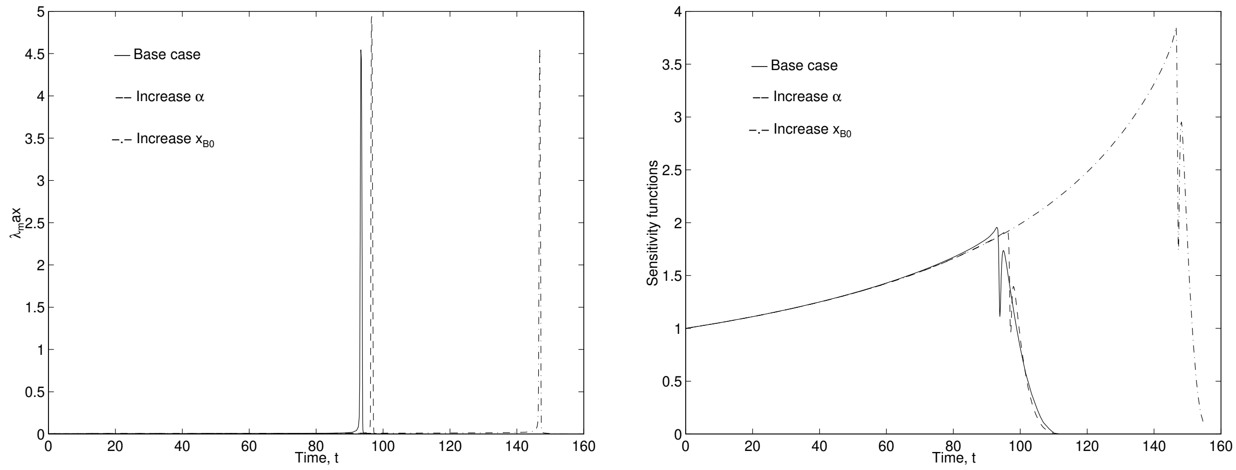


Figure 7: λ_{max} and sensitivity functions for L_w–configuration

4.3 Other Configurations

Among other possible configurations for column control we may consider the D_wV configuration. By following the treatment of the L_wV configuration, we find that conditions for sensitivity is in fact opposite to the L_wV case. Sensitivity is thus likely only for separations where $M_1 > M_2$. This result compares well to similar results on multiplicity for the continuous case (see Jacobsen and Skogestad [6] and [7]), where it is found that multiplicity with the D_wV configuration is unlikely. Sensitivity with the L_wV configuration may thus be avoided by changing condenser level control from using reflux L_w to distillate D_w.

5 Implications for Operation of Batch Columns

We have so far only considered the effect of perturbations in the initial states on one of the state variables, i.e. the composition of the reboiler. In practice, however, one is usually more concerned with other characteristics such as the distilllate composition x_D and the amount of accumulated distillate M_D. One should also consider the effect of changes in other parameters, such as mass reflux L_w. Even though parametric sensitivity may be independent of parameterisation [11], the magnitudes of the sensitivity functions may be different. The choice of operating strategy, that is the policy on how to stop the distillation of a cut, may also significantly influence the effect of small perturbations. In this section we provide results showing that small perturbations in the initial states and mass reflux may have dramatic effect on for instance the impurity in the accumulated distillate. We also demonstrate that greatest sensitivity is found if the distillation is stopped according to a given time.

Scaling of output variables. In order to make the variations in each output variable comparable, we introduce scaling as suggested by Skogestad and Morari [17]. Let x_D^* and x_B^* denote the nominal values for the accumulated distillate and reboiler composition. We use the following scaling

$$\Delta(1-x_D) = \frac{\delta(1-x_D)}{1-x_D^*}\frac{x_{B0}}{\delta x_{B0}} \tag{33}$$

$$\Delta x_B = \frac{\delta x_B}{x_B^*}\frac{x_{B0}}{\delta x_{B0}} \tag{34}$$

where $\delta(1-x_D) = x_D - x_D^*$ and $\delta x_B = x_B - x_B^*$ are deviations from nominal operation. This way we get percentage deviation in composition of impurity and reboiler composition for a 1% perturbation in x_{B0}. Note that the deviation for the distillate composition is, as for the reboiler composition, given in terms of the fraction of impurity.

5.1 Example column with tray holdups

In order to investigate an example of some industrial relevance, we looked at an example column where we also include holdups on all plates including the condenser. The process data given in table 2 are essentially the same as for the previous examples given in table 1, with a few minor changes in addition to including tray holdups. We may add the two specifications x_{Ds} and x_{Bs} since we have two degrees

Table 2: Process data for example column with holdups

Number of trays :	$N = 8$ + Total Condenser
Tray holdups :	$M_i = 0.1\ kmole$
Molar reflux :	$L = 4.1205\ [kmole/min]$
Mass reflux :	$L_w = 90.019\ [kg/min]$
Molar Boilup :	$V = 5\ [kmole/min]$
Relative volatility :	$\alpha = 3$
Molar weight of light component :	$M_1 = 20\ [kg/kmole]$
Molar weight of heavy component :	$M_1 = 40\ [kg/kmole]$
Initial composition in reboiler :	$x_{B0} = 0.5$
Initial amount in reboiler :	$H_{B0} = 100 kmoles$
Specifications :	$x_{Ds} = 0.98$
	$x_{Bs} = 0.05$

of freedom left, i.e. we may specify both the reflux policy and the final batch time for the separation. We will consider columns with molar boilup V and either molar or mass reflux as independent variables, i.e. $(L_w/V)V$– and $(L/V)V$–configuration.

From simulations we found that separation with constant $(L_w/V)V$ requires 70% longer batch time and 75% increase in energy consumption compared to operation with constant $(L/D)V$. The reason is that L decreases with time when $(L_w/V)V$ is constant, due to changes in composition. This is a non–optimal way of operating the column, since the ideal situation would be to *increase* the reflux at the end of the batch in order to improve the separation. In order to obtain both specifications on x_{Ds} and x_{Bs} the columns need to be operated under higher reflux during the production period, which off course increases both the time and energy to obtain the required specifications. As a comment to industrial operation of batch columns, this result actually means that for binary separations where $M_2 > M_1$, the optimal configuration for constant reflux will be the $(L_w/D_w)V-$ or the D_wV-configuration.

Nonlinear simulations. In tables 3 and 4 we give the scaled sensitivities Δx_B, ΔM_D and $\Delta(1-x_D)$ which are computed for two alternative operating strategies. We consider stopping the batch at a given time t_f or at a given composition on the top tray x_8. Sensitivities are computed for perturbations in x_{B0} and L_w. From the

Table 3: Scaled sensitivities for 1 % δx_{B0}

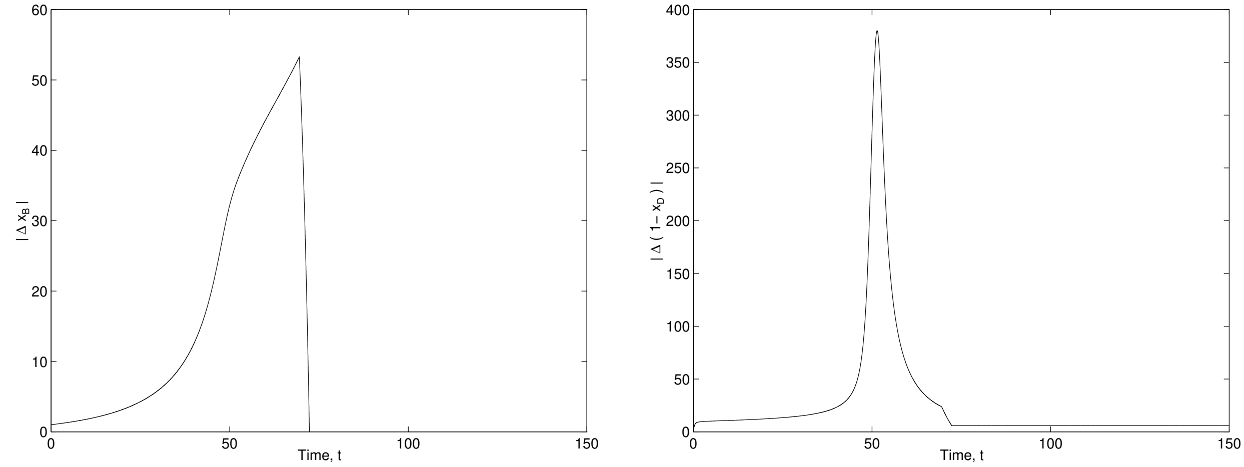
Stop at t_f	Δx_B	ΔM_D	$\Delta(1-x_D)$
LV	9.40	0.0	25.5
L_wV	16.90	4.4	206.0
Stop at x_8			
LV	0.10	1.0	2.1
L_wV	0.01	1.0	5.0

Table 4: Scaled sensitivities for 1% δL_w

Stop at t_f	Δx_B	ΔM_D	$\Delta(1-x_D)$
LV	32.7	4.44	124.6
L_wV	83.6	5.00	1317.0
Stop at x_8			
LV	5.2	0.13	7.5
L_wV	1.0	1.65	82.1

data in table 3 and 4 we see that the sensitivities decrease if the batch is stopped at a given composition. This is hardly surprising, and perhaps rather obvious. However stopping for a final composition requires an accurate and fast measurement, which only rarely is availiable. Reliable measurements in terms of GC"s typically have a delay of 15-15 minutes. In practice one would use a temperature measurement in the top of the column in order to estimate the compositions, or even better a cascade structure where both composition and temperature measurements are used. The results clearly demonstrates that very small changes in input specifications such as reflux, or changes in initial conditions may have a severe effect on the final products, e.g. distillate composition. Due to unavoidable measuring errors sensitivity will allways be present. It should be emphasized that uncertainty in the initial states is of special importance for batch processes that are operated within a chain of operations, which often is the case for batch columns.

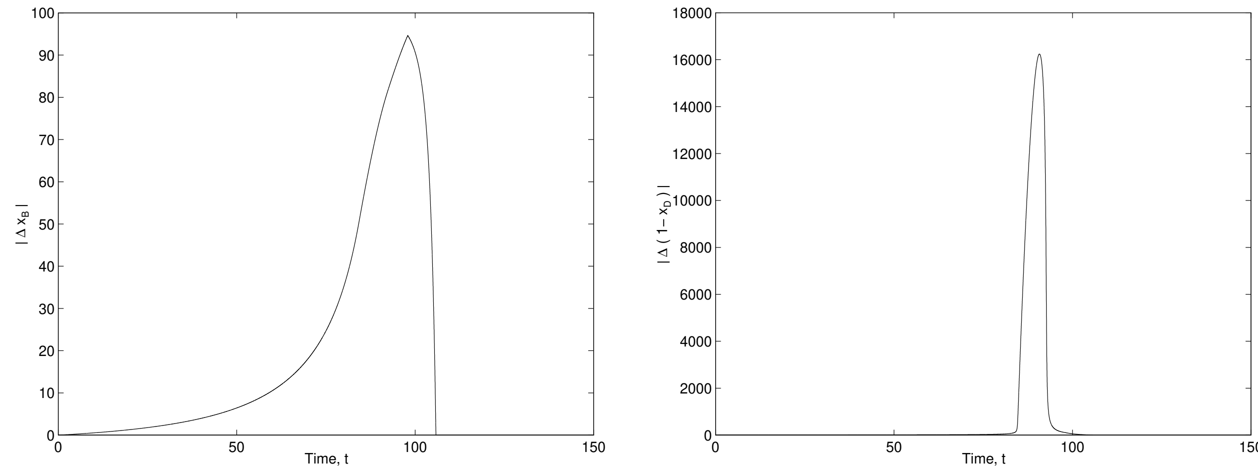
Figure 8 illustrates scaled sensitivities for a 1% perturbation in L for the $LV-$configuration, when the column is stopped at a given time. As can be seen from the plot,the sensitivities are large. Figure 9 shows in a similar fashion the scaled



(a) Scaled sensitivity for x_B (b) Scaled sensitivity for $1 - x_D$

Figure 8: Scaled sensitivity functions for example column with $LV-$configuration

sensitivities for the L_wV-configuration.



(a) Scaled sensitivity for x_B (b) Scaled sensitivity for $1 - x_D$

Figure 9: Scaled sensitivity functions for example column with L_wV-configuration

6 Conclusions

- Ideal binary batch columns may exhibit parametric sensitivity (PS), i.e. nominal trajectories are locally unstable

- PS is demonstrated even for columns with molar inputs, but the largest sensitivities are found in columns with mass inputs

- Evidence for sensitivity has been provided in terms of
  (1) analytical results (eigenvalues, λ)
  (2) numerical simulations

- We have demonstrated that occurrence of right half plane (RHP) λ normally serve as strong *indicators* of sensitivity, in that regions of sensitivity was enveloped by regions of RHP λ for all examples considered.

- Conditions that favor PS were found to be
  (1) Large relative volatilities
  (2) Large differences in molar weights
  (3) Large internal flows, i.e. L and V

- PS was shown to have greatest effect for columns operated with
  (1) L_wV- and $(L_w/V)V$-configurations.
  (2) Final time policy

- Implications for operation of batch columns was given, by considering nonlinear simulations of an example column

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