A NON-LINEAR WAVE MODEL WITH VARIABLE MOLAR FLOWS FOR DYNAMIC BEHAVIOUR AND DISTURBANCE PROPAGATION IN DISTILLATION COLUMNS

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A non-linear wave model for a distillation column has been extended and then examined for binary and ternary systems by including enthalpy and hold-up effects, these being significant for wide boilers and leading to variable molar flows and holdups. Application of the coherence condition to the system mass and energy balance equations confirms that, for an n-component system, any disturbance or eventual steady-state will be resolved into n-1 distinct, coherent waves (involving synchronized variations in composition, temperature, and flow-rate), provided that enthalpy and hold-up are made functions of composition. For *steady states*, the predictions of the wave-model and those of more rigorous plate-to-plate calculations show excellent agreement for the operating conditions required to obtain an optimal steady-state. In preliminary design calculations, the wave model thus quickly identifies an approximate, optimal steady state. For *disturbance propagation*, predictions of the wave model for the velocities of disturbance waves are in good agreement with those for the plate-to-plate model. For both models, "asymmetric dynamics" is predicted. The asymmetry is less than that predicted for a constant molar flow model; this agrees qualitatively with previous experimental results. In all cases, liquid and vapour flow variations across the waves are predicted correctly. When fully developed, wave theory can be used as a quick first step in design and optimisation, and its simplicity and speed offers good prospects for on-line control applications.

KEYWORDS: distillation dynamics, disturbance propagation, non-linear wave, variable molar flow, profile control

INTRODUCTION

Distillation columns producing high-purity products exhibit highly non-linear behaviour, particularly for wide boilers, leading to sharp composition and temperature profiles. Such behaviour is known to cause difficulties in column control and design. In particular, non-linear dynamic phenomena arise, such as high steady-state gains and large response lags, and the dependence of these on disturbances. Often, the transition in departing from a steady state is much faster than the return to it. This "asymmetric dynamics" implies desirable steady states are intrinsically difficult to control and maintain.

Wave theory, originally developed as a framework for the analysis of chromatography and ion-exchange [7], analyzes steady-state and dynamic composition variations

in a column in terms of "waves". Viewing the movement of the composition and temperature profiles as the propagation of such non-linear waves provides a much simpler, but nonetheless powerful, model for the dynamics, and an intuitive cause-and-effect analysis of the non-linear phenomena. Such an approach, developed by Hwang, Helfferich and Hankins [1,2], has already been applied successfully to fixed-bed processes and to continuous counter-current separation processes. It elucidates the development of "constant pattern waves" (ones that maintain a constant size and shape) governed by phase equilibrium, and their development into "standing waves" for the steady-state profiles as a result of their interaction with column ends. The propagation of feed disturbances on non-uniform, steady-state backgrounds, their interference, and the phenomenon of asymmetric dynamics has also been analysed [2] for both binary and multi-component distillation.

The wave analysis reveals that a multi-component column, when operated continuously at steady state, contains a set of standing (stationary) waves. These waves are separated by zones with negligible composition variation (i.e. pinched zones), and may sit balanced within the column (i.e. key waves) or sit bunched up near a column end. Any disturbance at the entry to such a column results in the triggering of a set of response waves. These waves travel and interfere with the standing waves of the stationary state.

In principle, the standing waves may be self-sharpening or non-sharpening, depending on phase equilibrium properties. Distillation systems almost always involve a marked relative volatility between components, analogous to a convex adsorption isotherm, and this leads to self-sharpening waves. On the other hand, disturbance waves normally involve small deviations and can be approximated as steps; they are indifferent to sharpening properties, but travel over a strongly non-uniform and nonlinear background of the steady-state pattern of standing waves. Ultimately, they may interfere with the key-wave, causing it to unbalance. This, in turn, leads to a highly non-linear response in column end conditions and thus product compositions.

Earlier theoretical work [3–6] on the steady-state and dynamic behaviour of continuous, counter-current distillation processes in single section operations is specifically extended here to include enthalpy effects, leading to non-constant molar flow rates and column hold ups, and reflux and reboil. It represents a further step towards the use of wave theory for improvements in the design, optimisation and control of multi-component fractionation columns, especially for wide boilers displaying highly non-linear behaviour.

THEORETICAL DEVELOPMENT

A differential model is developed here for a packed-bed distillation column, tuning the mass transfer parameters to select the theoretical number of plates. Such a model is well suited to a direct comparison with the wave theory, whilst retaining sufficient rigour to be realistic. For clarity, a single rectifying or stripping section of a distillation column is considered, and local thermal equilibrium is assumed.

EQUATIONS FOR PLATE DISTILLATION MODEL

The overall material balance for the liquid and vapour phases within the column is:

$$\frac{\partial W}{\partial t} + \frac{\partial U}{\partial t} - \frac{\partial L}{\partial z} + \frac{\partial V}{\partial z} = 0 \tag{1}$$

whilst a material balance for component i of n is:

$$\frac{\partial(Wx_i)}{\partial t} + \frac{\partial(Uy_i)}{\partial t} - \frac{\partial(Lx_i)}{\partial z} + \frac{\partial(Vy_i)}{\partial z} = 0 \qquad i = 1, n-1 \tag{2}$$

where t is time; z is the distance (related to the number of plates) from the top; L and V are the liquid and vapour molar flow rates per unit cross-sectional area; W and U are the liquid and vapour molar hold-ups per unit length (or per plate); and x_i and y_i are the liquid and vapour mole fractions of component i. The overall enthalpy balance governs changes in the molar flows:

$$\frac{\partial(WH_{liq})}{\partial t} + \frac{\partial(UH_{vap})}{\partial t} - \frac{\partial(LH_{liq})}{\partial z} + \frac{\partial(VH_{vap})}{\partial z} = 0 \tag{3}$$

where H_{liq} and H_{vap} refer to the molar enthalpies of liquid and vapour phases, respectively. A material balance for component i in the vapour phase is:

$$\frac{\partial(Uy_i)}{\partial t} + \frac{\partial(Vy_i)}{\partial z} = k_i a[f_i(x_1, x_2, \ldots, x_n) - y_i] \qquad i = 1, n \tag{4}$$

where $k_i a$ is a mass-transfer coefficient for i, and the driving force for mass transfer is taken to be the departure from equilibrium in the vapour phase i.e. it is liquid-film limited. The number of theoretical plates in the column is then $N = k_i a\, z_{col}/V$, where z_{col} is column length.

Note also that:

$$\sum_{i=1}^{n} y_i = 1 \text{ and } \sum_{i=1}^{n} x_i = 1 \text{ and that } H_{liq} = T_{liq} \sum_{i=1}^{n} (C_{pi})_{liq} x_i \tag{5a,b,c}$$

while

$$H_{vap} = \sum_{i=1}^{n} (\Delta H_i)_{vap,Tref} y_i + T_{ref} \sum_{i=1}^{n} (C_{pi})_{liq} y_i + (T_{vap} - T_{ref}) \sum_{i=1}^{n} (C_{pi})_{vap} y_i \tag{5d}$$

The volumes of liquid and gas phase hold-up per unit column volume and the liquid partial molar volumes are assumed to be constant; the gas is assumed to be ideal. Thus:

$$W = \frac{W_v}{\sum_{i=1}^{n} \bar{v}_i x_i} \quad \text{and} \quad U = \frac{PU_v}{R(T_{vap} + 273)} \tag{6a,b}$$

where T_{liq} and T_{vap} are liquid and vapour temperatures in $^\circ$C, T_{ref} is the reference temperature for the molar heat of vaporisation $(\Delta H_i)_{vap}$, $(C_{pi})_{liq}$ and $(C_{pi})_{vapi}$ are liquid and vapour molar heat capacities for i, W_v and U_v are the liquid and gas hold-up volumes per unit column volume, $\bar{v}_i$ is the liquid partial molar volume of i, P is pressure and R is the universal gas constant. Local thermal equilibrium ($T_{liq} = T_{vap} = T$) is assumed.

Thus, for given z, there are $2n + 3$ independent equations (1–4) and (5a,b) for the $2n + 3$ unknowns L,V,$x_1, \ldots, x_n, \ldots, y_1, \ldots, y_n$ and T. For a single section, boundary conditions are set by feed composition and rate at one end, and the reflux or reboil condition at the other.

WAVE MODEL

For the purposes of the wave model, local phase and local thermal equilibrium are assumed, reducing the number of variables to $n + 3$. To begin with, a binary system is considered. The equilibrium phase rule then implies that vapour composition, liquid and vapour enthalpies (with $T_{liq} = T_{vap} = T$), and phase molar holdups (under the assumptions of (5) and (6)) are all functions of liquid phase composition x. This means that the partial derivatives with respect to time in equations (1), (2) and (3) can all be collected on the right-hand side in the form $R_j \, \partial x/\partial t$ for equation j, where R_j is a function of x.

The important condition of coherence is now invoked: all systems tend to shake themselves down into simple modes, independent of initial conditions. For a full discussion of coherence, see [1–7]. At any point in a coherent wave, the propagation velocities for all variables are equal. Thus variations, or waves, of temperature, composition and flow-rate move and remain together relative to each other in a synchronized fashion. At a given point and time, the velocity of the set of synchronized variables on such a wave moves at a local wave velocity v_λ given by:

$$v_\lambda = \left.\frac{\partial z}{\partial t}\right|_{\alpha_i} = \lambda \frac{L}{W} \tag{7}$$

where α_i is one of the coherent variables, and λ is the local eigenvalue associated with the wave. Writing an expression for the total differential of α_I with respect to z and t, and taking the derivative under conditions of coherence and tracking of α_i (i.e. $d\alpha_I = 0$) and finally substituting (7):

$$\frac{\partial \alpha_i}{\partial z} \lambda \frac{L}{W} = -\frac{\partial \alpha_i}{\partial t} \tag{8}$$

This can be applied to $\partial x/\partial t$ in equations (1) to (3) and the whole set of equations rewritten, under conditions of coherence, in matrix form as follows:

$$
\begin{bmatrix}
-1 & 1 & R_1 \frac{L}{W}\lambda \\
-x & y & (R_1 \frac{L}{W}\lambda - L + Vy') \\
-H_L & H_V & (R_3 \frac{L}{W}\lambda - LH'_L + VH'_V)
\end{bmatrix}
\begin{bmatrix}
dL \\
dV \\
dx
\end{bmatrix} = 0
\tag{9}
$$

Here, a dash indicates differentiation with respect to x. Solving for a zero determinant, it is readily apparent that a linear equation for the eigenvalue λ is obtained, which yields:

$$
\lambda = \frac{(Vy' - L)(H_L - H_V) + (VH'_V - LH'_L)(y - x)}{\frac{L}{W}\{R_1(H_L y - H_V x) - R_2(H_L - H_v) + R_3(x - y)\}}
\tag{10}
$$

The existence of a single eigenvalue demonstrates that the system is monovariant, such that any disturbance or eventual steady-state will be resolved into a single wave. This wave will be a synchronized variation of L,V and x. The resulting eigen-vector or so-called "composition route," i.e. dL/dx and dV/dx, is obtained by re-substituting (1) into (9). In the case of constant relative volatility, by analogy with wave theory for fixed bed processes [7], the wave is expected to be a self-sharpening shock wave [3,6] (see also below). If the assumption of local composition equilibrium is relaxed by (4), a constant pattern wave is still expected, over which any disturbances will propagate with velocityλ. However, the natural velocity of a sharp, constant pattern wave in the column under conditions of coherence is derived from integral material balances and an energy balance. For binary systems, three such equations may be written, according to equations (1) to (3):

$$
u_\Delta \equiv \left[\frac{dz}{dt}\right]_{wave} = \frac{\Delta(L - V)}{\Delta(W + U)} = \frac{\Delta(Lx_i - Vy_i)}{\Delta(Wx_i + Uy_i)} = \frac{\Delta(LH_L - VH_V)}{\Delta(WH_L + UH_V)}
\tag{11}
$$

where Δ indicates difference across the wave. This wave will be coherent with respect to variations in L,V and x. Given a feed rate & composition at one end, and reflux or reboil conditions at the other, simultaneous solution yields the wave velocity and the values of the six key variables on either side of the wave. For an optimum design and operation, this wave sits balanced deep within the column at zero velocity. Movement of this constant pattern wave to either end tends to lower product purity at that end.

For ternary and n-component systems, there will be n − 1 independent terms associated with each $\partial x_i/\partial t$ in equations (1) to (3); following substitution of equation (8), the resulting matrix equation in (9) now has order n + 1. The equivalent of equation (10) will have n − 1 eigenvalues, and the system therefore has a variance n − 1. Hence, the variance is not increased by the enthalpy terms (and hence varying molar flows), or by varying holdups (note that if the assumption of liquid holdup being dependent only on composition is relaxed in equation (6) to include a liquid-flow dependence (through plate hydraulics), then the system variance will increase by one). For a ternary system,

there will be two such waves; the corresponding constant pattern waves of the steady-state require the simultaneous solution of three integral material balances (one overall and two for components) and one energy balance. At most, one of these waves will have zero velocity, and optimum design and operation will aim to place this "key wave" deep within the column, and thereby ensure key components lie below product specifications at the column ends.

PERFORMANCE OF WAVE MODEL
The wave model can now be tested by solving equations (9–11) and comparing its predictions with that of the plate model. For this, equations (1–6) are solved using the Numerical Method of Lines. Spatial derivatives are evaluated using a first-order upwind/downwind finite difference approximation in (1–4); temporal derivatives ($\partial x_i/\partial t$ and $\partial y_i/\partial t$) are evaluated by simultaneous solution of (2) and (4). The latter are integrated using a 4-step, 4th order Runge-Kutta scheme; at each step in the integration, the new values of L(z) and V(z) are calculated by solving the discretized set of equations (1) and (3) with the current values of x_i, y_i, $\partial x_i/\partial t$ and $\partial y_i/\partial t$. Parameters used for the binary and ternary systems studied are shown in Table 1.

STEADY-STATE CONDITIONS
Consider distillation of the binary system in Table 1 (methanol and 1-propanol) in a 1-metre rectifying section, with a saturated vapour feed of $0.1 \ kmol/m^2 \cdot$ sec, a total condenser and a reflux ratio of 1.2. Solution of wave equations (11) with u_Δ set to zero predicts that a feed vapour mole fraction y for 1-propanol of 0.658 is required for a balanced wave and an optimal steady-state. Figure 1 presents the results of the plate model under these conditions, for varying plate number (after large time; feed end at z = 1.0). The composition profile remains stationary, and sharpens with more plates; the wave model (which assumes local equilibrium) predicts a standing-step wave from y = 0.658 to y = 1.0. The final position of the wave is determined by the column end-effects; as the ends are

Table 1. Component physical properties

Property	Methanol (i = 1)	1-Propanol (i = 2)	1-Pentanol (i = 3)
$(Cp)_{liq,i}$ (J/mol °K)	81.59	144.4	209.0
$(Cp)_{vap,i}$ (J/mol °K)	43.93	87.45	140.0
$(\Delta H)_{vap,I}$ (kJ/mol)	37.57	45.0	52.3
Boiling Point, °C	65.2	97.4	137.3
Relative volatility with methanol	1.0	3.8 (binary mix) 3.45 (ternary mix)	15.87 (ternary mix)
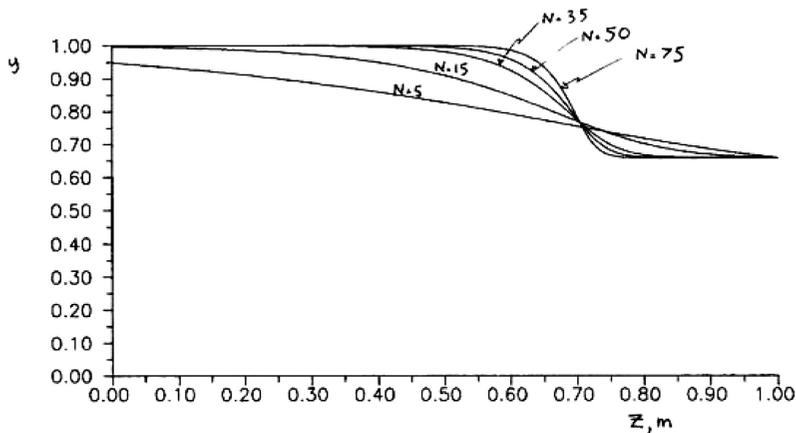
Figure 1. Plate-model prediction of optimal steady-state with varying plate number

not perfectly pinched (e.g. see z = 0 for N = 5), mass transfer effects tend to push the wave back inside. Furthermore, vapour rate and liquid rate are predicted to increase by 7 and 13% respectively across the wave, in excellent agreement with the plate model. In preliminary design calculations, the comparative simplicity of the wave model thus allows the identification of an approximate optimal state with relatively little effort.

DISTURBANCE PROPAGATION

The optimal steady-state identified in Figure 1 is now subjected to two feed composition disturbances. In the first, feed mole fraction decreases by 0.05; in the second, it increases by 0.05 back to the original value. The wave model prediction of the system response is shown schematically in Figure 2. The predictions of the plate model (N = 15) are shown in Figures 3a and b. Following the first feed disturbance, a disturbance wave propagates in Figure 2 (t = t_1) at velocity u_{dist}, given by equations (7) and (11), of −0.0954 m/s. In Figure 3a, the initial disturbance moves at velocity −0.05 to 0.15 m/s (exact value rather uncertain) to merge with the original optimal steady-state, and creates an unbalanced constant pattern key wave within 1 second. According to equation (11), the unbalanced key wave in Figure 2 (t = t_2) then moves to the left with velocity −0.004 m/s; the constant-pattern key wave in Figure 3a initially moves to the left at a velocity of −0.004 m/s. However, at 60 secs the constant pattern key wave slows down as it approaches the product (reflux) end of the column, and at 200 secs it is virtually stationary. In essence, the convective forces which move the unbalanced wave to the left are balanced by the column end-effect moving it back to the right: top product purity has dropped to y = x = 0.95, creating a non-equilibrium mass-transfer driving force. The original feed

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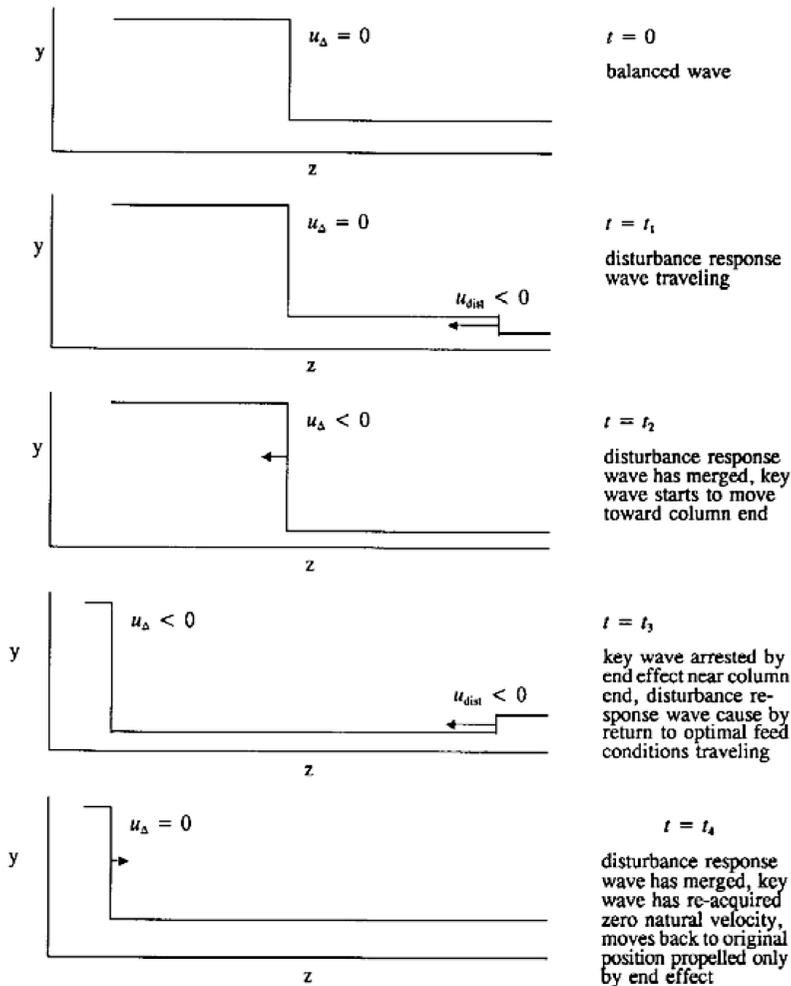
Figure 2. Departure from and return to optimal steady state due to disturbance in binary system

condition is then restored in Figure 2 (t = t$_3$), triggering a new disturbance wave with a velocity u$_{dist}$, given by equations (7) and (11), of -0.0949 m/s. In Figure 3b, the new disturbance propagates at a velocity -0.07 to -0.1 m/s (exact value rather uncertain) to merge with the key wave currently residing near the column top, and creates a balanced, zero natural velocity wave within 5 or so seconds (Figure 2, t = t$_4$). This new constant
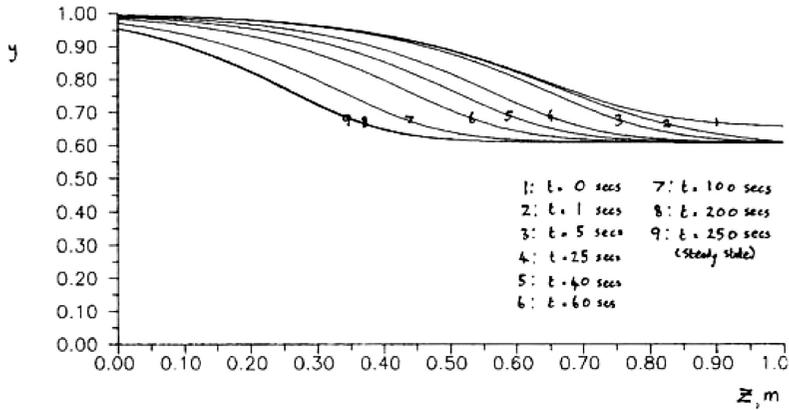
Figure 3a. Departure from optimal state: yf_{eed} decreases from 0.658 to 0.608

pattern key wave in Figure 3b initially moves to the right at 0.004 m/s under the unbalanced, column top end effect (this is reasonable, since the convective driving force in Figure 2, t = t_2 to t_3, is equivalent to a similar key wave velocity to the left). However, this wave soon slows down as it moves away from the top end. By 70 secs, the velocity has slowed to 0.001 m/s and by 200 secs to 0.0004 m/s. The original, optimal steady-state is not reached until after 900 seconds. Finally, it is again noted that the wave model predicts changes in molar flows around the key wave similar to those seen above
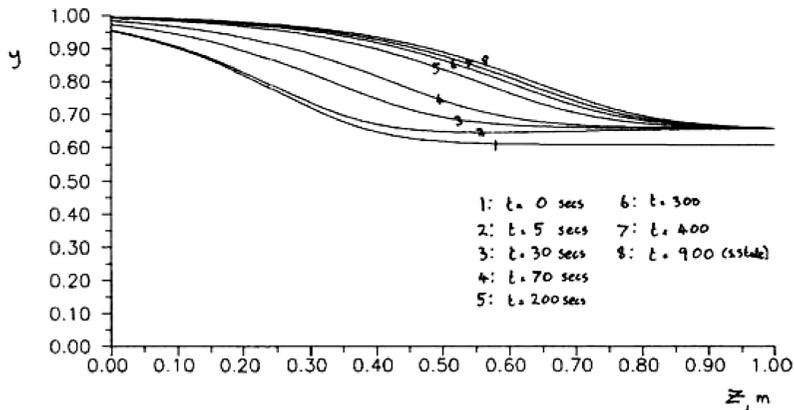
Figure 3b. Return to optimal state: yf_{eed} decreases from 0.608 to 0.658

for the balanced case (Figure 1), which is confirmed by the plate model predictions. The shift of molar flow profiles is also synchronized to those of the composition profiles, as expected above from coherence theory. In summary, the wave model is able to give a reasonably accurate quantitative prediction of the column dynamic response to disturb-ance propagation, with the exception that (as a consequence of assuming local equili-brium) it is unable to predict the velocity of return of the key wave to an optimal steady-state once it has been restored. It seems likely, however, that a constant pattern assumption can provide a means of predicting it, as suggested already for constant molar flow [8] and subsequently demonstrated experimentally [9].

The study of dynamic behaviour in Figures 2 and 3 highlights some important aspects of non-linear behaviour. First of all, it is apparent that small disturbances lead to high steady-state gains. A sensor placed in the middle of the column ($z = 0.5$ m) will first see a decrease in vapour mole fraction from 0.92 to 0.62 and then an increase back to 0.92. For a disturbance of ± 0.05, this represents a gain of 6. The gain increases further for a larger number of plates. Second, despite the restoration of the optimal feed condition in Figures 2 ($t = t_3$) and 3b, the time required to achieve the optimal steady-state of a key wave deep within the column is large. Thirdly, and as a consequence, the dynamic response to equal and opposite feed disturbances (in this case, of feed compo-sition) leads to a large asymmetry in response time – in this case, a factor of 5. Indeed, if constant molar flow is assumed, calculations show that the asymmetry factor increases further. This latter observation may help to explain why the asymmetry seems to be smaller in real experiments than predicted from constant flow models [9]. All of these effects are exacerbated as either the relative volatility (separation factor) or the number of plates (mass transfer efficiency) increases. This, in turn, suggests a way for improving on-line column control for such non-linear systems. A possible strategy might be based on profile control, where compositions are monitored in strategic positions. Furthermore, response time and asymmetry can be reduced if control can be made proactive rather than reactive; in this case, by reducing vapour feed rate in Figures 2 ($t = t_4$) and 3b in order to unbalance the re-established key wave long enough for it to occupy its optimal position.

TERNARY SYSTEMS
For a ternary system, the three equations in (11), along with an additional component material balance, were solved simultaneously for arbitrary feed and reflux conditions and confirmed composition routes as invariant.

CONCLUSIONS
- A non-linear wave model for a multi-component distillation column has been extended to wide boilers by including enthalpy and hold-up effects, which lead to variable molar flows and hold-up. Application of the coherence condition shows that, for an n-component system, the system variance is n − 1 in the absence of hydraulic effects.

Thus, composition, temperature and molar flow profiles move together in a synchronized fashion.

● A steady-state will consist of n − 1 constant pattern, standing waves, of which at most one will be a balanced key wave. For the conditions required for optimal steady-states, the predictions of the wave model agree with those for plate-to-plate calculations. This is highly useful in preliminary design.

● For wave propagation, predictions of the wave model for the dynamic response to feed disturbances are in good agreement with those of the plate-to-plate model, and demonstrate the high steady-state gains, large response times and asymmetry expected for non-linear systems, though the latter is less than calculated for constant molar flow. The simplicity, calculative speed and intuitive-predictive power of non-linear wave theory appears to offer a promising basis for both preliminary design and for on-line control.

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