corresponds to the phase contours and Eq. 10b to the x-axis so that the resulting plot conforms to the conventional Nichols chart. Figure 2 illustrates this from where it can be seen that incorporation of Eqs. 6, 10a, and 10b as above into the Nichols chart makes it so generalized and versatile as to permit both open- and closed-loop process identification. Thus, in addition to the usual M and α contours plotted on the A and θ coordinates, Figure 2 also provides loci of constant A and θ superimposed on the M and α coordinates. It may be noted from the chart that, while the M and A values coincide, the α and θ values differ from each other by a constant factor of 180° as per Eqs. 10a and 10b. Using Figure 2 the closed-loop (or open-loop) identification is achieved by the usual procedure of entering the chart through A and θ (or M and α) coordinates, and reading of M and α (or A and θ) contour values by interpolation. Any existing computer program describing the conventional Nichols chart may also be used for open-loop identification simply by incorporating Eqs. 6, 10a and 10b into the program.

NOTATION

A = open-loop magnitude ratio
C = controlled variable
$G(s)$ = open-loop process transfer function
$G^*(s)$ = closed-loop process transfer function
j = $\sqrt{-1}$
M = closed-loop magnitude ratio
R = set point
w = frequency, radians/time

Greek Letters

α = closed-loop phase angle, degrees
θ = open-loop phase angle, degrees

LITERATURE CITED

Coughanowr, D. R., and L. B. Koppel, *Process Systems Analysis and Control*, McGraw Hill, New York (1965).

Deshpande, P. B., "Process Identification of Open-loop Unstable Systems," *AIChE J.*, **26**, p. 305 (1980).

Koppel, L. B., "Sampled Data Control of Unstable Processes," *Ind. Eng. Chem. Fund.*, **5**, p. 396 (1966).

Luyben, W. L., "Sample-Data Control of Second-Order Open-loop Unstable Processes," *Ind. Eng. Chem. Fund.*, **1**, p. 557 (1972).

Luyben, W. L., "Effect of Reaction Rate on the Open-Loop Stability of Chemical Reactors," AICHE J., 26, p. 175 (1974).

Luyben, W. L., and M. Melcic, "Consider Reactor Control Lags," *Hydroc. Proc.*, **6**, p. 115 (1978).

Manuscript received February 23, and accepted December 17, 1982.

Accelerated Convergence for Newton-Type Iterations Applied to Multicomponent Distillation Problems

D. S. BILLINGSLEY

IBM Corp.
Two Riverway
Houston, TX 77056

INTRODUCTION

The component material balances and equilibrium relations on all the stages in a distillation column at steady state may be expressed in the well known form of a matrix-vector equation

$$A_i \Upsilon_i = f_i, \quad i = 1, \ldots, I \tag{1}$$

where A_i is a tridiagonal matrix involving equilibrium ratios, K_{ij}, of component i and ratios, L_j/V_{j+1}, of phase flow rates, but having no explicit dependence upon mole fractions. Υ_i is a vector of vapor flow rates of component i on all stages. f_i is a vector of molar feed rates of component i on all stages. Thus the elements of f_i are zero except for elements corresponding to feed stages.

Two computational procedures, successive approximation and simultaneous solution, are currently usually used for solving multicomponent staged distillation problems. The solution of Eq. 1 plays a central role in each approach. The scheme of Boston and Sullivan (1972) is probably the most efficient available for solving Eq. 1. This algorithm is the only one able to produce a solution while employing only multiplication and addition of positive numbers.

The successive approximation computational procedure consists of solving Eq. 1, correcting that solution, determining new estimates of stage temperatures as the bubble points of the corrected mole fractions, and using these temperatures in the heat balances to compute new estimates of phase flows. Various methods are used to correct the solution to Eq. 1. Holland (1963) multiplies all the product ratios, d_i/b_i, by a single correction factor, θ, and determines θ so that a product specification is satisfied. Boston and Sullivan (1974) in effect multiply all the ratios L_j/V_{j+1} by a single correction factor, S, and then determine S so that a product specification is satisfied. Alternately one could assume that all stage temperatures were multiplied by a constant factor or incremented by a constant addend. In any case the equation for determining the correction factor is nonlinear and usually solved by Newton iterations. Analytic partial derivatives with respect to the correction factor are simple to evaluate. For instance, partials with respect to S are readily obtained by differentiating Eq. 1.

As considered here the simultaneous solution computational procedure is based upon linearization of all equations under the assumptions that equilibrium ratios are independent of composition and that phase enthalpies may have an explicit linear composition dependence (Gentry, 1970; Billingsley and Boynton, 1971). A distinguishing feature of this procedure is that neither component flow rates nor mole fractions are "iteration variables." In effect, one formally solves Eq. 1, sums these solutions to have

$$(V_{J+1}, \ldots, V_1)^T = \sum_i \Upsilon_i = \sum_i A_i^{-1} f_i \tag{2}$$

and also substitutes the solutions of Eq. 1 into the heat balances. The result is a set of equations in which the only unknowns are the stage temperatures and the vapor phase flows. Note that vapor-phase

TABLE 1. ITERATIONS REQUIRED FOR CONVERGENCE

Prob. ID	Newton	Asymptotic Order of Convergence of Modification							
	2	$1+\sqrt{2}$	3	4	5	6	7	8	9
15	7	7	5	3	4	3	3	3	3
18	7	6	4	3	2	2	2	2	2
19	7	6	4	3	3	2	2	2	2
29	8	7	5	5	4	5	4	5	3
30	8	7	5	4	4	5	4	4	3
82	8	7	4	3	4	3	4	3	4
89	7	6	4	3	2	2	2	2	2
116	6	5	3	2	2	2	2	2	2
123	21	17	14	8	12	n.c.	9	n.c.	n.c.
126	6	6	4	3	2	2	2	2	2
141	9	8	5	n.c.	n.c.	7	7	5	5
1149	10	9	6	5	5	5	6	4	n.c.
159	8	8	6	n.c.	n.c.	4	n.c.	5	n.c.
164	8	7	5	4	4	4	3	3	3
179	11	15	n.c.	n.c.	n.c.	7	n.c.	n.c.	5
206	8	9	n.c.	8	n.c.	7	3	4	4
215	13	9	9	6	5	5	3	3	3
216	12	9	6	5	4	2	4	3	3

n.c. = no convergence under conditions of calculations

flows are given in terms of the phase flow ratios, L_j/V_{j+1}, by Eq. 1 when one sets all $K_{ij} \equiv 1$ and replaces f_i with $\Sigma_i f_i$. Analytical partial derivatives with respect to the unknowns are obtained by straightforward differentiation, and the equations are solved by Newton iterations.

ACCELERATED CONVERGENCE

Where $g = g(w)$ Newton iterations are given by

$$w_{n+1} = w_n - \left(\frac{\partial g}{\partial w}\bigg|_{w_n}\right)^{-1} g(w_n) \qquad (3)$$

The modified Newton iterations proposed by King (1972) for scalar equations are expressed by

$$\left.\begin{aligned} w_{n+1} &= w_n - \left(\frac{\partial g}{\partial w}\bigg|_{(w_n+u_n)/2}\right)^{-1} g(w_n) \\ u_{n+1} &= w_{n+1} - \left(\frac{\partial g}{\partial w}\bigg|_{(w_n+u_n)/2}\right)^{-1} g(w_{n+1}) \end{aligned}\right\} \qquad (4)$$

Equations 4 require the same number of function and derivative evaluations per iteration as does Eq. 3. However, for scalar equations the former have been shown (Werner, 1982; King, 1972) to possess an asymptotic convergence rate of $1 + \sqrt{2}$ under the same conditions for which Newton's method has an asymptotic convergence rate of 2. Consequently one should probably use Eqs. 4 to compute θ or S.

It apparently has not been shown that Eqs. 4 have $1 + \sqrt{2}$ order convergence in the vector case, wherein $\partial g/\partial w$ denotes the Jacobian. It is desirable then to see how they perform on distillation problems solved by the simultaneous solution computational procedure, in which stage temperatures and vapor-phase flows constitute the vector of unknowns. To this end Eqs. 4 were applied to a number of distillation problems collected over the years because a relatively powerful algorithm had been required for their solution. Some of these problems, for instance, are absorbers or strippers. In others some plates are nearly dry.

A pair of starting vectors is required for Eqs. 4, and the second vector of this pair was generated from the first by a single Newton iteration. Ordinary Newton iterations were also applied to these same problems using the same starting estimates as employed with Eqs. 4, results are shown in Table 1. The $1 + \sqrt{2}$ order method is clearly superior to Newton's method itself. The reprogramming to change a program from Newton's method to the $1 + \sqrt{2}$ order method is minimal.

Four additional problems were used for which Netwon's method did not converge when starting from their respective program generated initial estimates. The $1 + \sqrt{2}$ order method did not converge on these either. All four of these problems are best solved by a successive substitution method.

DISCUSSION

One may also consider the use of Eq. 3 under the restriction that only on every mth application thereof is the Jacobian recomputed. The asymptotic order of convergence achieved by such a procedure has been shown by Ortega and Rheinboldt (1970) to be $m + 1$. Thus, if the Jacobian be recomputed on every other application of Eq. 3 the asymptotic rate of convergence is 3. The iteration formula in this instance becomes

$$w_{n+1} = w_n - \left(\frac{\partial g}{\partial w}\bigg|_{w_n}\right)^{-1} \left(g(w_n) + g\left\{w_n - \left(\frac{\partial g}{\partial w}\bigg|_{w_n}\right)^{-1} g(w_n)\right\}\right) \qquad (5)$$

The numbers of iterations required for m values of 2 through 8 are given in the last seven columns of Table 1. Even for $m = 2$ the computation per iteration (after the first) required by Eq. 5 actually exceeds that for Eqs. 4. The former requires two distinct function evaluations while the latter needs only one new function calculation.

Now estimate the number of iterations saved using Eq. 5 compared to using Eqs. 4. Assume the current estimates of the unknowns accurate to one decimal digit. Assume further these are the earliest estimates to lie within the region in which the relevant asymptotic convergence rate prevails. If a single precision result is required (about 6.5 decimal digits) it is readily found that one Jacobian evaluation is eliminated by virtue of the cubic asymptotic convergence of Eq. 5. This is certainly a desirable saving. It is not more because so few iterations are required after the asymptotic convergence rate is achieved. It would be less if this rate were not attained until the unknowns were accurate to three decimal digits.

Where benefits are indicated in the fourth column of Table 1 they must therefore arise largely from

a. Improved convergence behavior outside the region of asymptotic convergence.

b. The various program limits for Newton iterations being more effective for this modification, having asymptotic cubic convergence, than for the $1 + \sqrt{2}$ order method.

The rationale for employing the $1 + \sqrt{2}$ order method is that it "projects ahead" to determine a location at which to evaluate the Jacobian for the upcoming iteration. The resulting Jacobian might better represent the Jacobian over the range $[w_n, w_{n+1}]$ than it would if evaluated at w_n. If so, the convergence behavior of the $1 + \sqrt{2}$ order method outside of its region of asymptotic convergence might be better than that of Newton's method or of some of its other modifications described in this section. Table 1, however, indicates this to be true only with respect to Newton's method itself when using the same program limits employed for Newton's method. Table 1 also suggests that these other modifications could have smaller regions of convergence.

Lastly, Scherule's (1979) quadratically convergent modification of Newton's method should be mentioned. This scheme avoids solving systems involving the inverse of the Jacobian. It thus requires less computation per iteration than does Newton's method. The author applied Scheurle's scheme to a set of collocation equations arising from a packed column model. Scheurle's modification exhibited a smaller region of convergence than did Newton's method; however, very few starting estimates were tested.

NOTATION

A = tridiagonal matrix in Eq. 1
b = molar rate of production of a component in the bottoms product stream
d = molar rate of production of a component in the distillate product stream
f = vector of feed rates of a single component
g = vector-valued function
I = number of components present
i = component index
j = stage index; reboiler is stage 0, J is top stage
K = equilibrium ratio
L = liquid leaving a stage
n = iteration number
S = correction factor of Boston and Sullivan
u,w = vectors of independent variables
V = vapor arriving at a stage
θ = correction factor of Holland
Υ = vector of vapor flow rates of a single component

LITERATURE CITED

Billingsley, D. S., and G. W. Boynton, "Iterative Methods for Solving Problems in Multicomponent Distillation at the Steady State," *AIChE J.*, **17**, p. 65 (1971).

Boston, J. F., and S. L. Sullivan, "An Improved Algorithm for Solving the Mass Balance Equations in Multistage Separation Processes," *Can. J. Chem. Eng.*, **50**, p. 663 (1972).

Boston, J. F., and S. L. Sullivan, "A New Class of Solution Methods for Multicomponent, Multistage Separation Processes," *Can. J. Chem. Eng.*, **52**, p. 52 (1974).

Gentry, J. W., "An Improved Method for Numerical Solution of Distillation Processes," *Can. J. Chem. Eng.*, **48**, p. 451 (1970).

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

King, R. F., "Tangent Methods for Nonlinear Equations," *Numer. Math.*, **18**, p. 298 (1972).

Ortega, J. M., and W. C. Rehinboldt, *Iterative Solution of Nonlinear Equations in Several Variables*, Academic Press, New York, p. 315 (1970).

Scheurle, J., "Newton Iterations Without Inverting the Derivative," *Math. Meth. in Appl. Sci.*, **1**, p. 514 (1979).

Werner, W., "Some Supplementary Results on the $1 + \sqrt{2}$ Order Method for the Solution of Nonlinear Equations," *Numer. Math.*, **38**, p. 383 (1982).

Manuscript received July 20, 1982; revision received March 31, and accepted May 10, 1983.

Absorption in Mixed Surfactant-Polymeric Films: A Novel Phenomenon

R. A. MASHELKAR
Chemical Engineering Div.
National Chemical Laboratory
Pune 411 008, India

M. SOYLU
Chemical Engineering Department
University of Salford
Salford, Lancashire, England

The influence of surface-active agents on gas absorption in turbulently falling films has been well known (Levich, 1962; Davies, 1972). The action of soluble surface-active agents presumably occurs by their selective adsorption at the interface. This leads to a gradient of surfactant concentration and therefore to a shear stress which opposes the motion. The effect of an insoluble surface-active agent is normally attributed to the surface convection and surface diffusion leading to a steady-state distribution of the concentration, which generates shear stresses opposing the motion. In either case, the net effect is to dampen the convective motion at the free interface thereby imparting certain rigidity. Such phenomena lead to a reduction in mass transfer rate at the free interface.

Our recent studies (Mashelkar, 1982) have indicated that the addition of soluble drag-reducing polymers (such as polyethylene oxide, polyacrylamide) in minute quantities actually brings in an enhancement in the mass transfer rate at the gas-liquid interface. This is at first sight somewhat surprising in view of the fact that such polymers are known to be mildly surface active (Mohan et al., 1976; Vocel and Ryan, 1971). Mashelkar (1982) explained this phenomenon. It was shown that the drag reduction phenomenon in freely falling films results in the generation of lower shear stresses at the solid-liquid interface. In a gravity-controlled film flow, the response of the fluid is to reduce the film thickness thereby gen-

---

Correspondence concerning this paper should be addressed to R. A. Mashelkar.