r = radius
r_1 = radius of smaller tube
r_2 = radius of larger tube
S = transformal axial length
u = velocity
u_m = mean velocity in large tube
u_{ms} = mean velocity in small tube
z = axial distance
Z = nondimensional axial length z/r_2
Z_+ = Z/N_{Re}

Greek Letters

ρ = density
ν = kinematic viscosity

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Application of Quasilinearization to Countercurrent CSTR'S

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Stagewise process problems commonly encountered in engineering design include the analysis of extractors, distillation towers, and reactor cascades. Solutions to these kinds of problems which may be resolved into linear equations have been established by either analytical or graphical techniques. By assuming a constant equilibrium or distribution coefficient or by assuming first order reaction, the equations become linear permitting the use of these standard techniques. If, however, the true nature of the equilibrium and/or rate expressions is known, it may be far more accurate to use the more rigorous system equations, although they may be nonlinear. The most popular method for handling stagewise nonlinear processes is that of linearizing the equations of the process matrix by the Newton-Raphson method. The current work is concerned with applying a relatively new technique, quasilinearization developed by Bellman and Kalaba (*1*), to the finite difference equations of stagewise reaction processes.

PURPOSE OF STUDY

A recent paper by Kowalczyk (*2*) shows that both the methods of solution and the analytical results obtained in applying finite difference calculus to a series of CSTR's are analogous to the solution of differential equations that are encountered in plug flow reactors. It is the intention of this communication to apply the method of quasilinearization to the nonlinear finite difference equations of cascaded CSTR's with boundary conditions at different stages (split conditions). Let it be known that this is simply an attempt to solve these difference equations by quasilinearization and not a theoretical proof of its validity or lack of validity for this application. The numerical method of quasilinearization which has been chosen has two major advantages. First of all, nonlinear equations using this technique converge rapidly to solutions (i.e., quadratic convergence). Secondly, solutions can be obtained even with very poor starting values of unknown initial conditions. Lee (*3*) and Lee and Noh (*5*) have shown that quasilinearization is a very powerful technique in solving nonlinear differential and difference equations occurring in chemical engineering (e.g., tubular reactor and distillation column).

Consider the following problem of a series of continuous stirred-tank reactors whose effluents and feed streams are flowing countercurrently (Figure 1). A steady material balance on reactor $n + 1$ for each component is made.

$$0 = QC_{An} + QC_{An+2} - 2QC_{An+1} - kC_{An+1}C_{Bn+1}V_R \quad \text{for } A \quad (1)$$

$$0 = QC_{Bn} + QC_{Bn+2} - 2QC_{Bn+1} - kC_{An+1}C_{Bn+1}V_R \quad \text{for } B \quad (2)$$

The generation rate equation used is

$$r_{An+1} = -kC_{An+1}C_{Bn+1}, \text{ i.e., } (A + B \rightarrow \text{products}).$$

Note that this term is nonlinear with respect to concentration C_{An+1} because C_{Bn+1} is also dependent on the concentration A.

The dimensionless variables introduced are

$$Y_{An+1} = C_{An+1}/C_{A0}, \quad Y_{Bn+1} = C_{Bn+1}/C_{A0}, \quad X = kC_{A0}\ V_R/Q$$

The material balance for constant X reduces to difference equations

$$0 = Y_{An} + Y_{An+2} - 2Y_{An+1} - X\,Y_{An+1}\,Y_{Bn+1} \quad (3)$$

$$0 = Y_{Bn} + Y_{Bn+2} - 2Y_{Bn+1} - X\,Y_{An+1}\,Y_{Bn+1} \quad (4)$$

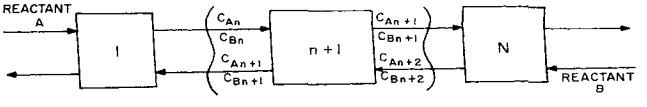

Fig. 1. Flow diagram of stage of countercurrent CSTR cascade.

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As these are finite difference equations, the operator E can be introduced, where $EY_{An} = Y_{An+1}$ (4). This operator can be considered analogous to the differential operator D. The equations may now be rearranged in terms of E notation and the terms collected

$$(E^2 - 2E + 1)\, Y_{An} = X\,(E\, Y_{An})\,(E\, Y_{Bn}) \qquad (5)$$

$$(E^2 - 2E + 1)\, Y_{Bn} = X\,(E\, Y_{An})\,(E\, Y_{Bn}) \qquad (6)$$

The CSTR problem has now been reduced to a pair of second-order inhomogeneous nonlinear finite difference equations. The boundary conditions for a system of N stages are

$$Y_{A0} = 1 \quad Y_{AN+1} = 0$$

$$Y_{B0} = 0 \quad Y_{BN+1} = C_{B0}/C_{A0}$$

The boundary conditions state that pure A enters from one side of the cascade, and pure B from the other.

The method of quasilinearization may now be applied to the finite difference equations. First, a further change in variable notation will prove useful. Let

$$U_1 = Y_{An};\quad U_2 = E\, Y_{An} = Y_{An+1};\quad U_3 = Y_{Bn};$$

$$U_4 = E\, Y_{Bn} = Y_{Bn+1} \qquad (7)$$

Then Equations (5) and (6) may be transformed to U notation which reduces the two second-order difference equations to four first-order equations as

$$EU_2 = 2U_2 - U_1 + X\, U_2U_4,\quad EU_1 = U_2 \qquad (8)$$

$$EU_4 = 2U_4 - U_3 + X\, U_2U_4,\quad EU_3 = U_4 \qquad (9)$$

The equations are valid for N countercurrent stages.

APPLICATION OF THEORY

The theory of quasilinearization can now be applied. Because there are $N + 1$ equations for U_1, U_2, and U_3, U_4, the maximization Equation (3) in vector form must be used, based on the analogy that $\dfrac{d\vec{V}}{dt} \leftrightarrow \vec{EV}$. Using this correspondence, it follows that

$$\vec{EV} = \max\,[\,\vec{f}\,(\vec{U}\,) + \vec{J}_u \times (\,\vec{V} - \vec{U}\,)] \qquad (10)$$

where $f_i = EU_i$. The matrix $\vec{J}_u$ is composed of elements which are partial derivatives of f_i, the values of which may be found by differentiating Equations (8) and (9)

$$\vec{J}_u = \begin{bmatrix} \dfrac{\partial f_1}{\partial U_1} & \cdots & \dfrac{\partial f_1}{\partial U_n} \\ \vdots & & \vdots \\ \dfrac{\partial f_n}{\partial U_1} & \cdots & \dfrac{\partial f_n}{\partial U_n} \end{bmatrix} \qquad (11)$$

The elements on both sides of Equation (10) may then be equated to derive the difference equations which are linear in V (i.e., quasilinear)

$$EV_1 = V_2,\quad EV_2 = 2V_2 - V_1 + XU_4V_2 - XU_2U_4 + XU_2V_4 \qquad (12)$$

$$EV_3 = V_4,\quad EV_4 = 2V_4 - V_3 + XU_2V_4 - XU_2U_4 + XU_4V_2 \qquad (13)$$

These equations are to be iterated upon with the U_i value being that of the previous solution; initial values of U_i must be guessed. Convergence is defined in terms of the approach of V_i to U_i. These equations represent each stage for any number of reactors, thus differing from the Newton-Raphson method in which the number of equations to be solved increases as the number of stages is increased.

The solution obtained should be a general solution for V, composed of a particular and two homogeneous solutions, that is

$$V_i = V_i^P + a\, V_i^{h1} + b\, V_i^{h2} \quad i = 1, 2 \qquad (14)$$

$$V_j = V_j^P + c\, V_j^{h1} + d\, V_j^{h2} \quad j = 3, 4 \qquad (15)$$

in which a, b, c, and d are constants which must be determined from the boundary conditions. The particular solution for arbitrary entrance boundary conditions is obtained directly from Equations (12) and (13). The two homogeneous solutions with different arbitrary entrance boundary conditions are generated by eliminating the U_2U_4 term (quasiconstant) from Equations (12) and (13). The constants of Equations (14) and (15) are then obtained from the stated boundary conditions as

$$V_1(0) = 1,\ V_3(0) = 0,\ V_1(N + 1) = 0,\ V_3(N + 1) = 1$$

The relationships are immediately found between the arbitrary and entrance boundary conditions. The other two relationships are found after $V_i^P(N + 1)$, $V_i^{h1}(N + 1)$ and $V^{h2}(N + 1)$ are generated. Once the constants are determined, the entire set V_i is generated and will serve as the U_i for the next iteration. A maximum allowable tolerance is taken on the difference between successive iterated values of V_i.

For concreteness, consider the case where the number of stages is set equal to ten, with $Y_{A0} = Y_{B11} = 1.0$ and $Y_{A11} = Y_{B0} = 0$. This is a symmetrical case and reduces to a situation for which a numerical solution has been obtained (via Newton-Raphson) and which therefore serves as a check on the validity of the quasilinearization method. One simplification which may be made even in nonsymmetrical cases is to substitute U_2V_4 for U_4V_2 in Equations (12) and (13), for in the limit $U_2V_4 \rightarrow U_4V_2$ and vice versa. An IBM 360/50 was used to perform the iterative computations.

RESULTS

Two runs with different initial guesses were made corresponding to the maximum and minimum values of relative concentration, $U_i(n) = 1.0$ and $U_i(n) = 0$, respectively, for all n stages. The arbitrary entrance conditions were chosen. Convergence was rapid in both cases and checked the Newton-Raphson solution. Ten iterations were required for the initial guesses of 1.0, while only eight were needed for the zero case. The convergence is illustrated in Figures 2a and b, the final iteration coinciding with the exact solution. After the third iteration, even with these poor starting values, convergence is rapid, characteristic of quadratic convergence. Probably because eight out of ten of the relative concentrations were chosen to equal zero rather than unity, the zero guess case converged more rapidly. Acceptable convergence was taken as three digits after the decimal place.

Results of the quasilinearization analysis may be compared with those obtained from a standard Newton-Raphson procedure. When initial guesses of 1.0 were used in the ten-stage problem, the execution time for the Newton-Raphson method was found to be 15.45 sec. as com-

pared to a 5.40 sec. value for quasilinearization. Since the Newton-Raphson and quasilinearization computer programs used were fundamentally different, the N-R program having a matrix-handling subroutine, the times can be considered only comparative to an order of magnitude. The computer programs and other calculations indicate that the Newton-Raphson method is more adversely affected by poor initial guesses than is the quasilinearization technique for the type of equation encountered.

CONCLUSIONS

1. The solutions converge to the very same answers obtained by the Newton-Raphson method. The material balance served as a check on both techniques. This verifies the numerical validity of the method of quasilinearization as applied to nonlinear finite difference equations of CSTR s in series.

2. Even with extremely poor starting guesses for $U_i(n)$, convergence was obtained to three significant figures in only seconds. Any reasonable guesses at all would have greatly improved rapidity of convergence. However, convergence, although rapid, is not quite quadratic. This is probably due to the highly coupled nature of the equations.

3. In the stagewise reactor problem described, quasilinear computation time was of the same order of magnitude as that of the Newton-Raphson computation. Unlike the Newton-Raphson method, the sub-problem does not become more complex as the number of stages increases, and matrix handling techniques, such as a Gauss-Jordan reduction, are not required.

In the future studies of the mathematical properties of quasilinearization as applied to other CSTR problems will be further investigated to determine under what conditions the technique may be validly used.

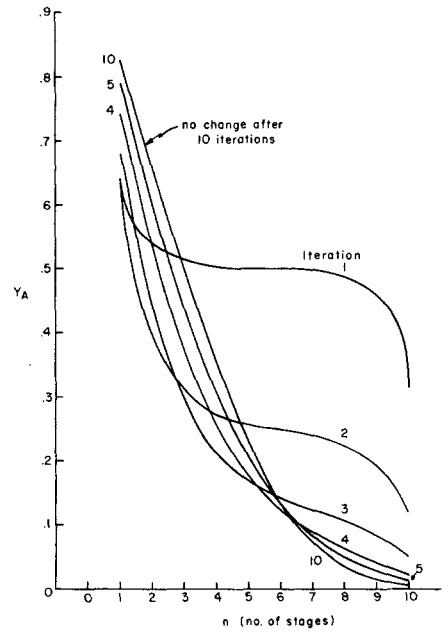

Fig. 2a. Ten-stage CSTR, countercurrent at $U_2(n) = 1.0$.

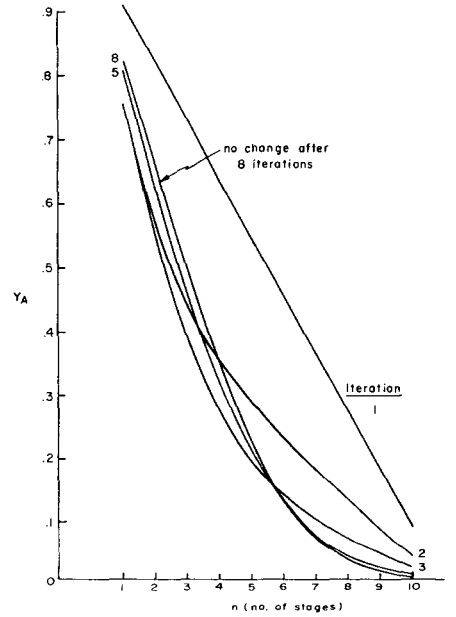

Fig. 2b. Ten-stage CSTR, countercurrent at $U_2(n) = 0.0$.

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NOTATION

A, B = reactants
a, b, c, d = coefficients in general solution of finite difference equation
C_{An}, C_{Bn} = concentration of a component leaving stage n of a CSTR
CSTR = continuous stirred-tank reactor
E = finite difference operator
$\vec{f}(\vec{U})$ = matrix of elements $f_i = EU_i$
J = Jacobi matrix of derivatives, $\partial f_i/\partial U_j$, as in Equation (11)
k = reaction rate constant
n = stage number
N = total number of stages
Q = volumetric flow rate of stream in CSTR
r = reaction rate
U = defined variable derived from Y_n
V_R = volume of a CSTR
V^P, V^h, V = particular, homogeneous, or general solution of quasilinearized equation
X = dimensionless variable $= kC_{A0}V_R/Q$
Y_{An}, Y_{Bn} = dimensionless concentration variable $= C_A/C_{A0}$, C_B/C_{A0}

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