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A Modified Naphtali-Sandholm Method for General Systems of Interlinked, Multistaged Separators

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Frequently, as shown by Stupin and Lockhart (1972) and Tedder and Rudd (1978), complex arrangements of interlinked distillation columns, as shown in Figure 1, can separate ternary mixtures into three products more economically than can simple sequential arrangements. For example, with a feed containing components R, S, and T in decreasing order of volatility, the complex arrangements in Figures 1*b* and *c* may be preferred over the arrangement in Figure 1*a* when the feed contains small amounts and large amounts of S, respectively. Complex interlinked arrangements can also be advantageous when feeds contain more than three components, and three or more products are required.

General systems of interlinked distillation columns have been devised by Sargent and Gaminibandara (1975), as shown, for example, in Figure 2 for the separation of a feed(s) into three products. The single-linked arrangement in Figure 1*b* can be obtained from Figure 2 by sending a feed to section 1, deleting sections 2*a* and *b*, combining sections 1 and 3*b* to form column I, letting section 3*a* be column II, and removing products from stages *P*, *L*, and *N*. In a similar manner, it can be shown that other complex and simple arrangements are embedded in the general system of Figure 2.

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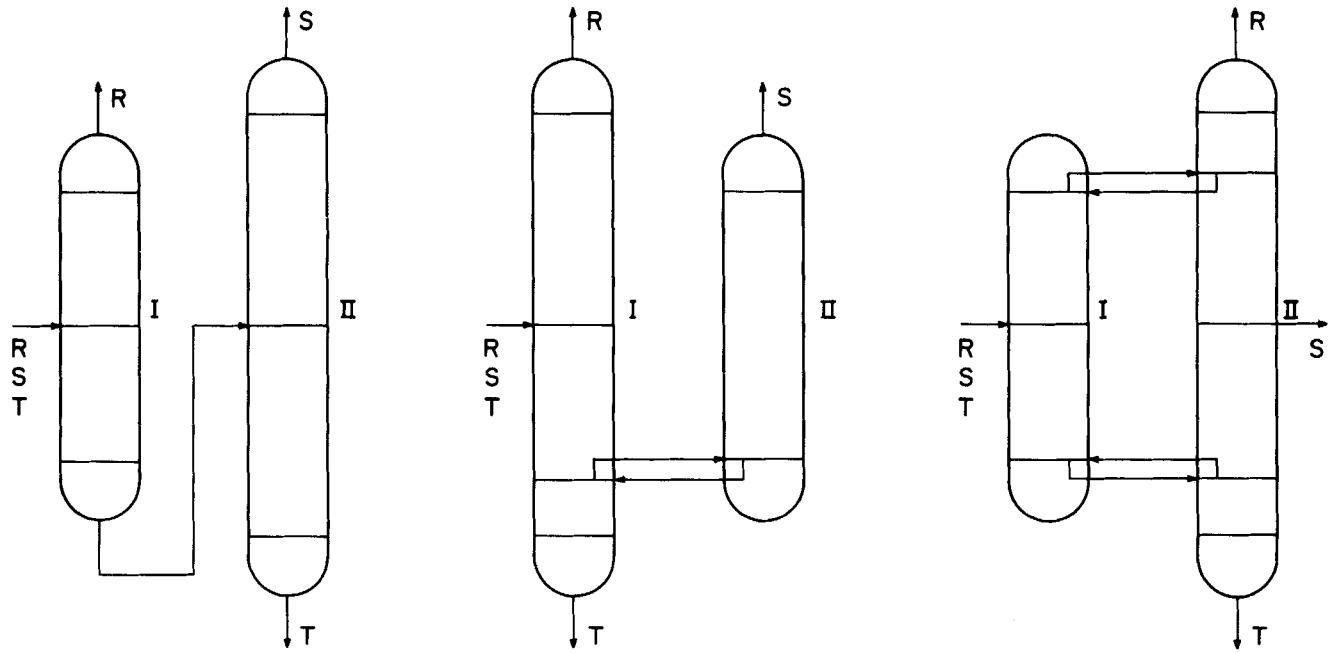
In this note, we extend the Naphtali-Sandholm method (1971), which was originally formulated to make stage calculations for a single distillation column, to the general interlinked system of Figure 2. The extension retains the technique of total linearization and simultaneous solution of all the equations for the system by a Newton-Raphson type of procedure. As discussed by Browne, Ishii, and Otto (1977), this type of approach is more advantageous than the iterative sequential approach.

CALCULATION PROCEDURE FOR INTERLINKED SYSTEM

For each stage in Figure 2, component material balances, equilibrium relationships, and an enthalpy balance are written in the manner of Naphtali and Sandholm except for some changes in subscripts at stages *P*, *J*, *Q*, and *M*, where interlinks occur. For example, the functions M_{Pj}, for component material balances for stage *P* are

$$M_{Pj} = (1 + S_P)V_{Pj} + (1 + s_P)L_{Pj} - V_{P+1,j} - L_{Jj} - f_{Pj} \quad (1)$$

where the term L_{Jj}, a linking flow rate, appears instead of an $L_{P-1,j}$ term which appears in the original Naphtali-Sandholm equation. To solve the equations for all stages simultaneously by a modified Newton-Raphson procedure, the functions are linearized in the usual manner, and then both the linearized equations and variables are grouped according to stage to form the matrix equation. However,



a. Simple Sequential Arrangement

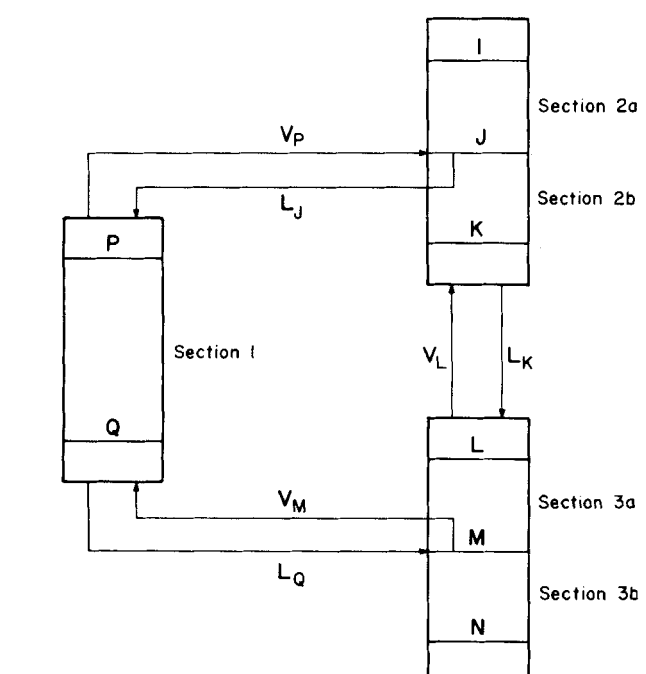
b. Complex Single-Linked Arrangement

c. Complex Double-Linked Arrangement

Note : Not shown are condensers and reboilers.

Fig. 1. Simple and complex arrangements for separation of a ternary mixture.

because of the effect of the interlinks, as observed in Equation (1), a number of different groupings are possible, none of which result in a completely block tridiagonal matrix of partial derivatives as is obtained in the original Naphtali-Sandholm procedure. Instead, a small number of nonzero, off-tridiagonal blocks occur in the matrix, and, consequently, the Thomas algorithm can not be directly applied. In order to solve the system efficiently, it is important to minimize the number of such nonzero blocks and their distance from the diagonal. One efficient grouping by stage is shown in Figure 3*a*, where, for simplicity, row-by-row indexing of A, B, and C submatrices on the diagonals is not shown, and the variable and constant vectors are omitted. This grouping is equivalent to taking the sections in Figure 2 in the order 2*a*, 2*b*, 3*a*, 1, and 3*b*. The alternative grouping of 2*a*, 1, 2*b*, 3*a*, and 3*b* is equally efficient.



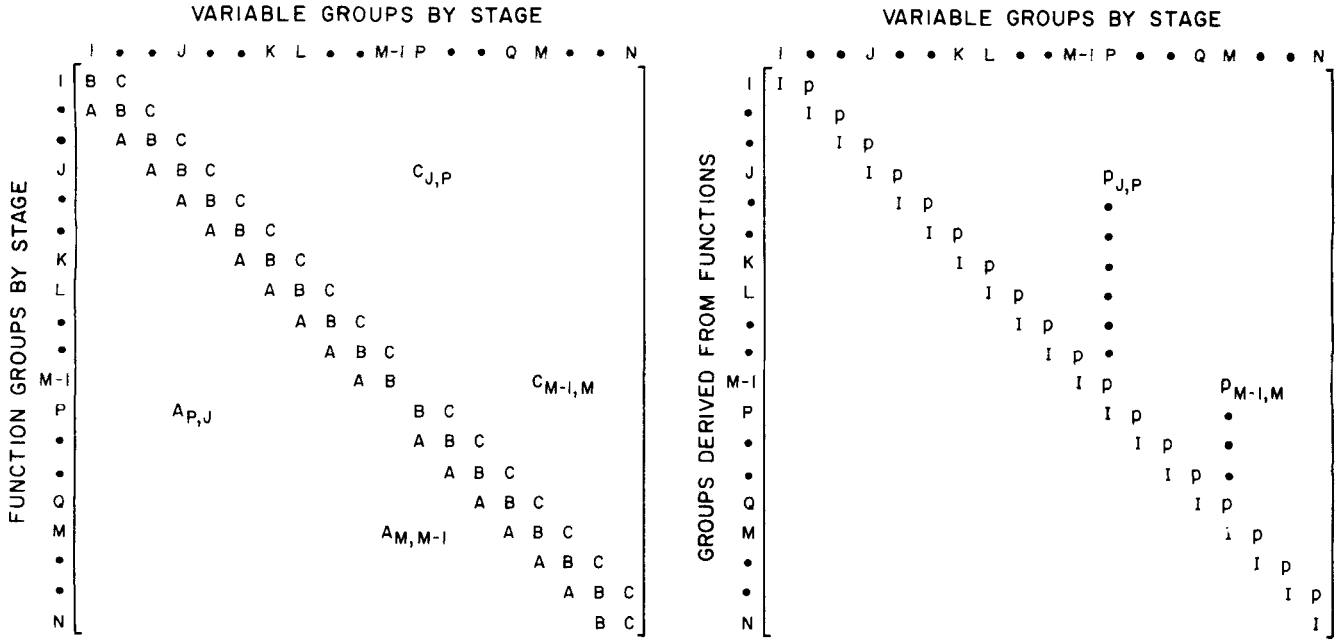
Note : Not shown are Feeds, Products, Sidestreams, and Heat Exchangers, which can be included at any stage.

Fig. 2. General system of Sargent and Gaminibandara for interlinked distillation columns.

A modification of the Thomas algorithm was developed to solve the matrix equation corresponding to Figure 3*a*. The forward substitution steps, which lead to the matrix in Figure 3*b*, are given in Table 1. Steps 1 and 2 are unchanged from the conventional Thomas algorithm. In steps 3, 4, and 5, the submatrix $C_{J,P}$ in row J causes a vertical column of nonzero values of $p_{i,P}$ to extend from row J to row $M - 1$, as seen in Figure 3*b*. In step 6, the submatrix $A_{P,J}$ in row P introduces variable vector $\overline{\Delta X}_J$, which is eliminated from row J by a back substitution chain extending from row $M - 1$ to J. Steps 7 to 11 are similar to the earlier steps. Because, as shown in Figure 3*b*, an upper triangular matrix is obtained, back substitution readily produces the solution vector. For a given number of components and total stages, computing time and storage requirements for solving the linearized set of equations are not increased greatly by the presence of the nonzero, off-tridiagonal submatrices.

CONSIDERATION OF BYPASS AND SPECIFICATIONS AT INTERMEDIATE STAGES

In order to preserve the block tridiagonal structure of the matrix of partial derivatives, Naphtali and Sandholm considered neither bypassing of flows around stages nor specifications of temperature, flow rates, or compositions



a Starting Matrix of Blocks of Partial Derivatives.

b. Matrix After Forward Substitution.

Fig. 3. Matrices for modified Naphtali-Sandholm procedure.

TABLE 1. FORWARD SUBSTITUTION STEPS FOR MODIFIED THOMAS ALGORITHM
(as applied to the matrix equation corresponding to Figure 3*a*)

Begin at each row i by setting up nonzero submatrices, A, B, C, and F for that row; complete each row i by replacing A_i with zero and B_i with I and by storing submatrix p_i and subvector q_i.

Step 1: row 1, $p_1 \leftarrow B_1^{-1}C_1$; $q_1 \leftarrow B_1^{-1}F_1$

Step 2: rows i, where $2 \leq i \leq J-1$, $B_i \leftarrow (B_i - A_ip_{i-1})^{-1}$; $p_i \leftarrow B_iC_i$; $q_i \leftarrow B_i(F_i - A_iq_{i-1})$

Step 3: row J, same as step 2, but add: $p_{J,P} \leftarrow B_JC_{J,P}$

Step 4: rows i, where $J+1 \leq i \leq M-2$, same as step 2, but add: $p_{i,P} \leftarrow -B_iA_ip_{i-1,P}$

Step 5: row $M-1$, $B_{M-1} \leftarrow (B_{M-1} - A_{M-1}p_{M-2})^{-1}$; $p_{M-1} \leftarrow -B_{M-1}A_{M-1}p_{M-2,P}$; $p_{M-1,M} \leftarrow B_{M-1}C_{M-1,M}$; $q_{M-1} \leftarrow B_{M-1}(F_{M-1} - A_{M-1}q_{M-2})$

Step 6: row P, set $\beta = -p_{M-1}$; iterate on $\beta \leftarrow -p_{i,P} - p_i\beta$ from $i = M-2$ to $i = J$; $B_P \leftarrow (B_P + A_{P,J}\beta)^{-1}$; $p_P \leftarrow B_PC_P$;
reset $\beta = -p_{M-1}$; iterate on $\beta \leftarrow -p_i\beta$ from $i = M-2$ to $i = J$; $p_{P,M} \leftarrow A_{P,J}\beta$
reset $\beta = 0$; iterate on $\beta \leftarrow q_i - p_i\beta$ from $i = M-1$ to $i = J$; $q_P \leftarrow B_P(F_P - A_{P,J}\beta)$

Step 7: rows i; where $P+1 \leq i \leq Q-1$, same as step 2, but add: $p_{i,M} \leftarrow B_iA_iP_{i-1,M}$

Step 8: row Q, $B_Q \leftarrow (B_Q - A_QP_{Q-1})^{-1}$; $q_Q \leftarrow B_Q(F_Q - A_Qq_{Q-1})$; $p_Q \leftarrow B_Q(C_Q - A_Qp_{Q-1,M})$

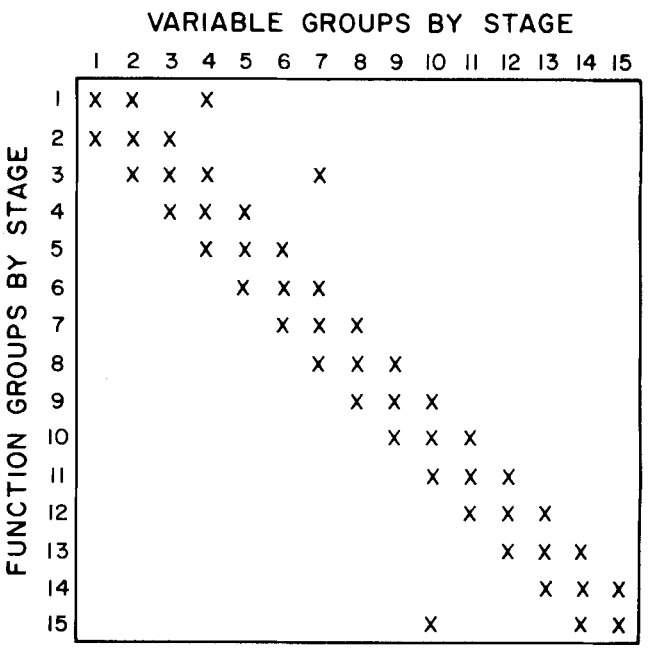
Step 9: row M, reset $\beta = 0$; iterate on $\beta \leftarrow -p_{i,M} - p_i\beta$ from $i = Q$ to $i = P$; $B_M \leftarrow [B_M - A_Mp_Q + A_{M,M-1}(-p_{M-1,M} - p_{M-1,P}\beta)]^{-1}$; $p_M \leftarrow B_MC_M$; reset $\beta = 0$; iterate on $\beta \leftarrow q_i - p_i\beta$ from $i = Q$ to $i = P$; $q_M \leftarrow B_M[F_M - A_Mq_Q - A_{M,M-1}(q_{M-1} - p_{M-1}\beta)]$

Step 10: rows i where $M+1 \leq i \leq N-1$, same as step 2

Step 11: row N, $q_N \leftarrow (B_N - A_NP_{N-1})^{-1}(F_N - A_Nq_{N-1})$

A single subscript refers to row of matrix. In a double subscript, the first index refers to the row, the second to the column.

at intermediate stages. Such considerations are permitted when the modified Thomas algorithm described here is employed. For example, consider a single distillation column with fifteen stages (including the condenser and reboiler). A liquid bypass flows from stage 7 to stage 3. Instead of the condenser and reboiler duties, the temperature of stage 4 and the vapor flow rate leaving stage 10 are specified. The resulting matrix structure, corresponding to Figure 4, is readily solved by the modified Thomas algorithm.



Note : X denotes a non-zero submatrix.

Fig. 4. Matrix for examples of single column with stage bypass and specifications at intermediate stages.

NOTATION

$A_{i,k}$ = submatrix of partial derivatives of linearized equations on stage i with respect to variables on stage k (if i, k is omitted, $i = i$, and $k = i - 1$)
B = submatrix of partial derivatives of linearized equations on stage i with respect to variables on stage i
$C_{i,k}$ = submatrix of partial derivatives of linearized equations on stage i with respect to variables on stage k (if i, k is omitted, $i = i$, and $k = i + 1$)
F_i = function vector for stage i
f_{ij} = flow rate of component j in feed to stage i
I = identity submatrix
L_{ij} = flow rate of component j in liquid leaving stage i that enters next stage in the system
M_{ij} = material balance equation for component j on stage i
$p_{i,k}$ = replacement submatrix for linearized equations on stage i with respect to variables on stage k (if i, k is omitted, $i = i$, $k = i + 1$)
q_i = replacement for function vector for stage i
S_i = ratio of vapor sidestream flow rate from stage i to vapor flow rate leaving stage i that enters next stage in the system
s_i = ratio of liquid sidestream flow rate from stage i to liquid flow rate leaving stage i that enters next stage in the system
V_j = flow rate of component j in vapor leaving stage i that enters next stage in the system
$\overline{\Delta X_i}$ = vector of Newton-Raphson corrections to variables for stage i
β = dummy submatrix
$\leftarrow$ = is replaced by

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Free Radical Transport in a Photochemical Reactor

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Although the field of photochemistry has expanded enormously in recent years, industrial exploitation of photochemical processes has been slow to develop. Photochlorination and photosulfoxidation processes have received industrial attention from time to time. However, the only large scale process apparently now in operation is the photooximation of cyclohexane to produce caprolactam, the monomer of Nylon 6, which is carried out by Toray Industries of Japan (Mellor et al., 1974; Pape, 1975). In view of the potential selectivity offered by the photochemical route, it is somewhat surprising that more widespread application has not occurred. Undoubtedly, operational difficulties inherent in photoprocesses have played a role in slowing such development. In particular, photodegradation of products and side reactions promoted by the high intensity sources used commercially as well as the ever present problem of opaque wall deposit formation frequently combine to make the photochemical route undesirable on a practical scale. Formation of wall deposits and tarry masses have been reported by many workers as common experimental problems to be overcome in practice (Chiltz et al., 1963; Cassano and Smith, 1966; Ziolkowski et al., 1967; Shah, 1968; Isaacson and Ting, 1970; Lucas, 1971).

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Lucas (1971) suggested that these problems might be eliminated entirely if the photoreaction process was separated into the two distinct operations of photoinitiation and subsequent thermal reaction and if these operations were carried out in different zones of the photoreactor. This would eliminate the direct irradiation of reaction products that frequently leads to undesired side reactions and would also prevent tar and deposit forming constituents from interacting at the radiation transmitting surfaces of the reactor. Such operation demands, of course, that the reactive species produced by photoinitiation be successfully transported to the point where the subsequent reactions may occur.

Lucas (1973) later enlarged on this idea and presented some experimental data for the gas-liquid photooximation of cyclohexane. The reaction was carried out in a segregated reactor divided into two zones by a teflon grid of low optical transparency and irradiated at one end by a mercury lamp. Gaseous NOCl and hydrochloric acid carrier gas were injected continuously into the zone closest to the lamp as well as into the liquid cyclohexane in the other zone of the reactor. The data reported by Lucas indicate that free radicals produced by the photodecomposition of NOCl were indeed transported intact through the grid and initiated reaction with the liquid cyclohexane on the other side. Furthermore, there was little or no evidence of wall deposit or tar formation found in this operation.