High Temperatures, IV. Carbondioxide in the Temperature Range 0°–600°C, and up to 50 Atmospheres," *J. Chem. Phys.*, **18**, 1269 (1950).

Martin, J. J., "Equations of State," *Ind. Eng. Chem.*, **59**, 34 (1967).

McKetta, J. J., D. C. K. Lin, and I. H. Silberberg, "Graphical Determination of Virial Coefficients by the Burnett Method: Isopentane and Neopentane," *J. Chem. Eng. Data*, **12**, 226 (1967).

Michels, A., H. Wouters, and J. de Boer, *Physica*, **1**, 587 (1934); as cited by J. H. Dymond and E. B. Smith, *the Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Michels, A., and G. W. Nederbragt, *Physica*, **2**, 1000 (1935); as cited by J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Michels, A., and G. W. Nederbragt, *Physica*, **3**, 569 (1936); as cited by J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Michels, A., and C. Michels, "Isotherms of CO_2 between 0° and 150°C and Pressures from 16 to 250 Atm," *Proc. R. Soc*, **A153**, 201 (1935).

Michels, A., and M. Geldermans, "Isotherms of Ethylene up to 3000 Atmospheres Between 0° and 150°C," *Physica*, **9**, 967 (1942).

Michels, Hub. Wijker, and Hk. Wijker, "Isotherms of Argon between 0 and 150°C and Pressures up to 2900 Atm.," *Physica*, **15**, 627 (1949).

Michels, A., T. Wassenaar, P. Louwerse, R. J. Lunbeck, and G. J. Wolkers, "Isotherms and Thermodynamic Functions of Propane at Temperatures Between 25°C and 150°C and at densities up to 340 Amagat," *Physica*, **19**, 287 (1953).

Michels, A., H. W. Schamp, and W. DeGraaf, "Compression Isotherms of Oxygen at 0°, 25° and 50°C and Pressures up to 135 Atm," *Physica*, **20**, 1209 (1954).

Michels, A., T. Wassenaar, and P. Louwerse, "Isotherms of Xenon at Temperatures Between 0° and 150°C and at Densities up to 515 Amagats," *Physica*, **20**, 99 (1954).

Michels, A., W. V. Straaten, and J. Dawson, "Isotherms and Thermodynamical Functions of Ethane at Temperatures Between 0° and 150°C and Pressures up to 200 Atm," *Physica*, **20**, 17 (1954).

Michels, A., J. M. Levelt, and W. DeGraaf, "Compressibility Isotherms of Argon at Temperatures Between −25°C and −155°C and at Densities up to 640 Amagat," *Physica*, **24**, 659 (1958).

Perez Masia, A., M. Diaz Pena, and J. A. Burriel Lluna, *An. R. Soc. Esp. Fis. Quim.*, **60B**, 229 (1964); as cited by J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Pfefferle, W. C., J. A. Goff, and J. G. Miller, "Compressibility of Gases I. The Burnett Method. An Improved Method of Treatment of the Data. Extension of the Method to Gas Mixtures," *J. Chem. Phys.*, **23**, 509 (1955).

Pitzer, K. S., and R. F. Curl, Jr., "The Volumetric and Thermodynamic Properties of Fluids. III Emperical Equation for the Second Virial Coefficient," *J. Am. Chem. Soc.*, **79**, 2369 (1957).

Pope, G. A., P. S. Chappelear, and R. Kobayashi, "Virial Coefficients of Argon, Methane and Ethane at Low Reduced Temperatures," *J. Chem. Phys.*, **59**, 423 (1973).

Prausnitz, J. M., "Molecular Thermodynamics of Fluid Phase Equilibria," Prentice-Hall, Englewood Cliffs, NJ (1969).

Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems, Volumetric Behaviour of Ethane," *I.E.Ch. Int. Ed.*, **36**, 956 (1944).

Schamp, Jr., H. W., and E. A. Mason, A. C. B. Richardson, and A. Altman, "Compressibility and Intermolecular Forces in Gases: Methane," *Phys. Fluids*, **1**, 329 (1958).

Tarakad, R. R., and R. P. Danner, "An Improved Corresponding States Method for Polar Fluids: Correlation of Second Virial Coefficients," *AIChE J.*, **23**, 685 (1977).

Tsonopoulos, C., "An Empirical Correlation of Secons Virial Coefficients," *AIChE J.*, **20**, 263 (1974).

Tsonopoulos, C., "Second Virial Cross-Coefficients: Correlation and Prediction of k_{ij}", A.C.S. series 182, Washington, DC (1979).

Van Ness, H. C., *Classical Thermodynamics of Nonelectrolyte Solutions*, McMillan, New York (1964).

Vukalovic, M. P., Ya. F. Masalov, *Teploenergetica*, **13**, 58 (1966); as cited by J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Warowny, W., P. Wielopolski, and J. Stecki, "Compressibility Factors and Virial Coefficients for Propane, Propene and their Mixtures by the Burnett Method," *Physica*, **91A**, 73 (1978).

Whalley, E., and W. G. Schneider, *Trans. Am. Soc. Mech. Eng.*, **76**, 1001 (1954): as cited by J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).

Whalley, E., Y. Lupien, W. G. Schneider, "The Compressibility of Gases at High Temperatures," *Can. J. Chem.*, 33, 633 (1955).

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Corrected Flowrates Estimation by Using θ Convergence Promoter for Distillation Columns

The main task of the θ convergence promoter is to afford a better estimate of liquid and vapor molar fractions in each tray of the column.

The assumptions implied by the promoter prove to be reliable for conventional columns, while they may cause numerical instability when dealing with nonconventional configurations. In these cases, corrected molar fractions may be computed only after making a supplementary assumption, which in principle is not unique. So, the paper presents a new methodology which gives rather satisfactory results.

S. J. PIERUCCI, E. M. RANZI,
AND G. E. BIARDI

Chemical Engineering Department,
Politecnico di Milano, Milano, Italy

SCOPE

The θ method for the simulation of distillation column is defined as a combination of numerical algorithms with a convergence promoter.

The former contribute to the iterative solution of the system of equations describing the column model. The latter (so far called as "θ-convergence promoter") accelerates the convergence of the whole numerical procedure by adopting the well-known θ multipliers. These can be distinguished into a primary θ multiplier and additional θ multipliers. Both of them refer to

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Correspondence concerning this paper should be addressed to S. J. Pierucci.

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recovery ratios; the primary θ between bottom products and top distillate, the additional ones between side-cuts products and top distillate.

This paper deals in particular with the way the θ-convergence promoter has to be applied. Basically, the main task of the θ-convergence promoter is to provide "corrected" liquid and vapor molar fractions after solving component material balances and before evaluating bubble (or dew) point conditions.

When dealing with conventional columns these corrections imply that the corresponding "corrected" liquid and vapor component flow-rates satisfy two conditions:

- **To be consistant with the definition of theta multipliers**
- **To satisfy component material balances in each tray of the column**

Our aim is to show that the above conditions are not valid any longer when dealing with nonconventional columns (multifeeds or multiside streams); therefore, a different procedure must be implemented to correct component flowrates.

For sake of clarity, we define three configurations: conventional, multifeeds and complex columns. For each of them, the new procedure is described in detail.

A common basic idea within this procedure may be found in terms of a new formulation of the primary theta multiplier. This is shown to be equivalent to an unique divisor of so-called "calculated" separation factors either of the feed tray for a conventional column, or of the section containing the trays where feed streams are present, for multifeeds or complex columns.

As a consequence, the condition of consistency with the definition of the primary θ is regarded as that the corrected flowrates give suitable values of the separation factors of a feed tray or of a section. We show here that, in principle, the way the corrected flowrates may be obtained is not unique for nonconventional columns. A methodology is suggested which may be considered by analogy, the closest to the unique one found for a conventional column.

CONCLUSIONS AND SIGNIFICANCE

Among the methods which partition the whole system of equations describing the model of a column, the theta method is one of the most reliable and efficient one for distillation columns.

Basically these peculiar features are due to the use of the θ-convergence promoter, that is the phase of predicting the values of liquid and vapor molar fractions after solving component material balance equations. These predictions are made under proper assumptions on the values of liquid and vapor component flowrates from which the corresponding molar fractions are obtained.

To ensure a more efficient use of the θ-convergence promoter, the implied assumptions have to be modified; thus, new ways of estimating liquid and vapor component flowrates are suggested.

The methodologies presented in this paper, even in a approximated version, seem to be more efficient as comparative examples show the advantages offered by their use.

INTRODUCTION

The θ method for solving distillation columns has been largely circulated in literature and a recent survey (Holland and Pendon, 1974; Holland and Eubank, 1974; Holland et al., 1975; Holland and Kuk, 1975; Gallum and Holland, 1976;Hess et al., 1977) showed the reliability of this method in solving a wide variety of instances. The method partitions the system of equations, describing the model of a distillation column. Three subsets are then solved in turn according to a major iterative loop:

- *Subset 1:* component material balances and equilibrium equations
- *Subset 2:* bubble point or dew point equations
- *Subset 3:* enthalpy balance equations, total material balance equations, and data equations

Subset 1 is solved in terms of component liquid and vapor flowrates, and Subset 2 in terms of tray temperatures. Subset 3 is then solved in terms of total liquid, vapor flowrates and duties to the column.

The way of solving the three subsets has been also discussed in literature. Subset 1 is readily solved for component flowrates by using the well-known recurrence formula (sometimes called Thomas algorithm) for tridiagonal matrices or by the method proposed by Boston and Sullivan (1972). The K_b method (Holland, 1963; Billingsley, 1970) is used for the determination of tray temperatures (solution of Subset 2), while "Constant Composition" procedure stated by Holland (1963) is adopted for the solution of Step 3.

The convergence characteristics of the θ method can be attributed both to the selection of the above-mentioned algorithms in use for the solution of each single subset, and to the θ-convergence promoter. Convergence rate is in fact accelerated by correcting the calculated flowrates of individual components after solving the component material balances (Subset 1) and before evaluating bubble or dew point conditions (Subset 2). According to Holland Pendon (1974)

$$(L_{j,i})_{co} = (L_{j,i})_{ca} \cdot R_j \cdot \psi_j (j = 1, \ldots np) \tag{1}$$

$$(V_{j,i})_{co} = (V_{j,i})_{ca} \cdot R_i \cdot \sigma_j (i = 1, \ldots ncp) \tag{2}$$

where ψ_j and σ_j are multipliers independent of i, and

$$R_j = \frac{(di)_{co}}{(di)_{ca}}$$

The subscript *co* stands for the corrected values, and *ca* for the calculated ones by the solution of component material balances.

The main task of the promoter is then to give a better estimate of the liquid and vapor molar fractions according to the following expressions:

$$(X_{j,i})_{co} = \frac{(L_{j,i})_{ca} \cdot R_i}{\sum_{1=i}^{ncp} (L_{j,i})_{ca} \cdot R_j} \qquad \begin{matrix} j = 1, np \\ i = 1, ncp \end{matrix} \tag{3}$$

$$(Y_{j,i})_{co} = \frac{(V_{j,i})_{ca} \cdot R_i}{\sum_{1=i}^{ncp} (V_{j,i})_{ca} \cdot R_i} \qquad \begin{matrix} j = 1, np \\ i = 1, ncp \end{matrix} \tag{4}$$

This correction substantially accelerates convergence in those problems which would converge without it and brings about convergence in most problems which would not converge otherwise (Billingsley, 1970).

For conventional distillation columns (one feed, no sidestreams)

$$R_i = \frac{(di)_{co}}{(di)_{ca}} = \frac{Fi}{(di)_{ca} + \theta (bi)_{ca}}$$

while for complex ones (multifeeds and sidestreams)

$$\frac{(di)_{co}}{(di)_{ca}} = \frac{Fi}{(di)_{ca} + \theta(bi)_{ca} + \theta_2^U(U_{2,i})_{ca} + \theta_2^W(W_{2,i})_{ca} + \ldots}$$

The theta multipliers θ, $\theta U/2$, $\theta W/2$, . . . are defined as follows:

$$\left(\frac{bi}{di}\right)_{co} = \theta\left(\frac{bi}{di}\right)_{ca}$$

$$\left(\frac{U_{2,i}}{di}\right)_{co} = \theta_2^U\left(\frac{U_{2,i}}{di}\right)_{ca}$$

$$\left(\frac{W_{2,i}}{di}\right)_{co} = \theta_2^W\left(\frac{W_{2,i}}{di}\right)_{ca}$$

They are calculated by imposing each component in overall component material balance and in agreement with the specified values of D and U_2, W_2, ...

Our attention is focused on the way the corrected flowrates have to be estimated. In fact, it is accepted that they have to agree with two basic conditions:

1) To be consistent with the definition of θ multipliers
2) To satisfy component material balances around each tray

This paper will prove that expressions 1 and 2 satisfy these conditions when applied to conventional columns. For nonconventional configurations, the latter of the two conditions is not valid any more. As in these cases, the corrections applied by expressions 3 and 4 may either cause instability, or the entire procedure to diverge, the following expressions will be applied throughout the paper:

$$(X_{j,i})_{co} = \frac{(L_{j,i})_{co}}{\sum\limits_{1=i}^{ncp}(L_{j,i})_{co}} \qquad \begin{matrix}(j = 1, np)\\(i = 1\ldots ncp)\end{matrix} \tag{5}$$

$$(Y_{j,i})_{co} = \frac{(V_{j,i})_{co}}{\sum\limits_{1=i}^{ncp}(V_{j,i})_{co}} \qquad \begin{matrix}(j = 1, np)\\(i = 1\ldots ncp)\end{matrix} \tag{6}$$

where the appearing corrected component flowrates are properly computed in a manner explained below.

It is worthwhile to note the entire θ method is regarded as a combination of suitable algorithms which solve each single equation subset and a convergence promoter based on proper θ multipliers. From this point of view, the improvement presented here only lies in the way the convergence promoter should be applied. For this purpose, we will analyze three cases which cover most of the possible configurations met in distillation problems:

- Conventional columns
- Multifeeds conventional columns (multifeeds)
- Multifeeds, sidestreams (complex)

CONVENTIONAL COLUMNS

A conventional distillation column will be defined as one which has one feed F, a distillate D, and a condenser which provides a liquid reflux and a reboiler which provides a vapor stream, Figure 1.

Considering that the a primary θ multiplier is defined by:

$$\left(\frac{bi}{di}\right)_{co} = \theta\left(\frac{bi}{di}\right)_{ca}$$

then

$$(bi)_{co} = (bi)_{ca}\cdot R_i\cdot\theta \text{ and } (di)_{co} = (di)_{ca}\cdot R_i\cdot$$

As the above relations belong to the class defined by Eqs. 1 and 2, their consistency with the θ definition (1st conditions) is proved (Holland and Pendon, 1974).

Let's now formulate Eqs. 1 and 2 in component material balances (2nd condition):
for the enriching section

$$(V_{j,i})_{co} = (L_{j-1,i})_{co} + (di)_{co} \qquad l < j \leq f$$

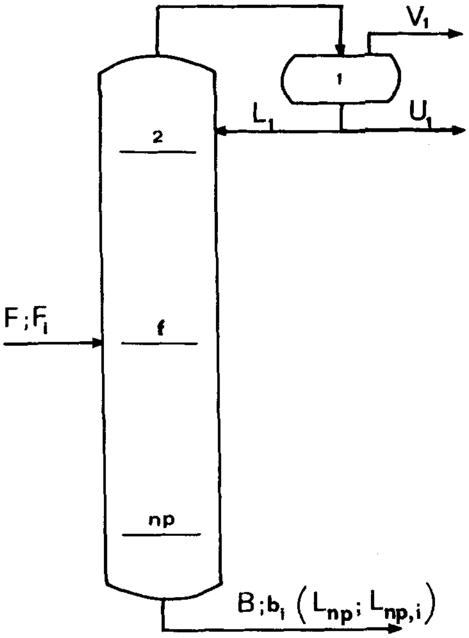

Figure 1. Conventional column.

by introducing Eqs. 1 and 2, we obtain:

$$(V_{j,i})_{ca} = R_i\cdot\sigma_j = (L_{j-1,i})_{ca}\cdot R_i\cdot\psi_{j-1} + R_i\cdot(di)_{ca}$$

by R_i elimination, and taking into account that:

$$(V_{j,i})_{ca} = (L_{j-1,i})_{ca} + (di)_{ca}$$

the result is:

$$(\sigma_j - 1) = \frac{L_{j-1,i}}{V_{j,i\ ca}}\cdot(\psi_{j-1} - 1)$$

the values σ_j and ψ_{j-1} are independent of component i when $\sigma_j = \psi_{j-1} = 1$.

Following a similar procedure, we immediately find that for the stripping section ($f < j \leq np$) is $\sigma_j = \psi_{j-1} = \theta$

In short, we proved that the expressions 1 and 2 satisfy the two required conditions; i.e., they are consistent with the θ multiplier definition and, they satisfy the tray-by-tray component material balances. Therefore, expressions 1 and 2 may be used to calculate, if necessary, the corrected flowrate by assuming:

$$\sigma_j = \psi_{j-1} = 1 \qquad \text{for } 1 < j \leq f$$

and

$$\sigma_j = \psi_{j-1} = \theta \qquad \text{for } f < j \leq np$$

The corrected molar fractions may be calculated by means of relations 5 and 6 or, more easily, by means of Eqs. 3 and 4.

As a consequence of the above treatment, it is easy to point out that in principle the corrected component flowrates may be calculated in a different way, i.e., by solving tray-by-tray component material balances having properly corrected the separation factors $S_{f,i}$ of the feed tray.

Provided the separation factors are defined as follows:

$$S_{j,i} = \frac{V_{j,i}}{L_{j,i}} = K_{j,i}\frac{V_j}{L_j}$$

then the component material balances stated in terms of liquid flow rates are represented by the following set of equations:

$$L_{1,i}\left(1 + \frac{U_1}{L_1} + S_1\right) - S_{2,i}L_{2,i} = 0$$

$$-L_{np-1,i} + L_{np,i}(1 + S_{np,i}) = 0$$

$$-L_{f-1,i} + L_{f,i}(1 + S_{f,i}) - S_{f+1,i}L_{f+1,i} - F_i = 0$$

$$-L_{j-1,i} + L_{j,i}(1 + S_{j,i}) - S_{j+1,i}L_{j+1,i} = 0 \quad (j \neq f \neq 1 \neq np)$$

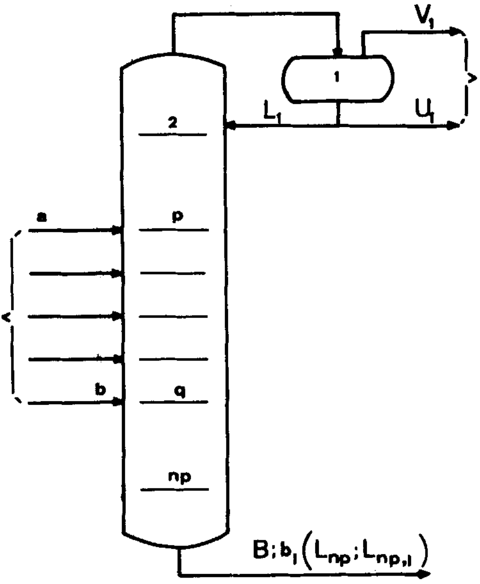

Figure 2. Multifeeds conventional column.

For any given set of values $S_{j,i}$ ($j = 1,np$), these equations are readily solved for $L_{j,i}$ by use of well-known recurrence formulas applied to tridiagonal matrices. Let $(S_{j,i})_{ca}$ be the values of the separation factors which give the $(L_{j,i})_{ca}$, and $(S_{j,i})_{co}$ those giving the values $(L_{j,i})_{co}$. The corrected molar liquid flowrates are obtained by solving the above system by means of the following set of separation factors:

$$(S_{j,i})_{co} = (S_{j,i})_{ca} \qquad (j \neq f)$$

$$(S_{f,i})_{co} = (S_{f,i})_{ca} \cdot \theta^{-1} \tag{7}$$

As the multipliers is usually calculated on the basis of the following conditions:

$$\sum (di)_{co} - D = 0$$

from relation 7, we can correctly assume that the primary θ multiplier, while modifying the feed tray separation factors, allows to match the specification of the output stream D in terms of component material balances (Pierucci et al., 1981). This formulation is the starting point of the analogue applied to the next distillation configurations.

MULTIFEEDS (CONVENTIONAL) COLUMN

A multifeeds (conventional) column will be defined as the one which satisfies all the conditions of a conventional one except for the presence of more than one feed stream.

Let's suppose that the feed streams are located between the trays p and q, Figure 2.

We define an enriching section above the tray p, a stripping section under the tray q, and a feed section containing the trays from p to q both included. For the two sections, enriching the stripping, the relations 3 and 4 may be applied under the same conditions found for a conventional column. Therefore, the corrected component flowrates may be calculated by means of Eqs. 1 and 2, where

$$\sigma_j = \psi_{j-1} = 1 \qquad \text{for } 1 < j \le p$$

and

$$\sigma_j = \psi_{j-1} = \theta \qquad \text{for } q < j \le np$$

The corrected molar fractions are calculated by 5 and 6 or more simply according to relations 3 and 4.

The following point is worth mentioning, provided that it is possible to define:

$$S_{p,q,i} = \frac{V_{p,i}}{L_{q,i}} \qquad i = 1 \ldots ncp$$

a global separation factor of the feed section, then the section may be reduced to a single tray when solving component material balances in the enriching and stripping sections.

The set of balance equations in terms of liquid flowrates is:

$$L_{1,i}\left(1 + \frac{U_1}{L_1} + S_{1,i}\right) - S_{2,i}L_{2,i} = 0$$

$$-L_{np-1,i} + L_{np,i}(1 + S_{np,i}) = 0$$

$$-L_{p-1,i} + L_{q,i}(1 + S_{p,q,i}) - S_{q+1,i}L_{q+1,i} - \sum_{p=j}^{q} F_{j,i} = 0$$

$$-L_{j-1,i} + L_{j,i}(1 + S_{j,i}) - S_{j+1,i}L_{j+1,i} = 0 \quad \begin{matrix}(1 < j \le p)\\(q < j < np)\end{matrix}$$

For any set of $S_{j,i}$ and $S_{p;q,i}$ the linear system is solved to give the liquid component flowrates above and below the feed section.

By attributing the subscripts *ca* and *co* to the separation factors which give respectively the calculated and corrected flowrates, we obtain:

$$(S_{j,i})_{co} = (S_{j,i})_{ca} \qquad 1 \le j < p \quad q < j < np$$

$$(S_{p,q,i})_{co} = (S_{p,q,i})_{ca}\,\theta^{-1}$$

As a consequence of the conditions previously obtained:

$$(V_{p,i})_{co} = (V_{p,i})_{ca} \cdot R_i$$

and

$$(L_{q,i})_{co} = (L_{q,i})_{ca} \cdot R_i \cdot \theta$$

Note that when p coincides with q, then Eqs. 8 becomes 7, as obtained for conventional columns.

Relation 8 may be viewed as a new formulation of the θ multiplier for multifeeds columns, namely: "leaving unchanged all the separation factors $S_{j,i}$($j < p$ and $j \le q$), find the unique multiplier θ^{-1} of the global separation factors $S_{p,q,i}$ of the feed section, so that the solution of tray-by-tray component material balances in the enriching and stripping sesctions may provide a value of the total flow of the distillate in agreement with the assigned value D."

A different approach must be used for the feed section as the relations 1 and 2 are not applicable to the section. Should, for instance, two nondistributed components a and b in the feeds stream, a presents only in the feed stream p and b only in the feed stream q.

The corrected flowrates according to relations 1 and 2 are calculated by associating to component a the multipliers $\sigma_j = \psi_{j-1} = \theta$, while the values $\sigma_j = \psi_{j-1} = 1$ to component b ($p < j \le q$ for both the cases).

The result is that the multipliers σ and ψ are no longer independent of components. Therefore, relations 3 and 4 can not be utilized any more. In other words, the liquid and vapor molar fractions have to be computed by means of relations 5 and 6 through a suitable calculation of the corrected flowrates. It is worth remembering that these corrected flowrates have to satisfy two conditions, that is to be both balanced in component material in each tray of the feed section, and in agreement with the θ multiplier definition.

The last condition has been proved to be equivalent to the statement that the corrected flowrates in the enriching and stripping section give a global separation factor of the feed section in agreement with Eq. 8.

The factors $S_{p,q,i}$ and the component flowrates at assigned input streams to the feed section [that is, feed streams of the column, and $(L_{p-1,i})_{co}$, $(V_{q+1,i})_{co}$] depend only on all $S_{j,i}$ for $p \le j \le q$. Therefore, the way of obtaining the required $(S_{p,qi})_{co}$ and $(L_{j,i})_{co}$ and $(V_{j,i})_{co}(p \le j \le q)$ by modifying the corresponding values of the $S_{j,i}$ is not unique.

The estimate of corrected flowrates inside the feed section, is made after formulating a further decision, that is, how to modify the values of the factor $S_{j,i}$.

By analogy with the conventional columns treatment, we find for each component i a multiplier, say θ_i^*, of the $S_{j,i}$ factors ($p \leq j \leq q$) so that the computed value $S_{p,q,i}$ is in agreement with relation 8. The θ_i^* may be computed for each component by an iterative procedure including the following steps:

i) Define $(S_{j,i})_{co} = (S_{j,i})_{ca} \cdot \theta_i^* \qquad p \leq j \leq q$

ii) Solve

$$-(L_{p-1,i})_{ca} R_i + L_{p,i}(1 + (S_{p,i})_{co}) - (S_{p+1,i})_{co} \cdot L_{p+1,i} - F_{p,i} = 0$$

$$-L_{j-1,i} + L_{j,i}(1 + (S_{j,i})_{co}) - (S_{j+1,i})_{co} \cdot L_{j+1,i} - F_{j,i} = 0 \qquad p < j < q$$

$$-L_{q-1,i} + L_{q,i}(1 + (S_{q,i})_{co}) - (V_{q+1,i})_{ca} R_i \cdot \theta - F_{q,i} = 0 \qquad p \leq j \leq q$$

$$V_{j,i} = (S_{j,i})_{co} L_{j,i}$$

iii) Compare the computed $S_{p,q,i} = (S_{p,i})_{co} L_{p,i}/L_{q,i}$ with the corrected one given by Eq. 8.

Restart the sequence with a new θ_i^*, if a nonacceptable disagreement is found. At the end of the procedure, the component material balances solution (step ii) gives the values of the component flowrates inside the feed section. They have been obtained on the basis of a certain not unique decision which, nevertheless, gives results which are consistent with the definition of the θ multiplier and with component material balance. Therefore, one may consider the obtained flowrates inside section as corrected ones.

In summary, the calculation of the corrected flowrates in each tray of a multifeeds column is reached through the following steps.

i) Calculate the θ parameter according to well-known methodologies (Holland, 1963; Holland and Pendon, 1974). The formulation presented here may be utilized in principle, even if not convenient.

ii) Estimate the corrected flowrates in the enriching and stripping sections by means of relations 1 and 2. The values of σ_j and ψ_{j-1} are: 1, for the enriching section; θ, for the stripping section.

iii) For each component, define the corrected separation factor $(S_{p,q,i})_{co}$ given by Eq. 8; by means of the above-described iterative procedure, estimate the θ_i^* parameter. The resulting component flowrates in the section will be the corrected ones.

The biggest drawback which discourages using the above calculation procedure in practice is related to the cumbersomeness and instability one meets in estimating the multipliers θ_i^*, when dealing with nondistributed components in the feed sections.

In order to reduce these difficulties we approximated the whole procedure by making it similar to the one given for conventional columns:

A unique multiplier $\theta^* = \theta_1^* = \theta_2^* = \theta_3^* = \theta_i^* \ldots$ is defined for the separation factors $S_{j,i}$ of each component in the trays of the feed section; its value is searched according to the following definition: "Leaving unchanged, all the $S_{j,i}$ factors ($j < p$ and $j > q$) find the unique multiplier θ^* of all the separation factors $S_{j,i}$ of the feed section ($p \leq j \leq q$) so that the distillate flowrates, obtained by the solution of component material balances in the whole column, agree with the assigned values D."

This formulation, which may be considered as an obvious extension of the one found for conventional columns (they both coincide when $p = q$), is simpler and overcomes the drawbacks met with the preceeding one; in any case, the disagreement of the results diminishes as much as the $S_{j,i}$ profiles are similar.

The present approximated procedure may be summarized as follows:

i) Define for all the components $i = 1, ncp$

$$(S_{j,i})_{co} = (S_{j,i})_{ca}\, \theta^* \qquad \text{for } p \leq j \leq q$$

$$(S_{j,i})_{co} = (S_{j,i})_{ca} \qquad \text{for } j < p \text{ and } j > q$$

ii) Solve

$$L_{1,i}\left(1 + \frac{U_1}{L_1} + (S_{1,i})_{co}\right) - (S_{2,i})_{co} L_{2,i} = 0$$

$$-L_{np-1,i} + L_{np}(1 + (S_{np,i})_{co}) = 0$$

$$-L_{j-1,i} + L_{j,i}(1 + (S_{j,i})_{co}) - (S_{j+1,i})_{co} L_{j+1,i} = 0 \qquad j < p \text{ and } j > q$$

$$-L_{j-1,i} + L_{j,i}(1 + (S_{j,i})_{co}) - (S_{j+1,i})_{co} L_{j+1,i} - F_{j,i} = 0 \qquad p \leq j \leq q$$

iii) Compare the computed distillate flowrate with the assigned one, namely:

$$f(\theta^*) = \sum(di)_{co} - D = \sum(L_{1,i})_{co}\left(\frac{U_1}{L_1} + S_{1,i}\right) - D$$

Restart the sequence with a new θ^* if a nonacceptable disagreement is found.

The value of θ^* may be updated by means of several techniques capable of rooting a single equation in one unknown. We found a Newton Raphson technique convenient, because it proved to be stable and efficient as a consequence of the fact that $f(\theta^*)$ was always (as intuitively assumed) monotously dependent on θ^* with positive first derivatives.

The values of the derivatives were numerically calculated. As a rule, few iterations are required to root the equation. Therefore, the overall computing time spent is in general an insignificant quantity when compared with the time needed by the convergence of the entire model.

Nevertheless, alternative methods as Quasi Newton, Broyden or others can be successfully applied if necessary in order to save computing time.

COMPLEX COLUMNS

A complex column is one where one or more feed streams are present with at least one side stream (liquid or vapor).

According to the theta method, for each side stream a new additional multiplier is introduced in analogy with the definition of the primary one.

For the column of Figure 3, for instance, two new θ's are introduced following the definition:

$$\left(\frac{W_{l,i}}{di}\right)_{co} = \theta_l^W \left(\frac{W_{l,i}}{di}\right)_{ca} \quad \text{and} \quad \left(\frac{U_{m,i}}{di}\right)_{co} = \theta_m^U \left(\frac{U_{m,i}}{di}\right)_{ca}$$

As a consequence, the factors R_i are defined as:

$$R_i = \frac{(di)_{co}}{(di)_{ca}} = \frac{F_i}{(di)_{ca} + \theta(bi)_{ca} + \theta_l^W (Wl,i)_{ca} + \theta_m^U (U_{m,i})_{ca}}$$

where F_i indicates the total feed-flowrate of component i.

The parameters θ, θ_l^W, θ_m^U are usually calculated by imposing each component in agreement with the assigned values D, W_l, U_m, namely:

$$\sum(di)_{co} - D = 0$$

$$\sum(W_{l,i})_{co} - W_l = 0$$

$$\sum(U_{m,i})_{co} - U_m = 0$$

We will then refer to Figure 3, even though the analysis and the results will appear basically general and applicable to any other configuration.

The column may be divided into three sections, upper ($j < l$), central ($l \leq j \leq m$), and lower ($j > m$); l and m are the trays delimiting the section containing feed or side streams.

For the two extreme sections upper and lower, relations 1 and 2 may be used under the same conditions found both for a conventional column and for a multifeed conventional one.

Therefore, the corrected component flowrates may be calculated by means of Eqs. 1 and 2, where:

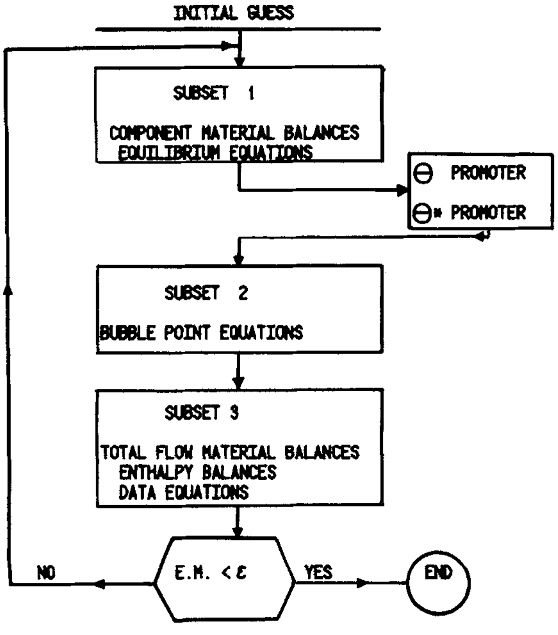

Figure 3. Complex column.

$$\sigma_j = \psi_{j-1} = 1 \qquad \text{for } 1 < j \le l$$

$$\sigma_j = \psi_{j-1} = \theta \qquad \text{for } m \le j \le np$$

The corrected molar fractions are calculated by Eqs. 5 and 6 or more simple by relations 3 and 4.

If we define, now, a global separation factor of the central section

$$S_{l,m,i} = \frac{V_{l,i}}{L_{m,i}}$$

then the section may be reduced to a single tray when solving component material balances in the lower and upper sections.

The set of balance equations stated in terms of liquid flowrate is:

$$L_{1,i}\left(1 + \frac{U_1}{L_1} + S_{1,i}\right) - S_{2,i}L_{2,i} = 0$$

$$-L_{np-1,i} + L_{np,i}(1 + S_{np,i}) = 0$$

$$-L_{l-1,i} + L_{m,i}(1 + S_{l,m,i}) - S_{m+1,i}L_{m+1,i} - \sum_{l=j}^{m} F_{j,i} + \\ + \theta_l^W (W_{l,i})_{ca} R_i + \theta_m^U (U_{m,i})_{ca} \cdot R_i = 0$$

$$-L_{j-1,i} + L_{j,i}(1 + S_{j,i}) - S_{j+1,i}L_{j+1,i} = 0 \qquad \begin{matrix} 1 < j < l \\ m < j < np \end{matrix}$$

By adopting as usual the subscripts *ca* and *co* to indicate separation factors giving respectively the calculated and the corrected flowrates, the result is the following:

$$(S_{j,i})_{co} = (S_{j,i})ca \qquad 1 \le j < l \text{ and } m < j \le np$$

$$(S_{l,m,i})_{co} = (S_{l,m,i})_{ca}\theta^{-1} \qquad (9)$$

The above relation may be considered in terms of a new formulation of the primary θ multiplier for complex columns, while the additional θ_l^W and θ_m^U still maintain the original one.

Therefore, "leaving unchanged all the separation factors $S_{j,i}$ ($j < l$ and $j > m$) find the multiplier θ^{-1} of the separation factors $S_{l,m,i}$ of the central section, and the multipliers θ_l^W and θ_m^U in order that, after solving the component material balances in the upper and lower sections, the calculated component flowrates in the distillate, and in the side streams are in agreement with the assigned values D, W_l, U_m."

For the trays of the central section, the corrected component flowrates are calculated with a different approach, because the relations 1 and 2 are no longer valid. For example, if those relations were applied to tray l, the component material balance around it would give.

$$(W_{l,i})_{co} + (V_{l,i})_{co} + (L_{l,i})_{co} = (L_{l-1,i})_{co} + (V_{l+1,i})_{co}$$

which may be rewritten as

$$(V_{l,i})_{ca}R_i + (W_{l,i})_{ca}\theta_l^W R_i + (L_{l,i})_{ca}\,\psi_l R_i = (L_{l-1,i})_{ca}R_i \\ + (V_{l+1,i})_{ca}\sigma_{l+1}R_i$$

But

$$(V_{l,i})_{ca} + (W_{l,i})_{ca} + (L_{l,i})_{ca} = (L_{l-1,i})_{ca} + (V_{l+1,i})_{ca}$$

than

$$(\sigma_{l+1} - 1) = \left(\frac{L_{l,i}}{V_{l+1,i}}\right)_{ca}(\psi_l - 1) + \left(\frac{W_{l,i}}{V_{l+1,i}}\right)_{ca}(\theta_l^W - 1)$$

If the values σ_{l+1} and ψ_l are independent of i, either the ratios $(L_{l,i}/V_{l+1,i})_{ca}$, $(W_{l,i}/V_{l+1,i})_{ca}$ are constant and independent from i (which is obviously an unacceptable condition), or θ_l^W is always unitary (which is contradicting the definition of the same θ_l^W multiplier).

Based on the preceeding proof, the following conclusions are drawn: first, accepting the independence of σ_l and ψ_{l+1} from the component i implicate imposing unreliable condition; secondly, the molar fractions have to be calculated by means of Eqs. 5 and 6 through a preliminary calculation of the corrected component flowrates.

It should be noted that at this point the theta multipliers, $\theta, \theta_l^W, \theta_m^U$ have known values which have been calculated in principle either by means of the original theta formulation (Holland, 1963) or by the new one presented in this paper.

This fact leads to the conclusion that the corrected component flowrates inside the central section only depend upon the values of $S_{j,i}$ inside the section.

This last statement reduces the present problem to the analog met for a multifeed conventional column. Therefore, for each component we may find a multiplier θ_i^*, of the $S_{j,i}$ factors ($l \le j \le m$) so that the computed value $S_{l,m,i}$ is in agreement with relation 9.

The θ_i^* may be searched for each component by an iterative procedure through the steps:

i) Define $(S_{j,i})_{co} = (S_{j,i})_{ca} \cdot \theta_i^* \qquad l \le j \le m$

ii) Solve

$$-(L_{l-1,i})_{ca} \cdot R_i + L_{l,i}(1 + (S_{l,i})_{co}) + (W_{l,i})_{ca} \cdot R_i \cdot \theta_l^W \\ - (S_{l+1,i})_{co}L_{l+1,i} = 0$$

$$-L_{j-1,i} + L_{j,i}(1 + (S_{j,i})_{co}) - S_{j+1,i}L_{j+1,i} - F_{j,i} = 0 \\ l < j < m$$

$$-L_{m-1,i} + L_{m,i}(1 + (S_{m,i})_{co}) + (U_{m,i})_{ca}R_i\theta_m^U \\ - (V_{m+1,i})_{ca}R_i\theta = 0$$

$$V_{j,i} = (S_{j,i})_{co}L_{j,i} \qquad l \le j \le m$$

iii) Compare the computed $S_{l,m,i} = (S_{l,i})_{co} \cdot L_{l,i}/L_{m,i}$ with the corrected one given by eq. 9.

Restart the sequence with a new θ_i^*, if an unacceptable disagreement is found, otherwise stop the sequence. The component flowrates obtained by step ii) will be the corrected ones.

In summary the estimation of corrected flowrates in each tray of the complex column, Figure 3, is done as follows:

i) Calculate all the parameters $\theta, \theta_l^W, \theta_m^U$ according to well-known formulations (Holland, 1963). The new one presented here may be utilized even if not convenient.

ii) Compute the corrected flowrates in the upper and lower sections by means of Eqs. 1 and 2. The values of σ_j and ψ_{j-1} are: 1 for the upper section, θ for the lower section.

iii) Compute the corrected output side streams flowrates by means of the additional theta multipliers:

$$(W_{l,i})_{co} = \theta_l^W (W_{l,i})_{ca} \cdot R_i$$

$$(U_{m,i})_{co} = \theta_m^U (U_{m,i})_{ca} \cdot R_i$$

iiii) For each component define the corrected separation factors $(S_{l,m,i})_{co}$ given by Eq. 9; estimate the θ_i^* parameters by means of the above-described iterative procedure. The resulting component flowrates inside the central section are the corrected ones.

The calculation of θ_i^* multipliers is unstable and cumbersome in the same situation considered for multifeed conventional columns. Therefore, a more stable and simpler methodology, besides the above-described one, has been developed which still gives good results.

With reference to a general configuration of a complex column with side streams and feed streams in each tray of a central section delimited by trays l and m, the approximate methodology is the one described here below.

A unique multiplier $\theta^* = \theta_1^* = \theta_2^* = \theta_i^*$ is defined for the separation factors $S_{j,i}$ of each component in the trays of the central section.

The original definitions of the additional theta multipliers,

$$(W_{j,i})_{co} = \theta_j^W (W_{j,i})_{ca} \cdot R_i$$

and (10)

$$(U_{j,i})_{co} = \theta_j^U (U_{j,i})_{ca} \cdot R_i \qquad l \leq j \leq m$$

are replaced by the following:

$$\left(\frac{W_j}{V_j}\right)_{co} = \theta_j^{*W} \left(\frac{W_j}{V_j}\right)_{ca}$$

and (11)

$$\left(\frac{U_j}{L_j}\right)_{co} = \theta_j^{*U} \left(\frac{U_j}{L_j}\right)_{ca}$$

The two definitions would be exactly the same if relations 1 and 2 were true. Therefore Eq. 11 may be considered as an equivalent formulation of Eq. 10 within the assumptions made by theta method.

In fact, according to relation 2

$$(W_{j,i})_{co} = (V_{j,i})_{co} \cdot \left(\frac{W_j}{V_j}\right)_{co} = (V_{j,i})_{ca} \cdot R_i \cdot \psi_j \left(\frac{W_j}{V_j}\right)_{co}$$

For θ_j^W definition it results:

$$(W_{j,i})_{co} = \theta_j^W (W_{j,i})_{ca} \cdot R_i = \theta_j^W (V_{j,i})_{ca} \cdot \left(\frac{W_j}{V_j}\right)_{ca} \cdot R_i \cdot \frac{\psi l}{\psi l}$$

The combination of the two equations gives the proof:

$$\left(\frac{W_j}{V_j}\right)_{co} = \frac{\theta_j^W}{\psi l} \left(\frac{W_j}{V_j}\right)_{ca} = \theta_j^{*W} \left(\frac{W_j}{V_j}\right)_{ca}$$

The second of Eq. 11 may be proved by analogous steps.

The values $\theta^*, \theta_j^{*W}, \theta_j^{*U} (l \leq j \leq m)$ are searched through the following steps:

i) Define for all component i:

$$(S_{j,i})_{co} = (S_{j,i})_{ca} \theta^* \qquad l \leq j \leq m$$

$$(S_{j,i})_{co} = (S_{j,i})_{ca} \qquad j < l \text{ and } j > m$$

ii) Define:

$$(W_j/V_j)_{co} = \theta_j^{*W} (W_j/V_j)_{ca}$$

and $l \leq j \leq m$

$$(U_j/L_j)_{co} = \theta_j^{*U} (U_j/L_j)_{ca}$$

iii) Solve tray-by-tray component material balances for the entire column.

iv) Compare the computed total flowrates of the distillate and side streams with the assigned values D, W_j^W, U_j^U.

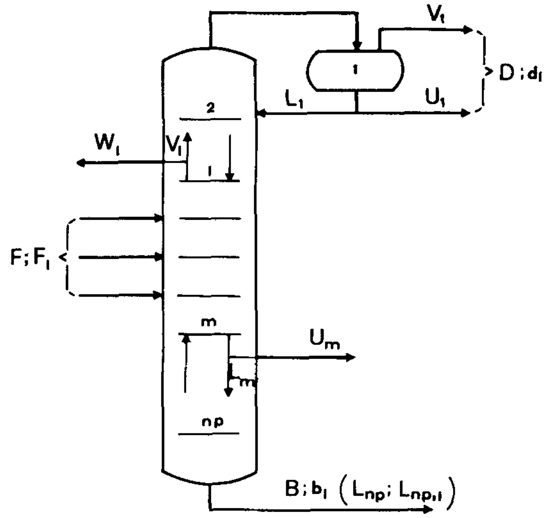

Figure 4. Decomposition and iterative calculation for solving distillation column models.

$$
\begin{aligned}
f_1(\theta^*, \theta_j^{*W}, \theta_j^{*U}, \ldots) &= \textstyle\sum (di)_{co} - D \\
f_2(\theta^*, \theta_j^{*W}, \theta_j^{*U}, \ldots) &= \textstyle\sum (W_{j,i})_{co} - W_j \qquad (12) \\
f_3(\theta^*, \theta_j^{*W}, \theta_j^{*U}, \ldots) &= \textstyle\sum (U_{j,i})_{co} - U_j \\
&\vdots
\end{aligned}
$$

Restart the sequence with new values $\theta^*, \theta_j^{*W}, \theta_j^{*U}$, if an unacceptable disagreement is found.

A Newton Raphson linearization technique has been found to be stable and efficient way to solve the above system (Eq. 12) in the unknown theta multipliers. The derivatives of the functions for the unknowns, have been calculated numerically and updated after each iteration.

Generally, few iterations are required to solve the system; therefore, the overall computing time spent to use this methodology normally is a small quantity when compared with the time needed by the convergence of the entire model.

Nevertheless, if necessary, alternative methods for the solutions of the system (Eq. 12) like Quasi Newton, Broyden or others may be successfully applied to save computing time.

COMPARATIVE EXAMPLES

Four examples will be presented to substantiate the improvement given to the θ-convergence promoter. For this purpose, a θ-method program for the simulation of distillation columns has been built up according to these main rules:

- Component material balance equations are solved by Boston and Sullivan (1972) algorithm.
- Bubble point equations are solved for tray temperatures by the Kb method stated by Holland (1963).
- Enthalpy and total flow balance equations are solved by "constant composition" method as described by Holland (1963). In this case, partial molar enthalpies have been always analytically calculated.

To this structure, either the original θ-convergence promoter (Holland, 1963) or the improved one (θ^*-promoter by this paper) may be applied.

The entire iterative procedure is synthetically shown in Figure 4.

An error measure of the computation procedure has been defined after the solution of subset 3) according to the following reaction:

$$E.M. = \frac{\sum_{1=j}^{np} \left\{ \left| \left(\sum_{1=i}^{ncp} L_{j,i} \right)_{ca} - L_j \right| + \left| \left(\sum_{1=i}^{ncp} V_{j,i} \right)_{ca} - V_j \right| + \sum_{1=i}^{ncp} \left| S_{j,i} (L_{j,i})_{ca} - (V_{j,i})_{ca} \right| \right\}}{\sum_{1=j}^{np} F_j}$$

TABLE 1. DATA SET OF EXAMPLE 1

Number of Trays = 10; Total Condenser $U_1 = 0.2$
Liquid Reflux $L_1 = 1.0$; Column Pressure = 20.7
Liquid Sidestreams $U_3 = 0.1$ and $U_7 = 0.2$

	Feed Tray: 5
Ethane	0.05
Propane	0.2
N-Butane	0.4
N-Pentane	0.2
N-Hexane	0.1
N-Decane	0.05
Temperature	378.1
Pressure	20.7

Initial Guess Profiles

$T_1 = 324.0$	$T_5 = 378.0$	$T_{10} = 378.0$
$V_1 = 0.0$	$V_5 = 1.2$	$V_{10} = 1.2$

Units: T (K), P (1.E + 5 Pa), Flows (mol/time)

TABLE 2. COMPARATIVE RESULTS FROM EXAMPLE 1

θ Method

Iter.	θ	θ-Promoter θ_3	θ_7	E.M.	θ^*	θ^*-Promoter θ_3^*	θ_7^*	E.M.
1	0.64107	0.50582	0.49047	17.784	1.1739	0.58501	0.76428	11.882
2	58.112	1.7363	9.2047	10.867	0.81425	1.0193	1.0026	2.4115
3	0.46370	0.94422	0.50989	8.8627	1.0272	1.0271	1.0079	0.25617
4	1.4631	1.0162	1.4368	3.1677	0.99765	0.99635	1.0001	0.02826
5	0.86174	0.99865	0.86364	1.5976	1.0002	1.0003	0.99988	0.00457
6	1.0638	1.0003	1.0641	0.63108	0.99996	1.0000	0.99999	0.00247
7	0.97542	1.0001	0.97519	0.26855	0.99996	1.0000	0.99999	0.00013
8	1.0101	0.99996	1.0102	0.10812				
9	0.99599	1.0000	0.99595	0.04402				
10	1.0016	0.99999	1.0016	0.01782				
CPU	3.9301				3.9298			

B.P. Method

Iter.	D_{CA}	E.M.	θ-Promoter θ	θ_3	θ_7	E.M.	θ^*	θ^*-Promoter θ_3^*	θ_7^*	E.M.
1	0.0562	19.58	0.6410	0.5058	0.4904	13.41	1.173	0.5850	0.7641	12.12
2	0.1505	11.09	2.414	1.264	2.418	5.832	0.8069	1.0213	1.009	4.249
3	0.2331	2.459	0.7637	0.9911	0.7689	3.010	1.042	1.0291	1.005	0.4377
4	0.2174	0.7018	1.071	0.9987	1.070	0.7010	0.9951	0.9946	1.000	0.0587
5	0.2076	0.2862	0.9821	1.000	0.9820	0.1985	1.000	1.000	0.9997	0.0088
6	0.2035	0.1381	1.004	0.9999	1.004	0.0524	0.9999	0.9999	1.000	0.0016
7	0.2017	0.0649	0.9986	0.9999	0.9987	0.0157	1.000	1.000	1.000	0.0007
8	0.2008	0.3121	1.000	0.9999	1.000	0.0034				
9	0.2004	0.0149								
10	0.2001	0.0069								
CPU	5.928		5.868				5.817			

TABLE 3. DATA SET OF EXAMPLE 2 (HENLEY, 1981)

Number of Trays: 16	Partial Condenser: $V_1 = 15.0$, $U_1 = 5.0$
Reflux $L_1 = 150$	Column Pressure: 16.5
Sidestreams:	$U_3 = 3.0$ and $W_{13} = 37.0$
Thermal Duties:	$Q_3 = -211.0\text{ E} + 6$

Feeds	Tray 6	Tray 9
Ethane	2.5	0.5
Propane	14.0	6.0
N-Butane	19.0	18.0
N-Pentane	5.0	30.0
N-Hexane	0.5	4.5
Temperature	350.0	383.0
Pressure	20.7	19.0

Initial Guess Profiles:

$T_1 = 255.0$	$T_6 = 305.0$	$T_{16} = 333.0$
$V_1 = 15.0$	$V_2 = 170.0$	$V_{16} = 170.0$

Units: T(K), P(1E + 5 Pa), Flows (mol/s) Duty (J/s)

TABLE 4. COMPARATIVE RESULTS FROM EXAMPLE 2

θ Method

		θ-Promoter				θ^*-Promoter		
Iter.	θ	θ_3	θ_{13}	E.M.	θ^*	θ_3^*	θ_{13}^*	E.M.
1	0.00087	0.00298	0.04539	6919.2	2.3527	1.4704	0.12771	53.195
2	28.280	14.481	1.2862	21.898	0.81998	0.62267	1.0182	10.277
3	0.34293	0.42363	1.0858	21.665	1.0709	1.1392	1.0199	2.6689
4	2.0629	1.9194	1.0376	8.7342	0.97192	0.95859	0.99216	1.0810
5	0.72558	0.74324	0.99156	5.6848	1.010	1.0131	1.0038	0.37079
6	1.1764	1.1669	1.0054	2.4757	0.99591	0.99586	0.99845	0.13567
7	0.93034	0.93294	0.99871	1.2028	1.0015	1.0013	1.0006	0.04787
8	1.0333	1.0324	1.0007	0.53057	0.99946	0.99957	0.99979	0.01682
9	0.98575	0.98606	0.99975	0.23752	1.0002	1.0001	1.0001	0.00584
10	1.0063	1.0062	1.0001	0.10288				
CPU	4.9152				5.1032			

B.P. Method

			θ-Promoter				θ^*-Promoter			
Iter.	D_{CA}	E.M.	θ	θ_3	θ_{13}	E.M.	θ^*	θ_3^*	θ_{13}^*	E.M.
1	2.493	18.17	0.0009	0.0030	0.0454	7617	2.353	1.470	0.1277	53.19
2	3.313	8.237	3.377	3.202	0.9541	13.77	0.9901	0.9532	0.8743	2.517
3	9.486	3.863	0.8595	0.8670	1.047	2.403	1.001	1.002	0.9836	0.1411
4	15.07	3.387	1.023	1.023	1.006	0.4136	0.9990	1.001	0.9995	0.0194
5	16.81	2.304	0.9951	0.9951	1.000	0.0912	0.9999	1.000	1.000	0.0041
6	17.65	1.545	1.001	1.000	0.9999	0.0094	1.000	1.000	1.000	0.0017
7	18.15	1.126	0.9999	0.9999	0.9999	0.0028				
8	18.51	0.8632								
9	18.77	0.6829								
10	18.98	0.5497								
CPU	6.511		5.747				5.350			

The calculation scheme, Figure 4 (if the convergence promoter is disregarded), is basically common to all the methods which adopt a partitioning of the whole equation system describing the distillation column. Distinction being the way each subset is solved. Among these methods, one of the most frequently used seems to the B.P. (Wang and Henke, 1966) method.

As the θ-promoter or the improved θ^*-promoter is structurally independent of the algorithm chosen for the solution of each equation subset, a practical possibility exists of implementing both convergence promoters an a B. P. structure [This type of implementaton is not a new once since the resulting calculation procedure (if referred to the θ-promoter) is similar to a pioneer version of the θ-method (Lyster et al., 1959).]

In this way, we mainly wanted to verify that better convergence characteristics of the θ^*-promoter over the θ-promoter are kept when these promoters are applied to a method different from the θ-one.

Each example reported here has been solved by five different runs according to the following procedures: 1) θ method with a θ-promoter; 2) θ-method with θ^*-promoter; 3) B.P. method, 4) B.P. method with θ-promoter; and 5) B.P. method with θ^*-promoter.

TABLE 5. DATA SET OF EXAMPLE 3 (FREDESLUND, 1977)

Trays Number: 30 Partial Condenser $V_1 = 0.4$
Liquid Reflux $L_1 = 0.7828$ Column Pressure = 1.013
Sidestream $U_{21} = 0.2$

	Feed Tray 8	Feed Tray 24
Ethanol	0.25	
Propanol	0.125	0.125
Water	0.125	0.125
Acetic Acid		0.25
Temperature	354.0	368.0
Pressure	1.013	1.013

Initial Guess Profiles:
$T_1 = 355.0$ $T_{23} = 361.0$ $T_{24} = 367.0$ $T_{30} = 370.0$
$V_1 = 0.4$ $V_2 = 1.2$ $V_8 = 1.2$ $V_9 = 0.67$ $V_{24} = 0.67$
$V_{25} = 0.7$ $V_{30} = 0.8$
Units: T(K), P (1.E + 5 Pa), Flows (mol/time)

The set of data for four examples have been reported in Tables 1, 3, 5 and 7, while the corresponding comparative results for ten iterations are shown in Tables 2, 4, 6 and 8. Table 1 is a one-feed two-sidestreams column; Table 3 refers to a two-feeds and two-sidestreams column taken from Henley (1981).

Table 5 (two-feeds column) and Table 7 (one-feed and one-sidestream column) are taken from Fredenslund (1977).

Equilibrium constants and molar enthalpies have been calculated by RKS (Soave, 1972) equation of state for Tables 1 and 3. Unifac method for liquid activity coefficient combined with a virial equation of state (Haiden and O'Connel, 1975) for vapor fugacity coefficient are used for the calculation of equilibrium constants in the remaining examples. In these cases, molar enthalpies have been estimated by polynomial expressions only depending on temperature.

All the data have been taken from Reid et al. (1977). The data set of each example also include the initial guess of temperature and total vapor flowrate in some trays; in the intermediate ones a linear interpolation has been assumed. The initial guess of total liquid flowrates has been derived by means of overall material balances, while the equilibrium constants have been initiated by assuming the ideal behavior of the mixture.

Tables 2, 4, 6 and 8 report the results obtained by executing the examples by five different runs as described above. Exception is made by the fourth example which diverged in the cases adopting the θ-method, due, probably, to the use of the Kb method. Better results, Table 8, were obtained, in fact, by substituting it with the bubble equations of B.P. method.

For each procedure adopted, the error measure (E.M.) and the following values of its main characteristic parameters are reported: θ or θ^* when adopting θ or θ^* convergence promoter, and the value of the calculated top distillate flowrate (D_{ca}) when the pure B.P. method is used. The total computing time (in s) is reported on the last row denoted by the item CPU. The runs were executed by an Univac 1100/60 computer.

All the examples show the benefit of adopting the θ^*-promoter.

The values quoted by CPU rows show that the computing time increment required by the θ^*-promoter is a nonsignificant figure

TABLE 6. COMPARATIVE RESULTS FROM EXAMPLE 3

θ Method

		θ-Promoter			θ*-Promoter	
Iter.	θ	θ_{21}	E.M.	θ^*	θ^*_{21}	E.M.
1	1.9426	2.3207	28.164	0.82752	1.7927	15.250
2	1.5934	1.8429	20.964	0.90949	1.3957	13.130
3	1.2761	1.3691	12.544	0.94386	1.2720	9.6978
4	1.2454	1.3282	11.821	0.95774	1.1853	7.0610
5	1.3045	1.3876	13.296	0.97100	1.1119	4.7530
6	1.0813	1.1013	5.1510	0.99354	1.0324	2.1523
7	1.1732	1.2268	9.5031	0.99281	1.0300	1.7268
8	1.2263	1.2562	10.480	0.99163	1.0266	1.4455
9	1.2726	1.3494	13.081	1.0062	0.98176	1.4991
10	1.2240	1.2687	15.703	1.0012	0.99709	1.1792
CPU	262.5			255.4		

B.P. Method

			θ-Promoter				θ*-Promoter	
Iter.	D_{CA}	E.M.	θ	θ_{21}	E.M.	θ^*	θ^*_{21}	E.M.
1	0.2627	30.73	1.943	2.321	29.30	0.8275	1.793	46.72
2	0.5011	11.81	1.581	1.821	22.17	0.9272	1.385	32.66
3	0.5119	12.88	1.280	1.374	12.92	0.9645	1.174	15.96
4	0.4788	10.01	1.244	1.326	13.12	0.9814	1.089	8.806
5	0.4705	11.20	1.297	1.378	14.69	0.9923	1.037	4.687
6	0.4460	6.305	1.092	1.115	6.312	1.001	1.004	1.925
7	0.4904	18.09	1.175	1.223	11.23	1.004	0.9883	1.697
8	0.4383	12.02	1.215	1.242	11.67	1.003	0.9884	1.667
9	0.5523	43.21	1.323	1.417	16.09	1.002	0.9911	1.382
10	0.5175	40.16	1.221	1.262	17.23	1.001	0.9933	0.9070
CPU	273.4		274.1			266.1		

TABLE 7. DATA SET OF EXAMPLE 4 (FREDESLUND, 1977)

Trays Number: 21; Total Condenser $U_1 = 0.1224$
Liquid Reflux $L_1 = 0.9914$; Column Pressure = 1.013

	Feed Tray 10	Feed Tray 15
Methylcyclohexane		0.1163
Toluene		0.1163
Phenol	0.7674	
Temperature	454.0	376.0
Pressure	1.013	1.013

Initial Guess Profiles:
$T_1 = 373.0$ $T_{21} = 425.0$
$V_1 = 0.0$ $V_2 = 1.114$ $V_{21} = 1.114$
Units: T(K), P(1.E+5 Pa), Flows (mol/time)

when compared with the time spent to conclude the calculations. In fact, the θ^* promoter demands something more which becomes vanishingly small along with the iterations. (In order to have meaningful comparisons, the θ^*- and θ-promoters have to be compared in the ambit of the same method B.P. or θ.)

Moreover, due to better convergence characteristics, the computing time increment may be compensated either by a minor time amount required by the remaining phases of the calculation procedure, or by a reduced number of iterations. Thus, a smaller global computing time may be obtained.

NOTATION

b = bottom product component molar flowrate
B = bottom product total molar flowrate
d = distillate product component molar flowrate
D = distillate product total molar flowrate
f = residual of the equation in the thetas unknowns
F = total feed molar flowrate
L = liquid stream molar flowrate
ncp = total number of components
np = total number of theoretical trays (condenser and reboiler included)
P = pressure
R = ratio between the corrected and the calculated component distillate flowrate
S = separation factor
T = temperature
U = liquid sidestream molar flowrate
V = vapor stream molar flowrate
X = liquid molar fraction
Y = vapor molar fraction
W = vapor sidestream molar flowrate

TABLE 8. COMPARATIVE RESULTS FROM EXAMPLE 4

	Iter.			B.P. Method				θ Method		
Iter.	D_{CA}	E.M.	θ	E.M.	θ^*	E.M.	θ	E.M.	θ^*	E.M.
1	0.2037	17.02	3.049	20.05	0.8062	29.54	3.049	15.60	0.8062	31.07
2	0.1384	16.54	0.1321	138.8	1.224	4.130	0.0377	341.9	1.609	0.452
3	0.1146	7.827	9.732	25.28	0.7803	2.512	40.19	24.92	0.5449	2.812
4	0.1335	5.427	0.2120	77.47	0.8933	1.301	0.0190	732.1	1.031	1.178
5	0.1496	7.997	6.809	23.42	0.9482	0.6338	24.84	26.34	0.9849	0.7299
6	0.1459	5.585	0.2470	64.85	0.9703	0.3349	0.0687	191.7	0.9766	0.4475
7	0.1310	2.449	5.523	22.27	0.9846	0.1607	24.50	23.14	1.018	0.2531
8	0.1281	0.9643	0.2683	59.11	0.9951	0.0762	0.0500	274.3	1.013	0.0791
9	0.1300	1.454	4.501	20.95	1.000	0.0513	21.73	24.39	0.9996	0.0337
10	0.1294	1.213	0.3117	48.41	1.000	0.0358	0.0640	211.3	0.9982	0.0283
CPU	29.46		29.73		29.83		11.73		11.79	

Greek Letters

ψ = correcting factor of the component liquid molar flowrate
σ = correcting factor of the component vapor molar flowrate
θ = theta multiplier

Superscripts

U = referred to a liquid-side stream
W = referred to a vapor-side stream
$*$ = theta parameter used in the proposed methodology

Subscripts

ca = calculated value
co = corrected value
f = feed tray number
i,k = component index
j,l,m,p,q = tray number
np = bottom tray

LITERATURE CITED

Billingsley, D. S., "On the numerical solutions of Problems in Multicomponent Distillation of the Steady State II," *AIChE J.*, **16**, 3 (1970).

Boston, J. F., and S. L. Sullivan, Jr., "An improved Algorithm for Solving Mass Balance equations in Multistage Separation Processes," *Can. J. of Chem. Eng.*, **50**, 664 (1972).

Fredenslund, A., J. Gmehling, and P. Rasmussen, "Vapor-Liquid Equilibria Using UNIFAC," Elsevier, Amsterdam (1977).

Gallun, S. E., and C. D. Holland, "Solve more Distillation Problems. Part 5. For Highly Non Ideal Solutions," *Hydrocarbon Processing*, **55**, 6 (1976).

Hayden, J. G., and J. P. O'Connel, "A Generalized Method for Predicting Second Virial Coefficients," *Ind. Eng. Chem. Process Des. Dev.*, **14**, 3 (1975).

Henley, E. J., "Equilibrium stage Separation Operations in Chem. Engineering," Wiley, N.Y.

Hess, F. E., S. E. Gallun, S. E. Bentzen, and G. W. Holland, "Solve more Distillation Problems. Part 8: Which Method to Use," *Hydrocarbon Processing*, **56**, 6 (1977).

Holland, C. D., "Multicomponent Distillation," Prentice-Hall Inc., Englewood Cliffs, NJ (1963).

Holland, C. D., and P. T. Eubank, "Solve more Distillation Problems. Part 2: "Partial molar enthalpies calculated," *Hydrocarbon Processing*, **53**, 11 (1974).

Holland, C. D., and P. G. Pendon, "Solve more Distillation Problems. Part 1. Improvements give Exact Answer," *Hydrocarbon Processing*, **53**, 7 (1974).

Holland, C. D., and M. S. Kuk: "Solve more distillation problems. Evaluate existing columns," *Hydrocarbon Processing*, **54**, 7 (1975).

Holland, C. D., G. P. Pendon, and S. E. Gallum, "Solve more distillation problems. Part 3: Application to absorbers," *Hydrocarbon Processing*, **54**, 1 (1975).

Lyster, W. N., S. L. Sullivan, D. S. Billingsley, and C. D. Holland, "Figure distillation This new way. Part 1: New Convergence Method will Handle Many cases," *Petroleum Refiner*, **38**, 6 (1975).

Pierucci, S. J., E. M. Ranzi, G. E. Biardi, and M. Dente, "T-method computes distillation," *Hydrocarbon processing*, **60**, 9 (1981).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, "The properties of Gases and Liquids," McGraw Hill, 3rd ed. (1977).

Soave, G., "Equilibrium Constants from a modified Redlich-Kwong equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Wang, J. C., and G. E. Henke, "Tridiagonal matrix for distillation," *Hydrocarbon Processing*, **45**, 155 (1966).

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A Residence-Time Model for Trickle-Flow Reactors Incorporating Incomplete Mixing in Stagnant Regions

A model for the liquid-phase residence time in a trickle-flow reactor has been derived and experimentally verified using a tracer input. The model, termed the Ideal Plug Flow Stagnancy Model, postulates that the prime liquid-phase dispersive mechanism in such reactors is the interchange between the dynamic and stagnant regions. Unlike previous models, however, it does not require the assumption of perfect mixing in the stagnant zones. While the results of the study confirm that the mixing is incomplete, they show clearly that back mixing rather than molecular diffusion is the dominant exchange mechanism.

KIN-MUN KAN and
P. F. GREENFIELD

Department of Chemical Engineering
University of Queensland
St. Lucia, Qld, 4067, Australia

SCOPE

Trickle-bed catalytic reactors find applications in situations where it is necessary or expedient to contact a gas and a liquid phase in a fixed-bed reactor. Such reactors are usually operated in the cocurrent mode to allow high flowrates of liquid and gas, which would cause flooding in countercurrent situations. Of course, cocurrent operation implies that the gas-liquid transfer resistance is not rate-limiting. The boundary between the gas and liquid phases is not fixed, but fluctuates in a highly complex manner as the fluids interact in finding their way through the packed bed.

Not surprisingly, the commercial design of trickle-bed reactors is based on extensive pilot plant and existing commercial

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Kin-Mun Kan is presently at the Ampol Research Laboratories, Lytton, Qld, Australia.

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