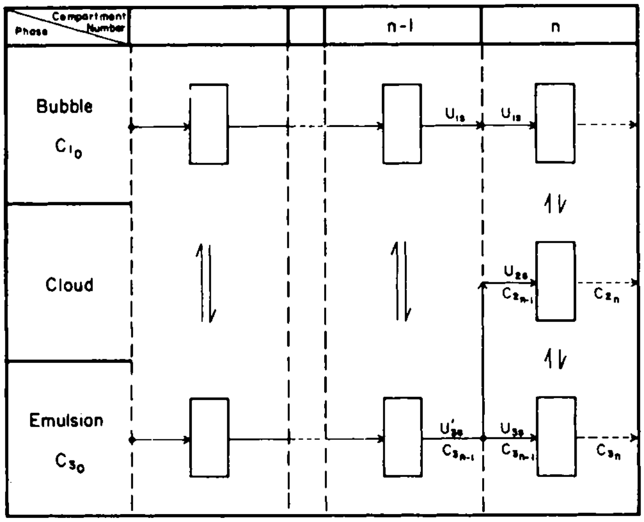

Figure A1. Compartments representation of slow bubble stage.

The volumes occupied by the bubble and emulsion phases in the nth compartment may be obtained from a straightforward simplification of Eqs. 22 and 26–29 as:

$$N = \frac{6S(\epsilon - \epsilon_{mf})}{\pi D_{1_n}^2 (1 - \epsilon_{mf})}$$

$$V_{1_n} = N(1/6)\pi D_{1_n}^3$$

$$V_{3_n} = SD_{1_n} - V_{1_n}$$

APPENDIX 2: TWO PHASE THEORY FOR ESTIMATING SUPERFICIAL GAS VELOCITIES

Determination of the superficial gas velocities in each phase is the same here as that presented by Fan and Fan (1980),

$$U_{1s} = U_o - U_{mf}$$

$$\bar{\delta}_1 = \frac{U_{1s}}{\bar{U}_1 \epsilon_1}$$

$$\bar{\delta}_2' = \frac{3U_{mf}}{\epsilon_{mf}\bar{U}_1 - U_{mf}}$$

$$\bar{\delta}_2 = \bar{\delta}_2' \bar{\delta}_1$$

$$U_{2s} = \frac{\bar{\delta}_2}{\bar{\delta}_1} \frac{\epsilon_2}{\epsilon_1} U_{1s}$$

$$U_{3s} = U_{mf} - U_{2s}$$

and $\bar{U}_1$ is computed from Eq. 10. Note that under these assumptions it necessarily follows that $Y = 1$ in Eq. 20.

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An Approximate Mathematical Model for Three-Phase Multistaged Separators

An approximate method is developed for the simulation of three-phase, multistaged multicomponent separators in which one of the two liquid phases can be regarded as being constituted of almost one component only.

Comparisons with the complete three-phase model shows a large reduction of the required computation time and a satisfactory agreement of the obtained results.

G. BUZZI FERRARIS
and M. MORBIDELLI
Istituto di Chimica Industriale
Politecnico di Milano
20133 Milano, Italy

SCOPE

Multistaged, multicomponent separators in which three phases coexist are present in many industrial processes. The mathematical model of these units consists on a large algebraic system of non linear equations, and therefore all the numerical methods proposed so far in the literature for their solution require a relatively large amount of computation time (Block and Hegner, 1976; Buzzi Ferraris and Morbidelli, 1981).

This work aims at providing a simplified approach to this problem so as to solve it more efficiently, even if approximately. In fact, in many cases of import, when the liquid phase separation occurs, each component is soluble almost only in one of the two immixible liquid phases. This is the case, for example, of many organic aqueous solutions, in which two liquid phases can coexist: an organic phase, in which all the components are present, and an aqueous phase in which all the organic components are slightly soluble. In these cases it is possible to consider the aqueous liquid phase as constituted of pure water. This

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Correspondence concerning this paper should be addressed to G. Buzzi Ferraris. M. Morbidelli is with Ist. di Chimica Fisica, Politecnico di Milano, Italy.

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approximation can be applied to all those cases in which a liquid, multicomponent phase is present in the whole distillation column; in some stages, the separation of another liquid phase constituted of almost only one component occurs.

CONCLUSIONS AND SIGNIFICANCE

Two numerical methods, the bubble point method and the global Newton-Raphson method, for the simulation of three-phase distillation columns in which one of the two liquid phases can be approximate as pure, are developed. These methods make it possible to largely reduce the computation time with respect to the complete methods (Block and Hegner, 1976; Buzzi Ferraris and Morbidelli, 1981) due to the reduced size of the solving system of equations. In fact the proposed approximation makes it possible to neglect all the equations describing the second liquid phase composition, and therefore the amount of the required computation time is of the same order of a two-phase distillation problem.

As a consequence also the thermodinamic description of the system is largely simplified. Namely the activity coefficients are required to cover only a small portion of the state diagram, in particular that related to the liquid phase described as multicomponent.

Another simplification coming out from the proposed approximation is that the trivial solution (that is the solution in which the two liquid phases have the same compositions) is obviously always automatically avoided. In the complete three-phase model instead this difficulty needs to be overcome with a suitable solution strategy (Buzzi Ferraris and Morbidelli, 1981).

The proposed methods can also be successfully employed to estimate the first trial for the solution procedure of the complete three-phase problem. In fact a large amount of the computation time required by the exact methods is devoted to the evaluation of the phase pattern of the column. This evaluation is largely simplified in the proposed methods and the estimated phase pattern is usually very close to the correct one. Therefore the so evaluated first trial solution can greatly reduce the computation time of the complete methods.

Careful attention has been given to allow the solution of problems with different choices of the specified and the unspecified variables a possibility that can be very useful in the operation conditions optimization of separation units in which three phases can coexist.

Finally some examples of application of the developed methods are reported.

Comparison of the so obtained results with those obtained by the exact procedure shows the reliability of the proposed approximation. The accuracy appeared to be satisfactory also in those cases in which the solubility of the present components in the liquid phase, approximate as a pure phase, was significant.

BASIC EQUATIONS

The system under consideration consists of a mixture of M components, which at equilibrium conditions can be split in three phases: one vapor and two liquids. If all the components from 1 to $(M - 1)$ are slightly soluble in one of the two liquid phases, it is possible to approximate this phase as constituted of the pure Mth component (in the following this phase will be indicated with an apex). The other liquid phase and the vapor phase will be considered, as usual, as multicomponent mixtures of M components.

The mathematical model of the multistaged separator is constituted of the following set of equations, with reference to Figure 1:

—Material balance of the ith component on the jth stage ($L_0 = L'_0 = V_{N+1} = 0$):

$$L_{j-1}x_{i,j-1} - (L_j + U_j)x_{i,j} - (V_j + W_j)y_{i,j} + V_{j+1}y_{i,j+1} + F_j z_{i,j} = 0 \qquad (i = 1, M - 1; j = 1, N) \quad (1)$$

$$L_{j-1}x_{M,j-1} + L'_{j-1} - (L_j + U_j)x_{M,j} - (L'_j + U'_j) - (V_j + W_j)y_{M,j} + V_{j+1}y_{M,j+1} + F_j z_{M,j} = 0 \qquad (j = 1, N) \quad (1')$$

—Equilibrium relationship of the i-th component on the j-th stage:

$$y_{i,j} - K_{i,j}x_{i,j} = 0 \qquad (i = 1, M; j = 1, N) \quad (2)$$

—Enthalpy balance on the jth stage:

$$L_{j-1}h_{j-1} + L'_{j-1}h'_{j-1} - (L_j + U_j)h_j - (L'_j + U'_j)h'_j - (V_j + W_j)H_j + V_{j+1}H_{j+1} + F_j HF_j - Q_j = 0 \qquad (j = 1, N) \quad (3)$$

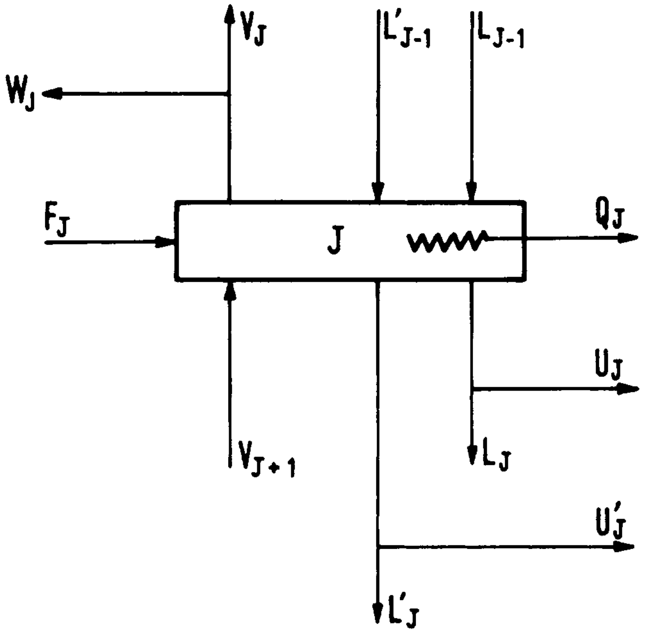

Figure 1. Schematic diagram of the separator stage.

—Stoichiometric equation on the jth stage:

$$\sum_n (y_{n,j} - x_{n,j}) = 0 \qquad (j = 1, N) \quad (4)$$

—Overall material balance on the jth stage:

$$L_{j-1} + L'_{j-1} - (L_j + U_j) - (L'_j + U'_j) - (V_j + W_j) + V_{j+1} + F_j = 0 \qquad (j = 1, N) \quad (5)$$

—Liquid-liquid equilibrium equation for the pure component M on the jth stage:

$$a_{M,j} - a'_{M,j} = 0 \qquad (j = 1, N) \qquad (6)$$

In the previous equations the "standard unknowns" of the two-phase problems: $x_{i,j}, y_{i,j}, L_j, V_j, T_j$ and the new unknowns L'_j, which represent the mole flow rate of the pure liquid phase, appear.

The new equations are the liquid-liquid equilibrium of the Mth component in the two coexisting phases. Recalling that the activity of one component in a liquid mixture is given by:

$$a_i = \gamma_i x_i$$

and that the activity coefficient $\gamma_i \rightarrow 1$ if $x_i \rightarrow 1$, we can conclude, according to our approximation, that

$$a'_{M,j} \simeq 1$$

and Eq. 6 can be then rewritten as

$$\gamma_{M,j} x_{M,j} - 1 = 0 \qquad (6')$$

Equation 6 can be considered only for those stages in which a liquid phase separation occurs. If this is not the case then the second liquid phase does not exist on the jth stage and Eq. 6 is replaced by

$$L'_j = 0 \qquad (6'')$$

The system of Eqs. 1 to 6 is the mathematical model of the multistaged separators and its solution defines the values of the $2N(M+2)$ unknowns. Obviously, in different problems, the set of specified and unspecified variables can be different. In the following we will refer to: $x_{i,j}, y_{i,j}, T_j, L_j, L'_j$, and V_j as the "standard set of unspecified variables", and to: $F_j, U_j, U'_j, W_j, P_j, z_{i,j}$ and Q_j as the "standard set of specified variables."

BOILING POINT METHOD

This method is an extension of the two-phase boiling point method proposed by Wang and Henke (1966) summarized as follows:

1. A first trial profile of $x_{i,j}, y_{i,j}, L_j, L'_j, V_j$, and T_j through the column is assumed.
2. The linear tridiagonal system of Eqs. 1, in which the variable $y_{i,j}$ is substituted from Eq. 2, for all the stages, is solved separately for each component i in the unknowns $x_{i,j}$. This system is rapidly solved by the solution formulas for tridiagonal linear systems given by Boston and Sullivan (1972).
3. Normalization of the obtained values of $x_{i,j}$.
4. Evaluation of the temperature T_j on each stage by solving the implicit Eq. 4. Substituting Eq. 2, Eq. 4 can be rewritten in the more convenient form

   $$f(1/T_j) = \log \left| \sum_n K_{n,j} x_{n,j} \right| = 0 \qquad (4')$$

   where $f(1/T_j)$ is an almost linear function of the unknown $1/T_j$.
5. Evaluation of the vapor phase composition $y_{i,j}$ in all the stages and for each component from Eq. 2.
6. Solution of the block tridiagonal linear system of Eqs. 3 and 5 in the unknowns L_j and V_j.

The modifications of the proposed method involve only step 2: the evaluation of the liquid phase composition through the material balance of each component, and only for the Mth component, while for all the other components the procedure is unchanged. In particular if on the jth stage there are only two phases, then the procedure for the evaluation of $x_{M,j}$ is unchanged and L'_j is simply set equal to zero. If instead on the jth stage there are two coexisting liquid phases then the material balance of the Mth component is removed from the system and it is replaced by the equilibrium Eq. 6 or 6′. It is worthwhile to note that the resulting system retains its tridiagonal form, because Eq. 6′ is explicit in the variable $x_{M,j}$. The flowrate of the second liquid phase L'_j is then obtained separately from the material balance of the Mth component on the jth stage ($L'_0 = 0$):

$$L'_j = L_{j-1} x_{M,j-1} + L'_{j-1} - (L_j + U_j) x_{M,j} - (V_j + W_j) y_{M,j} + V_{j+1} y_{M,j+1} + F_j z_{M,j} \quad (7)$$

The possibility this method has of solving problems with "nonstandard set" of specified and unspecified variables is limited by the block structure of the solving procedure, i.e., it is impossible to give some specification equations involving unknowns which are evaluated from different steps. It is instead possible to exchange specified and unspecified variables comparing in the step 4. So, U_j, U'_j, W_j, F_j and Q_j can be regarded as unknowns and, correspondently, any linear relationships between L, L', and V can be introduced. In this way the original coefficient matrix is changed by introducing the new unknowns after the last column on the right hand side and the new equations after the last row of the matrix. Except for the new columns and rows the new coefficient matrix still retains its block tridiagonal structure. The numerical solution of the system is then still straightforward by using the procedure reported by Buzzi Ferraris (1981).

It is worthwhile to note that in the particular "nonstandard" problem, in which L_1 and V_1 are specified, while Q_1 and Q_N are unknown, the solution of the system of step 4 can be efficiently and simply obtained through the de-coupling of the overall material and enthalpy balances, as proposed by Wang and Henke (1966).

In conclusion, this method appeared to be very efficient in solving distillation problems where the relative volatility of the present components are not too different (Friday and Smith, 1964). Further it can always be very useful to improve the first trial solution enough to allow the global Newton-Raphson method convergence. It is also important to remark that this method requires that the number of phases present on each stage is assigned as an imput.

NEWTON-RAPHSON GLOBAL METHOD

The Newton-Raphson global method deals with the whole system of Eqs. 1 to 6, and solves it as a whole without any block solving procedure, as for example the boiling point method. All the equations of the system are linearized with a Taylor's series truncated after the first term, and the resulting linear system is then solved in the unknowns $\delta x_{i,j}$, $\delta y_{i,j}$, δL_j, $\delta L'_j$, δV_j and δT_j. The linearized equations, obtained from Eqs. 1 and 5, are the same as those obtained for the two-phase problem except for the presence of the unknown $\delta L'$ in the material balances of the Mth component, and in the enthalpy and overall material balances. The new linearized equations, correspondent to the new unknowns $\delta L'_j$, are obtained from Eqs. 6′ or 6″ as follows:

—if on the jth stage there is liquid phase separation

$$\gamma_{M,j} \delta x_{M,j} + x_{M,j} \sum_n \frac{\partial \gamma_{M,j}}{\partial x_{n,j}} \delta x_{n,j} + x_{M,j} \frac{\partial \gamma_{M,j}}{\partial T_j} \delta T_j = r_j$$

—if on the jth stage there is not liquid phase separation

$$\delta L'_j = 0$$

It clearly appears that this method requires an *a priori* knowledge of the number of phases present on each stage.

The obtained linear system has a block tridiagonal structure (Naphtali and Sandholm, 1971) with submatrices dimensions of $2M+4$.

A significant reduction of computation time can be obtained in the problems where the vapor phase is not highly non-ideal, so that the terms $\partial K_{i,j}/\partial y_{n,j}$ in the linearized equations can be neglected. In these cases the unknowns $\delta y_{i,j}$ can be explicitly obtained from the linearization of Eq. 2, and then substituted in all the equations of the linearized system. This reduces the size of the submatrices to $M+4$, and therefore simplify the numerical solution of the linearized system.

Due to the fact that the Newton-Raphson method faces the system altogether, it can be applied to the solution of problems in which the specified and unspecified variables are very different from the "standard set."

Each new unknown is introduced in a column on the right hand side of the last column, and each new linearized equation after the last row of the original coefficient matrix, that is the one correspondent to the "standard set" of specified and unspecified variables. The so obtained matrix has again a block tridiagonal structure, except for the last rows and columns and its solution can be obtained as reported by Buzzi Ferraris (1981).

Finally, the Newton-Raphson method appears to be extremely efficient and fast in reaching the solution, even if it always requires a good first trial solution as do all numerical procedures of this type. This solution can be provided by the user or directly obtained by the boiling point method.

DETERMINATION OF THE PHASE PATTERN OF THE SEPARATOR

As mentioned above, both the proposed numerical methods require an *a priori* knowledge of the number of phases present on each stage. However this is not a limitation of the methods but is required from the intrinsic feature of the examined system. Namely, as it has been shown by Henley and Rosen (1969), a three-phase equilibrium system always admits also a pseudo two-phase solution. Therefore, as reported by Buzzi Ferraris and Morbidelli (1981), a multicomponent multistaged three-phase separator admits not only the correct solution but also all the pseudo-solutions in which, in some of the stages where three phases coexist, only two phases are considered. Then it is *necessary* to assign the number of phases on each stage as an input, in order to have a *unique* solution problem.

The solution procedure of these separators is so constituted to the following steps:

1. First trial phase pattern of the column.
2. Solution of the problem.
3. Verification that on all the stages in which the presence of only two phases were assumed, the liquid phase separation does not occur.
4. Iteration of the procedure until the number of phases on each stage given as an input is verified.

It is worthwhile to note that if the trial phase pattern of the column involves a liquid phase separation in some stages, in which actually there are only two phases, the problem does not admit any solution. Therefore, a new trial phase pattern has to be given by the user with a decreased number of stages in which the presence of three phases is assumed.

If, instead, the solution of the problem with the trial phase pattern of the column is obtained, it is necessary to verify (step 3) all the stages in which only two phases were assumed, to determine whether or not the liquid phase separation occurs. This can be performed by comparing the fugacity of the Mth component in the vapor phase and in the possible present new liquid phase constituted of the pure Mth component.

In particular the following cases may arise:

$f_M^{L'} \geq f_M^V$: The new liquid phase is not formed; the obtained two-phase solution is correct.

$f_M^{L'} < f_M^V$: The liquid phase separation is thermodinamically favored; the presence of three coexisting phases on the stage is predicted, and the two-phase solution is wrong.

Where the fugacity of the Mth component in the vapor phase is given by:

$$f_M^V = P y_M \phi_M(P) \tag{8}$$

while the fugacity in the new liquid phase is:

$$f_M^{L'} = P_M^\circ \phi_M(P_M^\circ)\, x_M' \gamma_M' \tag{9}$$

According to our approximation the values of x_M' and γ_M' should be set equal to 1. However, in order to obtain a more realistic evaluation of the fugacity $f_M^{L'}$, and then of the possibility of the liquid phase separation occurrence, a more precise estimation of x_M' can be introduced. Namely it is possible to evaluate, also from rough solubility data, the sum s_j of the molar solubilities of all the i ($i \neq M$) components in the second liquid phase and then estimate the mole fraction of the Mth component as

$$x_{M,j}' = 1 - s_j$$

The value of $x_{M,j}$ in the here considered problems being close to one, the activity coefficient γ_M' can still be approximate to 1. If this more accurate approximation is introduced also Eq. 6′ has to be consequently modified as follows:

$$\gamma_{M,j} x_{M,j} - (1 - s_j) = 0 \tag{6‴}$$

The presence of two phases on each stage can be then verified by simply comparing the value of the vapor pressure $P_{M,j}^\circ$, with the value of the group $P y_{M,j} \phi_M(P_j) / \phi_M(P_{M,j}^\circ)\,(1 - s_j)$ evaluated on the basis of the previous obtained solution.

Finally, it is worthwhile pointing out that this approach requires the thermodinamic description of only one of the liquid phases, in particular of that considered as a multicomponent mixture. This fact is very useful in the evaluation of the activity coefficients, which are then required to cover only a small portion of the state diagram.

CONVERGENCE CHARACTERISTICS

The two proposed numerical methods have been combined in a computer program, which switches from one to the other in order to minimize the required computation time. Due to the above mentioned characteristics of the two methods, the boiling point method is usually used to move from the first trial solution to a new trial solution, close enough to the correct one, so that the Newton-Raphson method, which is indeed the more powerful in reaching the solution, could converge.

The convergence of each method in the computer program is tested by evaluating at each iteration, the value of the objective function SQR. This function is defined as the square root of the sum of the weighted squared residuals of all the Eqs. 1 to 6. The weights for each equation are evaluated so that a SQR value of for example 10^{-6} means that the average error in the residuals of all the equations involves the sixth significant digit. The control remains on the same method until the objective function, from one iteration to the next, increases (or does not decrease enough). At this point the control switches to a different method able to further decrease the function SQR.

It is worthwhile to notice that, in order to increase its efficiency, the global Newton-Raphson method has to be coupled with a one-dimensional optimum research. This procedure makes it possible to determine, along the lines predicted by the global Newton-Raphson method, a point in which the starting solution is improved. This point is then assumed as the starting point of the new iteration. This procedure appeared to be extremely useful in the whole computer program; in fact it is not time consuming and in many situations it improves the efficiency of the Newton-Raphson method, and, even more important, its stability.

The solution is considered as being reached when the value of SQR is less than 10^{-6}; if no one of the numerical methods is able to decrease the SQR value below 10^{-6}, the procedure is interrupted and the problem is considered unsolvable. This situation arises when the liquid phase separation in some stages, in which only two phases are present, is required by the trial phase pattern given as an input. In these cases, as already mentioned, the solution procedure has to be repeated assuming a new phase pattern, in which the number of stages where three coexisting phases are present is decreased.

Actually it can also happen that the solution of the problem exists, but the computer program is not able to find it. This fact is usually due to a "too bad" first trial solution, that is a solution too far from the correct one so that no one of the numerical methods can converge, or even move in the right direction. This can obviously be avoided through a better knowledge of the behavior of the column. However in many situations a good first trial solution can be also

TABLE 1. PHYSICO-CHEMICAL CHARACTERISTICS OF THE MIXTURE: ACRYLONITRILE (1)-ACETONITRILE (2)-WATER (3)

Component	1	2	3
C_p^L	26.50	22.18	18.00
ΔH_{ev} (25°C)	7,800.	8,330.	10,681.0
A	7.03855	7.33986	8.07131
B	1,232.53	1,482.29	1,730.63
C	−50.690	−22.637	−39.734
a_0	6.75	4.756	8.22
a_1	0.03327	0.02854	0.0015
a_2	−1.091-05	−0.9776-05	0.134-05

$$\log P^o = A - B/(T + C)$$
$$C_p^V = a_o + a_1 T + a_2 T^2$$

NRTL Parameters

i–j	$(g_{i,j} - g_{j,j})$	$(g_{j,i} - g_{i,i})$	$\alpha_{i,j}$
1–2	−438.180	485.852	0.302
1–3	536.851	1.857.103	0.295
2–3	512.936	1,058.453	0.272

obtained from the pseudo-homogeneous solution, that is the solution of the problem in which only two phases are considered on each stage. In our experience this first trial solution appeared to be always close enough to the correct solution to allow the convergence of the two numerical methods.

APPLICATION EXAMPLES

In this section, two demonstration examples of the use of the computer program are reported. The obtained solutions are compared with those given by the complete three-phase model in order to give an estimate of the accuracy of the approximate method here developed.

The first example is a eighteen stages separator, fed with an acrylonitrile-acetonitrile-water mixture. This column, which is very important in the synthesis process of acrylonitrile, is devoted to the separation of acrylonitrile and acetonitrile using water as extractive solvent. In the top of the column the liquid phase separation occurs and an aqueous phase is formed. Due to the slight solubility of acrylonitrile and acetonitrile in water (an overall mole fraction of approximately 5%), the use of the approximate method here developed is promising. The aqueous phase formed in the top of the column is almost completely refluxed to improve the above mentioned separation between acrylonitrile and acetonitrile. The problem is then to determine the amount of solvent which it is necessary to reflux to the column in order to obtain the desired separation. It clearly appears in this case that the possibility of giving non standard specification equations to the problem can be very useful in the optimization of the operating conditions of these equipments.

For demonstration purposes, we will consider the problem to determine the amount of water which it is necessary to reflux to the column to obtain a mole fraction of acetonitrile in the distillate equal to 0.05 and an acrylonitrile mole fraction in the bottom equal to 0.06. The vapor-liquid equilibrium is described by means of the NRTL equation with the parameters values reported by Gmehling and Onkes (1977). These values together with all the other physico-chemical properties employed in the simulation are reported in Table 1.

In order to estimate a good first trial solution, the problem has been solved by considering only two phases present in the whole column. The following specification equations have been considered.

$$\text{Specified: } x_{2,1} = 0.05 \quad x_{1,18} = 0.06 \quad V_1 = 0$$
$$\text{Unspecified: } Q_1, Q_{18}, U_1$$

The speudo-homogeneous solution so obtained is fully reported in Table 2. Starting from this solution, the problem was then solved with the approximate three-phase method. It is important to point out that two more data have to be added to the problem if the third coexisting phase is taken into account. In particular the amount of distillate of the aqueous phase is fixed at 5 mol/h and the overall solubility of acrylonitrile and acetonitrile is set at $s_j = 0.05$ mol/total mol. All the other specification equations are unchanged. The first trial phase pattern of the column has been obtained from the number of coexisting phases verification procedure applied to the pseudo-homogeneous solution reported in Table 2. The results of this analysis show that in stages one to five the two-phase solution is thermodinamically unstable, and then the liquid phase separation is predicted.

The results obtained with the here developed methods are reported in Table 3. It is remarkable that the phase pattern of the column predicted by the pseudohomogeneous solution was correct. From the comparison of the results reported in Tables 2 and 3 it appears that the differences between the values of the reflux rate of the organic phase and the duties of the condenser and the reboiler are significant. On the other hand the compositions profiles of the organic liquid phase and the vapor phase are quite similar. This is due to the fact that the compositions in the distillate and in the bottom were in both cases fixed as an input.

In Table 4, the exact solution of the same problem, obtained with the complete three-phase model (Buzzi Ferraris and Morbidelli, 1981), is fully reported. A comparison with the results reported in

TABLE 2. PSEUDO-HOMOGENEOUS SOLUTION OF EXAMPLE 1

j	$x_{1,j}$	$x_{2,j}$	$x_{3,j}$	$y_{1,j}$	$y_{2,j}$	$y_{3,j}$	T_j	V_j	L_j
1	0.6490	0.0500	0.3010	0.6648	0.0353	0.2998	343.0	0.0000	996.3
2	0.6275	0.0700	0.3025	0.6490	0.0500	0.3010	343.2	1054.0	994.5
3	0.6006	0.0953	0.3042	0.6287	0.0689	0.3024	343.4	1052.0	992.3
4	0.5679	0.1262	0.3059	0.6033	0.0928	0.3040	343.7	1050.0	989.8
5	0.5295	0.1628	0.3078	0.5724	0.1220	0.3057	344.1	1048.0	986.9
6	0.4860	0.2045	0.3095	0.5361	0.1566	0.3074	344.5	1045.0	983.8
7	0.4391	0.2499	0.3110	0.4951	0.1959	0.3090	344.9	1042.0	980.7
8	0.3905	0.2972	0.3123	0.4507	0.2388	0.3105	345.4	1038.0	977.5
9	0.3426	0.3442	0.3132	0.4049	0.2834	0.3116	345.9	1035.0	974.6
10	0.2977	0.3888	0.3135	0.3598	0.3277	0.3125	346.3	1032.0	972.0
11	0.2576	0.4299	0.3125	0.3174	0.3698	0.3128	346.8	1030.0	970.2
12	0.2246	0.4684	0.3070	0.2796	0.4086	0.3119	347.2	1028.0	1068.0
13	0.1817	0.5113	0.3070	0.2314	0.4564	0.3122	347.6	1025.0	1065.0
14	0.1437	0.5501	0.3062	0.1867	0.5010	0.3122	348.1	1023.0	1063.0
15	0.1118	0.5855	0.3027	0.1472	0.5414	0.3114	348.4	1021.0	1062.0
16	0.0869	0.6230	0.2901	0.1140	0.5783	0.3077	348.8	1020.0	1065.0
17	0.0699	0.6767	0.2534	0.0880	0.6173	0.2947	349.1	1022.0	1074.0
18	0.0600	0.7597	0.1803	0.0703	0.6733	0.2564	349.6	1032.0	42.27

$$U_1 = 57.727 \quad Q_1 = 8.7016{+}06 \quad Q_{18} = -8.7031{+}06 \quad P = 1.0$$

$$F_{12} = 100.0 \quad z_{1,12} = 0.40 \quad z_{2,12} = 0.35 \quad z_{3,12} = 0.25 \quad HF_{12} = 107{,}090.0$$

TABLE 3. APPROXIMATE SOLUTION OF EXAMPLE 1

j	$x_{1,j}$	$x_{2,j}$	$x_{3,j}$	$y_{1,j}$	$y_{2,j}$	$y_{3,j}$	T_j	V_j	L_j	L'_j
1	0.6817	0.0500	0.2683	0.6757	0.0345	0.2898	343.0	0.0000	1276.0	39.35
2	0.6585	0.0693	0.2722	0.5697	0.0484	0.2919	343.2	1375.0	1275.0	37.56
3	0.6287	0.0936	0.2777	0.6390	0.0663	0.2946	343.4	1372.0	1274.0	34.44
4	0.5913	0.1234	0.2853	0.6128	0.0892	0.2981	343.7	1369.0	1275.0	29.03
5	0.5455	0.1585	0.2960	0.5802	0.1174	0.3024	344.0	1364.0	1281.0	17.84
6	0.4938	0.1987	0.3075	0.5418	0.1515	0.3067	344.4	1359.0	1295.0	0.0000
7	0.4451	0.2458	0.3091	0.4996	0.1919	0.3084	344.9	1355.0	1290.0	0.0000
8	0.3940	0.2956	0.3104	0.4532	0.2369	0.3100	345.4	1351.0	1286.0	0.0000
9	0.3428	0.3458	0.3114	0.4043	0.2845	0.3112	345.9	1346.0	1282.0	0.0000
10	0.2942	0.3940	0.3118	0.3555	0.3324	0.3122	346.4	1342.0	1278.0	0.0000
11	0.2504	0.4385	0.3111	0.3091	0.3783	0.3126	346.9	1339.0	1275.0	0.0000
12	0.2135	0.4796	0.3069	0.2672	0.4208	0.3120	347.3	1336.0	1372.0	0.0000
13	0.1703	0.5232	0.3066	0.2181	0.4698	0.3122	347.8	1332.0	1369.0	0.0000
14	0.1331	0.5624	0.3046	0.1736	0.5146	0.3118	348.2	1329.0	1367.0	0.0000
15	0.1031	0.6000	0.2969	0.1353	0.5549	0.3098	348.6	1327.0	1368.0	0.0000
16	0.0814	0.6462	0.2725	0.1044	0.5937	0.3019	348.9	1328.0	1375.0	0.0000
17	0.0680	0.7174	0.2145	0.0820	0.6413	0.2767	349.3	1336.0	1396.0	0.0000
18	0.0600	0.8095	0.1305	0.0683	0.7147	0.2170	350.2	1356.0	39.83	0.0000

$U_1 = 55.172 \quad U'_1 = 5.000 \quad Q_1 = 1.1315{+}07 \quad Q_{18} = -1.1317{+}07 \quad P = 1.0$

$F_{12} = 100.0 \quad z_{1,12} = 0.40 \quad z_{2,12} = 0.35 \quad z_{3,12} = 0.25 \quad HF_{12} = 107{,}090.0$

TABLE 4. EXACT SOLUTION OF EXAMPLE 1

j	$x_{1,j}$	$x_{2,j}$	$x_{3,j}$	$x'_{1,j}$	$x'_{2,j}$	$x'_{3,j}$	$y_{1,j}$	$y_{2,j}$	$y_{3,j}$	T_j	V_j	L_j	L'_j
1	0.6698	0.0500	0.2802	0.0540	0.0093	0.9367	0.6714	0.0348	0.2938	343.0	0.0000	1293.0	26.70
2	0.6477	0.0697	0.2825	0.0539	0.0132	0.9329	0.6557	0.0491	0.2953	343.2	1381.0	1291.0	26.28
3	0.6194	0.0948	0.2858	0.0537	0.0185	0.9278	0.6351	0.0676	0.2972	343.4	1378.0	1289.0	25.15
4	0.5840	0.1258	0.2902	0.0535	0.0255	0.9210	0.6090	0.0913	0.2997	343.7	1375.0	1287.0	22.73
5	0.5412	0.1626	0.2963	0.0531	0.0347	0.9122	0.5768	0.1206	0.3026	344.1	1371.0	1285.0	19.70
6	0.4890	0.2037	0.3073	0.0000	0.0000	0.0000	0.5376	0.1556	0.3068	344.5	1366.0	1301.0	0.0000
7	0.4399	0.2512	0.3089	0.0000	0.0000	0.0000	0.4948	0.1967	0.3085	344.9	1362.0	1297.0	0.0000
8	0.3885	0.3013	0.3102	0.0000	0.0000	0.0000	0.4479	0.2420	0.3100	345.4	1357.0	1292.0	0.0000
9	0.3374	0.3514	0.3111	0.0000	0.0000	0.0000	0.3989	0.2898	0.3113	345.9	1353.0	1288.0	0.0000
10	0.2891	0.3993	0.3116	0.0000	0.0000	0.0000	0.3501	0.3377	0.3122	346.4	1349.0	1284.0	0.0000
11	0.2458	0.4433	0.3109	0.0000	0.0000	0.0000	0.3041	0.3834	0.3126	346.9	1345.0	1282.0	0.0000
12	0.2095	0.4839	0.3066	0.0000	0.0000	0.0000	0.2627	0.4254	0.3119	347.3	1342.0	1378.0	0.0000
13	0.1668	0.5271	0.3061	0.0000	0.0000	0.0000	0.2139	0.4740	0.3121	347.8	1339.0	1375.0	0.0000
14	0.1302	0.5661	0.3037	0.0000	0.0000	0.0000	0.1699	0.5185	0.3116	348.2	1336.0	1373.0	0.0000
15	0.1011	0.6043	0.2946	0.0000	0.0000	0.0000	0.1323	0.5586	0.3091	348.6	1334.0	1375.0	0.0000
16	0.0803	0.6532	0.2666	0.0000	0.0000	0.0000	0.1023	0.5980	0.2998	348.9	1336.0	1384.0	0.0000
17	0.0678	0.7284	0.2038	0.0000	0.0000	0.0000	0.0809	0.6483	0.2709	349.3	1345.0	1407.0	0.0000
18	0.0600	0.8206	0.1194	0.0000	0.0000	0.0000	0.0680	0.7258	0.2062	350.4	1367.0	39.20	0.0000

$U_1 = 55.804 \quad U'_1 = 5.000 \quad Q_1 = 1.1374{+}07 \quad Q_{18} = -1.1376{+}07 \quad P = 1.0$

$F_{12} = 100.0 \quad z_{1,12} = 0.40 \quad z_{2,12} = 0.35 \quad z_{3,12} = 0.25 \quad HF_{12} = 107{,}090.0$

TABLE 5. NUMERICAL SOLUTION OF EXAMPLE 2

j	$x_{1,j}$	$x_{2,j}$	$x_{3,j}$	$y_{1,j}$	$y_{2,j}$	$y_{3,j}$	T_j	V_j	L_j	L'_j
1	0.3500	0.0279	0.6221	0.3807	0.0133	0.6061	361.8	0.0000	87.00	0.0000
2	0.2997	0.0528	0.6475	0.3500	0.0279	0.6221	362.2	116.0	87.56	0.0000
3	0.2495	0.0785	0.6720	0.3123	0.0466	0.6412	362.8	116.6	88.14	0.0000
4	0.2091	0.1011	0.6898	0.2744	0.0660	0.6596	363.3	117.2	88.64	0.0000
5	0.1879	0.1248	0.6874	0.2439	0.0831	0.6731	363.7	117.8	139.2	0.0000
6	0.1611	0.1393	0.6996	0.2141	0.0988	0.6872	364.1	118.2	139.8	0.0000
7	0.1364	0.1560	0.7077	0.1825	0.1160	0.7015	364.5	118.8	140.3	0.0000
8	0.1252	0.1962	0.6787	0.1533	0.1357	0.7110	364.8	119.3	124.5	16.28
9	0.1074	0.2357	0.6570	0.1231	0.1563	0.7206	365.2	119.8	114.0	27.29
10	0.0872	0.2729	0.6398	0.0947	0.1760	0.7293	365.5	120.3	106.5	35.26
11	0.0675	0.3064	0.6261	0.0700	0.1935	0.7366	365.8	120.8	101.0	41.16
12	0.0494	0.3355	0.6151	0.0493	0.2084	0.7424	366.0	121.1	16.96	4.004

$U_1 = 29.036 \quad Q_1 = 1.2463{+}06 \quad Q_{12} = -1.2474{+}06 \quad P = 1.0$

$F_5 = 50.0 \quad z_{1,5} = 0.22 \quad z_{2,5} = 0.13 \quad z_{3,5} = 0.65 \quad HF_5 = 68{,}151.$

Table 3 shows that the agreement with the approximate solution is satisfactory.

It can be summarized that the method here developed provides a good estimation of the behavior of the examined three-phase column, also if the amount of organic compounds in the aqueous phase is significant (an overall mol fraction of about 0.08, Table 4).

This result constitutes an empirical guideline to the selection of

TABLE 6. COMPARISON OF THE OVERALL FLOWRATES OF EACH COMPONENT CALCULATED WITH THE APPROXIMATE AND THE EXACT METHOD

	Exact			Approximate		
Component	Propanol	Butanol	Water	Propanol	Butanol	Water
Distillate	10.00	0.797	17.78	10.16	0.810	18.16
Bottom	0.992	5.701	14.70	0.831	5.682	14.43

TABLE 7. COMPUTATION TIME, s, REQUIRED ON UNIVAC 1100/80 BY THE EXACT AND THE APPROXIMATE METHOD

	Exact	*Approximate*
Example 1	57.0	8.0
Example 2	34.0	5.0

systems for which this method is applicable. Further, the determination of the first trial phase pattern of the column through the solution of the pseudo-homogeneous problem appears to be quite satisfactory, and then very efficient in reducing the required computation time.

It is also noticeable that the activity coefficients required by the here developed approximate method are related only to the organic phase. In fact in the description of the aqueous phase no activity coefficients are necessary but simply the solubility value of the present organic compounds. This fact greatly simplify the thermodinamic description of the liquid-liquid-vapor equilibria of the mixture under consideration.

The second example is a twelve stages separator of a propanol-butanol-water mixture, with the operating conditions and the physico-chemical characteristics reported by Buzzi Ferraris and Morbidelli (1981). In Table 5 the full numerical solution obtained with the approximate method is reported.

The value of the molar solubility of propanol and butanol in water, s_j, has been obtained from an examination of the phase diagram reported by Block and Hegner (1976). The mean value $s_j = 0.035$ has been chosen and kept constant in all the stages of the column in which the liquid phase separation is present.

A comparison with the results obtained by means of the exact method, which has been fully reported by Buzzi Ferraris and Morbidelli (1981) (Table 2 of this work), shows a satisfactory agreement of the temperature, flow rate and compositions profiles along the column. In Table 6, the comparison of the distillate and the bottom flowrates of each component is reported. It is also remarkable that the phase pattern of the column is correctly predicted by the approximate method.

Finally the computation time, required by both the complete and the approximate method, for the solution of both the above reported examples is reported in Table 7.

NOTATION

a = activity in the liquid phase
C_p = molar specific heat
f = fugacity
F = feed stream molar flow rate
h = liquid stream molar enthalpy
H = vapor stream molar enthalpy
HF = molar feed enthalpy
K = vapor-liquid equilibrium ratio
L = liquid stream molar flow rate
M = number of components of the mixture
N = number of stages, including reboiler and condenser
P = pressure
P° = vapor pressure
Q = rate of heat leaving the stage
s = sum of the mole fraction of all the components ($i \neq M$) in the second liquid phase
SQR = objective function
T = temperature
U = molar flow rate of the liquid stream leaving the stage
V = vapor stream molar flow rate
W = molar flow rate of the vapor stream leaving the stage
x = liquid mole fraction
y = vapor mole fraction
z = feed mole fraction

Greek letters

γ = activity coefficient
ΔH_{ev} = molar enthalpy of evaporation
τ = residual of Eq. 6′
ϕ = fugacity coefficient

Superscripts

L = liquid phase
V = vapor phase
$'$ = second liquid phase

Subscripts

i = component index
j = stage index

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