CALCULATION OF MASS TRANSFER IN A BACK-FLOW MODEL WITH NON-LINEAR EQUILIBRIUM AND VARIABLE BACK-FLOW

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If material balances are taken around each nth stage and around the first n stages in a N-stage cascade, a set of N linear and N nonlinear equations with $2N$ concentration variables is obtained. On substitution of the general solution of the linear equations into the nonlinear ones the resulting set of N nonlinear equations is solved by an iteration method using linear programming technique.

There are two models commonly used for the description of flow of phases in a countercurrent equipment: the so-called diffusion model suitable for differential contact equipment and so-called back-flow model suitable for stage equipment.

If the equilibrium relationship is linear, the solution of mass transfer problem in either of these models can be expressed in analytical forms, which are summarized in a paper of Hartland and Mecklenburgh[1]. As far as more general cases are concerned, several numerical methods for the solution of mass transfer in the back-flow model are available. The simple boundary iteration method consists of guessing the concentrations in both phases at one end of the contactor and calculating the concentration profile from stage to stage to the other end of the contactor. A new guess of the initial values must be made and the calculation repeated until the boundary conditions are satisfied. Mecklenburgh and Hartland[2] have shown that, because of its instability, this method is reliable only when the back-mixing is high in one phase or completely absent from one phase. The mentioned authors proposed the so-called unsteady state procedure consisting of formulating this problem in unsteady state and integrating the resulting differential equations with respect to time until the profiles become steady. This procedure requires minimum amount of computer storage but tends to converge slowly if high accuracy is required.

By writing material balance equations of each stage of a N-stage cascade for feed and solvent phase separately, a set of $2N$ nonlinear equations is obtained. Procházka and Landau[3] derived expressions for the coefficients of the system matrix using the concept of stage efficiency. In general case of nonlinear equilibrium, these coefficients are dependent on the concentration profiles and hence an iteration procedure is needed. McSwain and Durbin[4] have formulated the expressions for the variable coefficients of the resulting quidiagonal matrix system by means of the defined curvarature of the equilibrium relationship. Using the modified Newton-Raphson technique combined with Gaussian elimination procedure for matrix inversion, they have achieved a satisfactory convergence of the solution.

The presented method is based on the solution of N nonlinear equations by means of iterative linear programming technique. The reduced set of N nonlinear equations

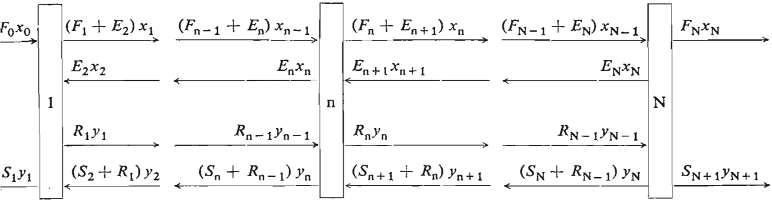

FIG. 1. Model of Countercurrent Cascade with Back-Flows

is obtained after the elimination of N concentration variables from the set of $2N$ properly formulated material balance equations.

Formulation of Material Balances

Schematic representation of the back-flow model with variable flow of phases and variable back-flow is shown in Fig. 1. The solute material balance of the feed phase in n^{th} stage of the N stage cascade is expressed by the following equation:

$$\left(F_{n-1} + E_n\right)x_{n-1} - \left(F_n + E_n + E_{n+1}\right)x_n + E_{n+1}x_{n+1} = KaV\left(x_n - x_n^+\right). \quad (1)$$

Taking the material balance so that its envelope encloses the x-phase inlet and cuts between stage n and $n + 1$, we get

$$F_0x_0 + E_{n+1}x_{n+1} - \left(F_n + E_{n+1}\right)x_n - S_1y_1 - R_ny_n + \left(S_{n+1} + R_n\right)y_{n+1} = 0\,, \quad (2)$$

where x_0 and y_{N+1} are known inlet concentrations. Eqs (1) and (2) are applied for each stage including both end stages of the cascade with respect to the boundary conditions

$$E_1 = E_{N+1} = R_0 = R_N = 0\,. \quad (3)$$

In case of constant flows of phases, when

$$F_n = F = \text{const.}\,, \quad S_n = S = \text{const.}\,, \quad F/S = Q\,, \quad (4)-(6)$$

we define the back-flow coefficients

$$f_n = E_n/F\,, \quad (7)$$

$$s_n = R_n/S\,, \quad (8)$$

and the mass transfer number

$$t = KaV/F\,. \tag{9}$$

Using dimensionless concentration variables

$$X_n = x_n/x_0\,, \quad Y_n = y_n/x_0 \qquad (10), (11)$$

we can rearrange Eqs (*1*), (*2*) and (*3*) into

$$(1 + f_n)\,X_{n-1} - (1 + f_n + f_{n+1})\,X_n + f_{n+1}X_{n+1} - t(X_n - X_n^+) = 0\,, \tag{12}$$

$$1 + f_{n+1}X_{n+1} - (1 + f_{n+1})\,X_n - (1/Q)\,Y_1 - (s_n/Q)\,Y_n + (1/Q)(1 + s_n)\,Y_{n+1} = 0\,, \tag{13}$$

$$f_1 = f_{N+1} = s_0 = s_N = 0\,. \tag{14}$$

Calculation Procedure

As it is apparent from Eqs (*12*) and (*13*), this way of formulating material balances leads to a set of $2N$ equations, from which N are nonlinear of the type (*12*) and N linear of the type (*13*). The set of N linear equations may be solved generally with respect to X_n, which results in

$$X_n = \sum_{k=n}^{N} A_{n,k}U_k\,, \tag{15}$$

where

$$U_k = (1/Q)\,[s_kY_k - (1 + s_k)\,Y_{k+1} + Y_1] - 1 \tag{16}$$

and

$$A_{n,n} = -(1/1 + f_{n+1}) \tag{17}$$

$$A_{n,k} = A_{n,n} \prod_{m=n+1}^{k} (f_m/1 + f_{m+1})\,, \quad k = n + 1, n + 2, \ldots N, n = 1, 2, \ldots N\,. \tag{18}$$

On substitution of expressions (*15*) into Eq. (*12*) we get the set of nonlinear equations

$$F_n(\mathbf{Y}) \equiv Y_1 + QX_n^+(Y_n) + \sum_{k=n-1}^{N+1} C_kY_k - Q = 0\,, \tag{19}$$

where

$$C_{n-1} = -\frac{s_{n-1}}{t},$$

$$C_n = \frac{1 + s_{n-1}}{t} + \frac{1 + t + f_{n+1}}{1 + f_{n+1}} \frac{s_n}{t},$$

$$C_{n+1} = -\frac{1}{1 + f_{n+1}}\left(1 + s_n - \frac{f_{n+1}}{1 + f_{n+2}} s_{n+1}\right) - \frac{1 + s_n}{t},$$

$$C_k = A_{n,k-1}\left(1 + s_{k-1} - \frac{f_k}{1 + f_{k+1}} s_k\right) \quad \text{for} \quad k > n + 1,$$

$$f_k = 0 \quad \text{for} \quad k > N \quad \text{and} \quad k = 1\,; \quad s_k = 0 \quad \text{for} \quad k \geqq N \quad \text{and} \quad k = 0\,.$$

$\bar{\mathbf{Y}}$ denotes here a vector $(Y_1, Y_2, \ldots Y_N)$.

If the equilibrium relationship is expressed as

$$x_n^+(y_n) = by_n + cy_n^2\,, \quad \text{resp.} \quad X_n^+(Y_n) = bY_n + cx_0Y_n^2\,. \tag{20}$$

Eq. (*19*) takes the form

$$F_n(\bar{\mathbf{Y}}) \equiv Y_1 + QbY_n + QBY_n^2 + \sum_{k=n-1}^{N+1} C_kY_k - Q = 0\,, \tag{19'}$$

where $B = cx_0$.

Values of Y_n giving the concentration profiles in the solvent phase are obtained by the solution of the set of equations (*19*) or (*19'*). Knowing the end concentrations Y_1, Y_{N+1}, we can calculate X_N from the relation

$$X_N = 1 - (1/Q)(Y_1 - Y_{N+1})\,. \tag{21}$$

The concentration profile in the feed phase can then be determined from Eqs (*15*)–(*18*).

The whole problem is thus reduced to the solution of the set of nonlinear equations (*19*) or (*19'*). From the point of convergency, it has proved convenient to apply the method published previously[5], which uses the linear programming technique, for this purpose.

The calculation procedure can be summarized as follows:

A. Given N, Q, Y_{N+1}, f_n ($n = 2, 3, \ldots N$), s_n ($n = 1, 2, \ldots N - 1$), t, $X^+ = X^+(Y)$, δ

B. Find the starting approximation of $\overline{Y}$ from

$$Y^{(o)}_{n} = Q - (Q - Y_{N+1})\frac{n-1}{N} \tag{22}$$

and let $\overline{\mathbf{Y}} = \overline{\mathbf{Y}}^{(0)}$

C. Calculate $F_n(\overline{\mathbf{Y}})$ from Eq. (*19*) or (*19'*). Denote all those functions $F_n(\overline{\mathbf{Y}})$, for which

$$|F_n(\overline{\mathbf{Y}})| < \delta$$

(if any) as $F_r(\overline{\mathbf{Y}})$, ($r = r_1, r_2, \dots r_\omega$; $1 \leqq \omega \leqq N$) and all those functions $F_n(\overline{\mathbf{Y}})$, for which

$$|F_n(\overline{\mathbf{Y}})| \geqq \delta$$

as $F_s(\overline{\mathbf{Y}})$ ($s = s_1, s_2, \dots s_\beta$; $1 \leqq \beta \leqq N$; $\beta + \omega = N$). Choose as $F_\alpha(\overline{\mathbf{Y}})$ one function of all $F_s(\overline{\mathbf{Y}})$ which satisfies the condition

$$|F_\alpha(\overline{\mathbf{Y}})| = \min_{s} [|F_s(\overline{\mathbf{Y}})|] . \tag{23}$$

D. Solve the LP problem: Find values of vector $\overline{\mathbf{g}}\,(g_1, g_2, \dots g_N)$ which yields minimum of the function*

$$u = \text{sign}\left[g_1 + Q\frac{\mathrm{d}X^+_\alpha(Y_\alpha)}{\mathrm{d}Y_\alpha}g_\alpha + \sum_{k=\alpha-1}^{N} C_k g_k\right]$$

(take sign + if $F_\alpha(\overline{\mathbf{Y}}) > 0$
and sign − if $F_\alpha(\overline{\mathbf{Y}}) < 0$)
at the restrictions

$$|g_j| \leqq 1 \quad j = 1, 2, \dots N\,^{**}$$

and

$$g_1 + Q\frac{\mathrm{d}X^+_r(Y_r)}{\mathrm{d}Y_r}g_r + \sum_{k=r-1}^{N} C_k g_k = 0\,^{*}$$

$r = r_1, r_2, \dots r_\omega$; $1 \leqq \omega < N$
(if any, *i.e.* if $\omega < 0$).

* The general form of the functions chosen for the solution of the LP-problem is derived from the functions $F_n(\overline{\mathbf{Y}}) = 0$ as

$$f_n'(\overline{\mathbf{Y}}) \equiv g_1 + Q\frac{\mathrm{d}X^+_n(Y_n)}{\mathrm{d}Y_n}g_n + \sum_{k=n-1}^{N} C_k g_k = 0 .$$

** In the computing program the substitution

$$g_j' = g_j + 1\,; \quad j = 1, 2, \dots N$$

is used.
That leads to the restrictions

$$g_j' \geqq \quad \text{and} \quad g_j' \leqq 2\,,$$

which are more convenient for computations than the restrictions $|g_j| \leqq 1$ mentioned above.

E. Determine the least root $t > 0$ of the equation

$$F_\alpha(\overline{\mathbf{Y}} + \overline{\mathbf{g}}t) = 0\,.$$

F. Calculate the new values of variables

$$Y'_n = Y_n + g_n t\,.$$

G. Let $\overline{\mathbf{Y}} = \overline{\mathbf{Y}}'(Y'_1, Y'_2, \ldots Y'_N)$, return to *C.* and stop the calculation if $|F_n(\overline{\mathbf{Y}})| < \delta$ for all n, *i.e.* $\omega = N$. The calculation of the X-profile by the Eqs (*15*)—(*18*) follows.

EXAMPLE

A. $N = 4$; $Q = 0{\cdot}4$; $x_0 = 4$; $y_{N+1} = 0$; $f_n = 1$ $(n = 2, 3, 4)$; $s_n = 0{\cdot}5$ $(n = 1, 2, 3)$; $t = 5$; $x^+ = by + cy^2$; $b = 1$; $c = 0{\cdot}2$; $\delta = 0{\cdot}0010$.

B. Starting approximation (Eq. (*22*))

$$Y_n^{(o)} = 0{\cdot}4 - 0{\cdot}4\,.\,\frac{n-1}{4};\; Y_1^{(0)} = 0{\cdot}4;\; Y_2^{(0)} = 0{\cdot}3;\; Y_3^{(0)} = 0{\cdot}2;\; Y_4^{(0)} = 0{\cdot}1.$$

C. Set of nonlinear equations (Eq. (*19'*)):

$B = 0{\cdot}2 \times 4 = 0{\cdot}8$

$$F_1(\overline{\mathbf{Y}}) \equiv 1{\cdot}95 Y_1 + 0{\cdot}32 Y_1^2 - 0{\cdot}925 Y_2 - 0{\cdot}3125 Y_3 - 0{\cdot}1875 Y_4 - 0{\cdot}4 = 0$$

$$F_2(\overline{\mathbf{Y}}) \equiv 0{\cdot}9 Y_1 + 1{\cdot}05 Y_2 + 0{\cdot}32 Y_2^2 - 0{\cdot}925 Y_3 - 0{\cdot}375 Y_4 - 0{\cdot}4 = 0$$

$$F_3(\overline{\mathbf{Y}}) \equiv Y_1 - 0{\cdot}1 Y_2 + 1{\cdot}05 Y_3 + 0{\cdot}32 Y_3^2 - 1{\cdot}05 Y_4 - 0{\cdot}4 = 0$$

$$F_4(\overline{\mathbf{Y}}) \equiv Y_1 - 0{\cdot}1 Y_3 + 0{\cdot}7 Y_4 + 0{\cdot}32 Y_4^2 - 0{\cdot}4 = 0$$

$F_1(\overline{\mathbf{Y}}^{(0)}) = +0{\cdot}07245 \qquad (|F_1(\overline{\mathbf{Y}})^{(0)})| > \delta)$

$F_2(\overline{\mathbf{Y}}^{(0)}) = +0{\cdot}08130 \qquad (|F_2(\overline{\mathbf{Y}}^{(0)})| > \delta)$

$F_3(\overline{\mathbf{Y}}^{(0)}) = +0{\cdot}08780 \qquad (|F_3(\overline{\mathbf{Y}})^{(0)})| > \delta)$

$F_4(\overline{\mathbf{Y}}^{(0)}) = +0{\cdot}05320 \qquad (|F_4(\overline{\mathbf{Y}}^{(0)})| > \delta) \ldots F_\alpha(\overline{\mathbf{Y}}) = F_4(\overline{\mathbf{Y}})$

D. Solution of the LP problem

$u^{(1)} = +[g_1 - 0{\cdot}1 g_3 + (0{\cdot}7 + 2 \times 0{\cdot}32 Y_4^{(0)})\, g_4] \overset{!}{=}$ minimum at the restrictions

$$\left.\begin{aligned} g_j &\leqq 1 \\ -g_j &\leqq 1 \end{aligned}\right\} j = 1, 2, 3, 4$$

gives values of vector $\overline{\mathbf{g}}^{(1)}$:

$g_1^{(1)} = -1;\; g_2^{(1)} = +1;\; g_{(3)}^1 = +1;\; g_4^{(1)} = -1.$

E. $F_\alpha(\overline{\mathbf{Y}}^{(0)} + \overline{\mathbf{g}}^{(1)}t) = F_4(Y^{(0)} + \overline{\mathbf{g}}^{(1)}t) =$
$= (0{\cdot}4 - t) - 0{\cdot}1(0{\cdot}2 + t) + 0{\cdot}7(0{\cdot}1 - t) + 0{\cdot}32(0{\cdot}1 - t)^2 - 0{\cdot}4 = 0$

The least root $t > 0$ of this equations is $t = 0{\cdot}0287$.

F. Thus the approximation of $\bar{\mathbf{Y}} = \bar{\mathbf{Y}}^{(1)} = \bar{\mathbf{Y}}^{(0)} + \bar{\mathbf{g}}^{(1)} . t$, *i.e.* $Y_1^{(1)} = 0{\cdot}3713$; $Y_2^{(1)} = 0{\cdot}3287$; $Y_3^{(1)} = 0{\cdot}2287$; $Y_4^{(1)} = 0{\cdot}0713$.

C_1.

$F_1 \bar{\mathbf{Y}}(^{(1)}) = -0{\cdot}02073 \qquad (|F_1(\bar{\mathbf{Y}}^{(1)})| > \delta) \ldots F_\alpha(\bar{\mathbf{Y}}) = F_1(\bar{\mathbf{Y}})$
$F_2 \bar{\mathbf{Y}}(^{(1)}) = +0{\cdot}07559 \qquad (|F_2(\bar{\mathbf{Y}}^{(1)})| > \delta)$
$F_3(\bar{\mathbf{Y}}^{(1)}) = +0{\cdot}12045 \qquad (|F_3(\bar{\mathbf{Y}}^{(1)})| > \delta)$
$F_4(\bar{\mathbf{Y}}^{(1)}) = -0{\cdot}00003 \qquad (|F_4(\bar{\mathbf{Y}}^{(1)})| < \delta) \ldots F_4(\bar{\mathbf{Y}}^{(1)}) = 0$

D_1. Solution of the LP problem

$u^{(2)} = -[(1{\cdot}95 + 2 \times 0{\cdot}32 Y_1^{(1)})\, g_1 - 0{\cdot}925 g_2 - 0{\cdot}3125 g_3 - 0{\cdot}1875 g_4] \stackrel{!}{=}$ minimum
at the restrictions

$$\left.\begin{aligned} g_j &\leqq 1 \\ -g_j &\leqq 1 \end{aligned}\right\} j = 1, 2, 3, 4$$

and

$$g_1 - 0{\cdot}1 g_3 + (0{\cdot}7 + 2 \times 0{\cdot}32 Y_4^{(1)})\, g_4 = 0$$

gives values of vector $\bar{\mathbf{g}}^{(2)}$:

$g_1 = +0{\cdot}6456$; $g_2 = -1$; $g_3 = -1$; $g_4 = -1$.

E_1. From $F_1(\bar{\mathbf{Y}}^{(1)} + \bar{\mathbf{g}}^{(2)} t) = 0$

$$t = 0{\cdot}0074$$

F_1. Thus the approximation of $\bar{\mathbf{Y}} = \bar{\mathbf{Y}}^{(2)}$, *i.e.* $Y_1^{(2)} = 0{\cdot}3761$; $Y_{(2)}^2 = 0{\cdot}3213$; $Y_3^{(2)} = 0{\cdot}2213$; $Y_4^{(2)} = 0{\cdot}0639$; *etc.*

The results of all particular approximations of the solution are summarized in the Table on p. 2089.

More than 50 problems have been solved using computer Tesla 200 in order to check the convergence of the proposed method. Folowing range of the parameters has been used: number of stage 4–20, back-flow coefficients 0–10, mass transfer number 0·1–100. The evaluation of the course of computation of particular problems has shown that the number of iterations and the computing time increases approximately with the square of the number of stages while the proportionality constant depends on the required accuracy of the solution. A change in accuracy of one order causes approximately a 30 per cent change in the number of iterations. Computing time of one iteration amounts to about $2N$, seconds the number of iterations falls within N to $2N$.

TABLE

Number of approx. i	$\bar{\mathbf{Y}}^{(i)}$	$F(\bar{\mathbf{Y}}^{(i)})$	$\bar{\mathbf{g}}^{(i+1)}$	t_{i+1}
0	0·4	+0·0724	−1	0·0287
	0·3	+0·0813	+1	
	0·2	+0·0878	+1	
	0·1	+0·0532	−1	
1	0·3713	−0·0207	+0·6456	0·0074
	0·3287	+0·0756	−1	
	0·2287	+0·1204	−1	
	0·0713	−0·0000	−1	
2	0·3761	+0·0003	−0·2403	0·0313
	0·3213	+0·0802	−1	
	0·2213	+0·1249	+1	
	0·0639	+0·0000	+0·4593	
3	0·3686	+0·0004	−0·3064	0·0823
	0·2900	+0·0001	−0·4419	
	0·2526	+0·1430	−1	
	0·0783	+0·0001	+0·2751	
4	0·3434	+0·0006		
	0·2536	+0·0005	$\lvert F_i(\bar{\mathbf{Y}}^{(4)})\rvert < \delta, i = 1, 2, 3, 4$	
	0·1703	+0·0002		
	0·1009	+0·0003		

Using the 4th approximation $Y_1 = 0{\cdot}3434$, $Y_2 = 0{\cdot}2536$; $Y_3 = 0{\cdot}1703$; $Y_4 = 0{\cdot}1009$, as the solution, we obtain from Eqs *(15)*—*(18)* $X_1 = 0{\cdot}5034$; $X_2 = 0{\cdot}3437$; $X_3 = 0{\cdot}2243$; $X_4 = 0{\cdot}1415$.

Overall balance check (Eq. *(21)*):

$$X_4 = 1 - \frac{1}{0{\cdot}4}(0{\cdot}3434 - 0) = 0{\cdot}1415.$$

LIST OF SYMBOLS

- a specific interfacial area
- b, c constants in equilibrium relationship
- E back-flow in feed phase
- f back-flow coefficient in feed phase
- F flow of feed phase
- g elements of direction vector $\bar{\mathbf{g}}$
- K mass transfer coefficient related to feed phase

n stage number counted from feed phase inlet
N number of stages
R back-flow in solvent phase
s back-flow coefficient in solvent phase
S flow of solvent phase
t step size in LP problem
u objective function in LP problem
V volume of a stage
x solute concentration in feed phase
X dimensionless solute concentration in feed phase
x^+ solute concentration in feed phase in equilibrium
X^+ dimensionless solute concentration in feed phase in equilibrium
y solute concentration in solvent phase
Y dimensionless solute concentration in solvent phase
δ positive number characterizing the accuracy of the calculation

Subscript

n stage number

Superscript

i iteration number

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