# Acceleration of Cyclic Steady State Convergence for Pressure Swing Adsorption Models

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## Abstract

A new solution algorithm is presented that accelerates the convergence of pressure swing adsorption dynamic models. The algorithm combines the desirable properties of Quasi-Newton and successive substitution methods to obtain a significant acceleration factor.


## Introduction

Pressure swing adsorption (PSA) separation processes are carried out in fixed-bed adsorbers which contain a porous adsorbent solid phase, usually pellets. Mathematical models are needed to understand the dynamics of the systems thereby predicting and explaining the separation results. The models should yield the temperature, pressure, velocity, and composition profiles as a function of time and location within the bed.

The most rigorous way to model a PSA system is to model it as a convective-diffusive phenomena with transfer between two phases, the gas or void space phase and die solid or adsorbent phase. In the gas phase, mass is being transferred by diffusion, convection, and adsorption/desorption. Components are either adsorbed onto or desorbed off of the solid phase depending on the equilibrium conditions. The two phases are thus coupled by the rate of mass transfer between them.

The major commercial applications of PSA processes involve bulk separations which are highly nonisothermal, and the flow velocity is not spatially constant during the adsorption and purge operations. The solution of these complex models can be very numerically intensive. An alternative solution procedure is presented here that can decrease the computations necessary to solve some systems.

## Cyclic Steady State Operation

For any fixed-bed adsorption process, the sorbate concentrations in the gas and solid phases are functions of both time and location resulting from the movement of the concentration and temperature fronts axially along the bed. Thus, all adsorption operations operate in an unsteady state manner; so, unlike steady state separation systems, the continuous processing model is time dependent and cannot be written in terms of algebraic relationships only. Even though the concentration and temperature profiles

are dynamic for a PSA system, they do approach a pseudo steady state which is termed the cyclic steady state (CSS).

At CSS the movement of the concentration and temperature profiles axially along the bed becomes the same for each subsequent cycle. Figure 1 illustrates this cyclic steady state behavior. The CSS

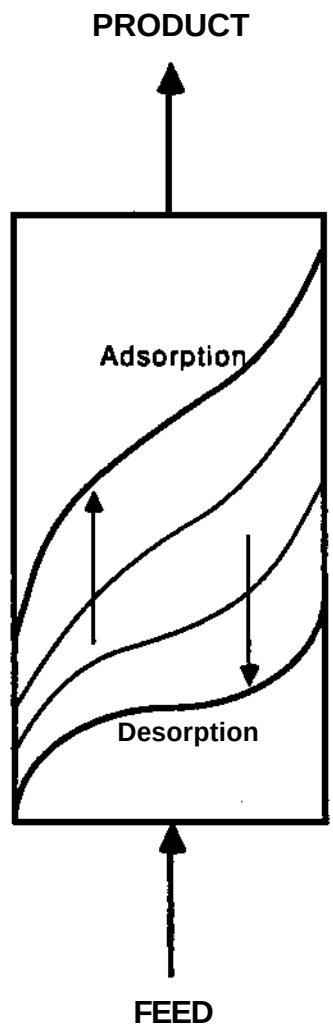



**Figure 1: Cyclic Steady State Profiles in a Fixed-Bed Adsorber**

behavior occurs for the solid phase as well as for the gas phase. TTius, we can form the conditions for a *CSS as:*

$$Y_i(z,t=0) - Y(z,t=T) \qquad q_i(z,t=0) - q(z,t=T) \qquad i - 1, \cdots n \tag{1}$$

where 7 is the system cycle time.

## Solution of an Example Cyclic Steady State Problem

Consider the following mathematical model of the Skarstrom PSA system similar to that of Raghavan et al. (Raghavan et al., 1985) with the following approximations:

1. The feed consists of a single trace component in an inert carrier.
2. The system is isothermal with negligible axial pressure drop.
3. The concentration of the solid phase is frozen during the depressurization and repressurization operations.
4. Axial dispersion is negligible.

The dimensionless component mass balance equation for this problem becomes:

$$\frac{\partial Y_i}{\partial \tau} = -\frac{u\, t_{end}}{L}\frac{\partial Y_i}{\partial \bar{z}} - \frac{(1-\varepsilon)}{\varepsilon}\frac{RTq_{scale}}{Pt_{end}}\frac{\partial \bar{q}_i}{\partial \tau} \tag{2}$$

where $t_{tnd}$ is the duration of the operation and $q_{scaU}$ is the solid concentration in equilibrium with the feed gas. The dimensionless parameters are:

$$X = \frac{L}{t_{end}} \qquad F = \frac{L}{L} \qquad \$ = \frac{*}{q_{scale}} \tag{3}$$

The mass transport processes are assumed to be well described by the linear driving force (LDF) model so the solid phase concentration is modeled by:

$$\frac{\partial \bar{q}_i}{\partial \tau} = \frac{k_{op}\, t_{end}}{q_{scale}}(q_i - R^* a_i \bar{*} 1_i) \tag{4}$$

where $k_{op}$ is the LDF mass transfer coefficient for the modeled operation. The equilibrium isotherm is assumed to be linear and is given by:

$$q_i^* = K_{eq}\frac{P Y_i}{R T} \quad (5)$$

Equations 2 and 4 are the ordinary differential equations that describe the gas and solid phase concentration profiles, respectively. These equations are written for the adsorption and purge operations of the Skarstrom cycle using the model parameters given in Table 1. The boundary condition for the adsorption and purge operations were respectively:

$$I\text{^}F\text{-}O.T) - 1? \quad (6)$$

$$y,\{F=l,T) = 0 \quad (7)$$

The initial conditions for each operation were taken to be the final conditions of the previous operation. The adsorption operation for cycle #1 was started with initially clean beds so:

$$Y\pounds\bar{z},x=0) = \text{^}(F.T\text{-}O) = 0 \quad (8)$$

In the depressurization and repressurization operations, the solid phase concentration of the adsorbable component, $\bar{q}_{i9}$ is assumed to not change (frozen solid assumption) during the operation. For the depressurization operation, the gas phase concentration, $Y_{i9}$ is averaged across the whole bed at the end of the operation while the gas phase concentration after the repressurization operation was taken to be the feed concentration.

The CSS of the above model was determined using a method of lines (MOL) solution method. The F spatial domain was discretized using five-point biased upwind finite differences. This discretization method was used since it has been shown that convective phenomena can be analyzed effectively using a fixed grid numerical method of lines technique with upwind approximations of the spatial derivatives (Carver and Schiesser, 1980). The problem was implemented using the DSS/2 system (Pirkle and Schiesser, 1987) to calculate the spatial derivatives and using LSODE (Hindmarsh, 1980) as the initial value problem ODE integrator. Thirty unequal spatial intervals were used, the smallest interval being at F = 0 and the largest being at F = 1.

Figures 2 and 3 show the solid and gas phase profiles at the end of the adsorption operation for a number of consecutive cycles.

| | | Adsorption | Purge |
|---|---|---|---|
| $k_{op}$ | | 2.78 x lCT$^4$ $\frac{1}{s}$ | 2.78 x 10-^ $\frac{1}{s}$ |
| $i_{eHd}$ | | 2705 | 270 s |
| u | | 0.255 $\frac{m}{s}$ | -0.5 $\frac{m}{s}$ |
| | E | 0.4 | |
| | $K_{eq}$ | 9084 | |
| | $L$ | 0.5m | |
| | $T$ | 298* | |

**Table 1:** Model Parameters used for CSS Example Problem

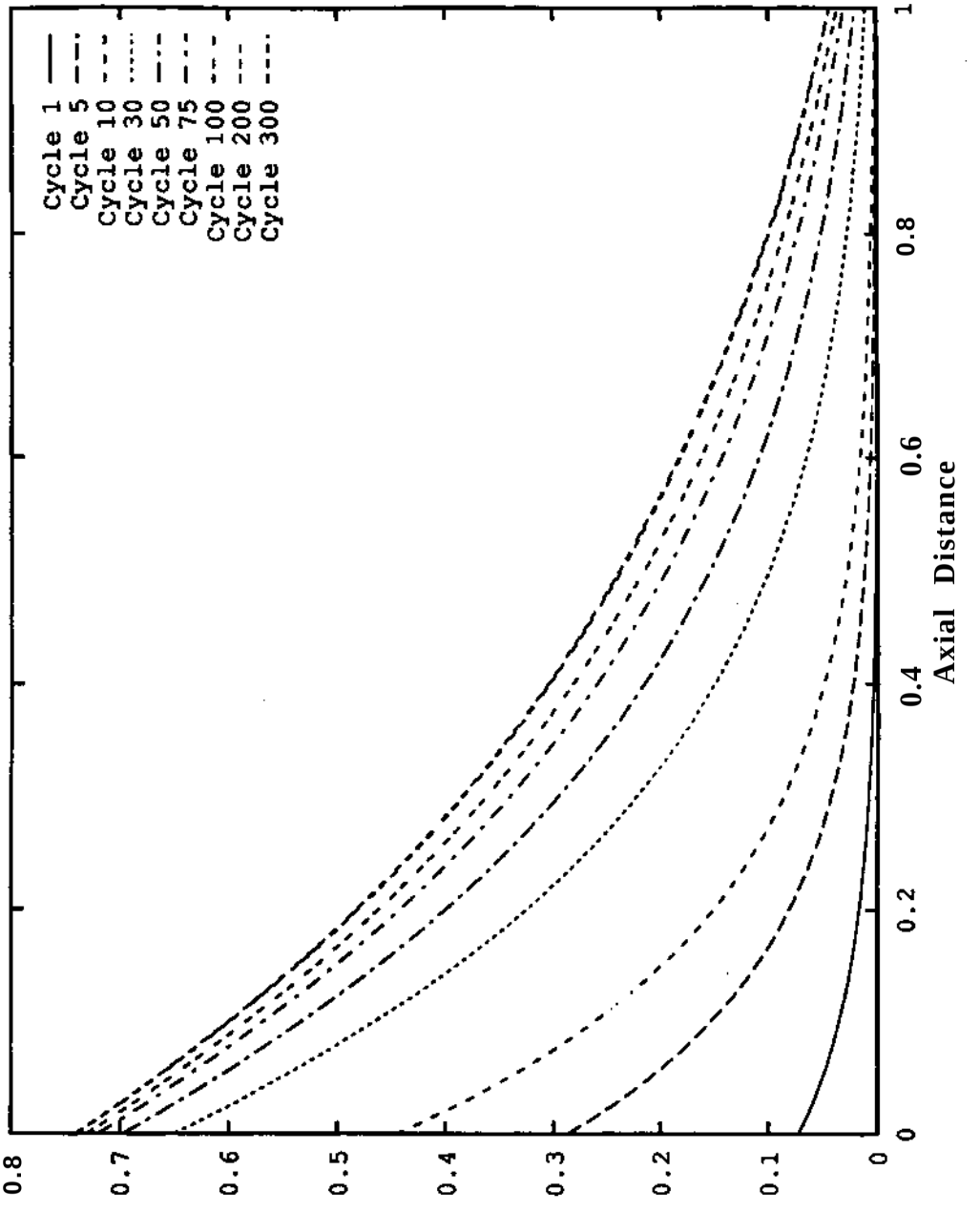
As can be seen, the curves do not become coincident for at least 300 cycles at which time it may be concluded that the CSS has been obtained. A better measure of the attainment of CSS is the error of equation 1 for the current cycle which is calculated as:

$$e = X(z, r=7) - X(z, r=0) \tag{9}$$

where $X$ is the vector of all the state variables such as $Y_{i9}$ $q_{i9}$ and $T$. If $e^T e$ £ *eps*, where *eps* is a small number, then the CSS has be achieved. Figure 4 shows a semilog plot of the error for the solid phase concentration profile as a function of the cycle number. Due to the linear behavior of the plot, the system is approaching the CSS exponentially **and** thus theoretically the CSS will never be perfectly achieved. **For all practical purposes though, the CSS for this system can be assumed to be achieved after 275 iterations when $e^T e$ £ 1.0 x 10$^{-9}$.**

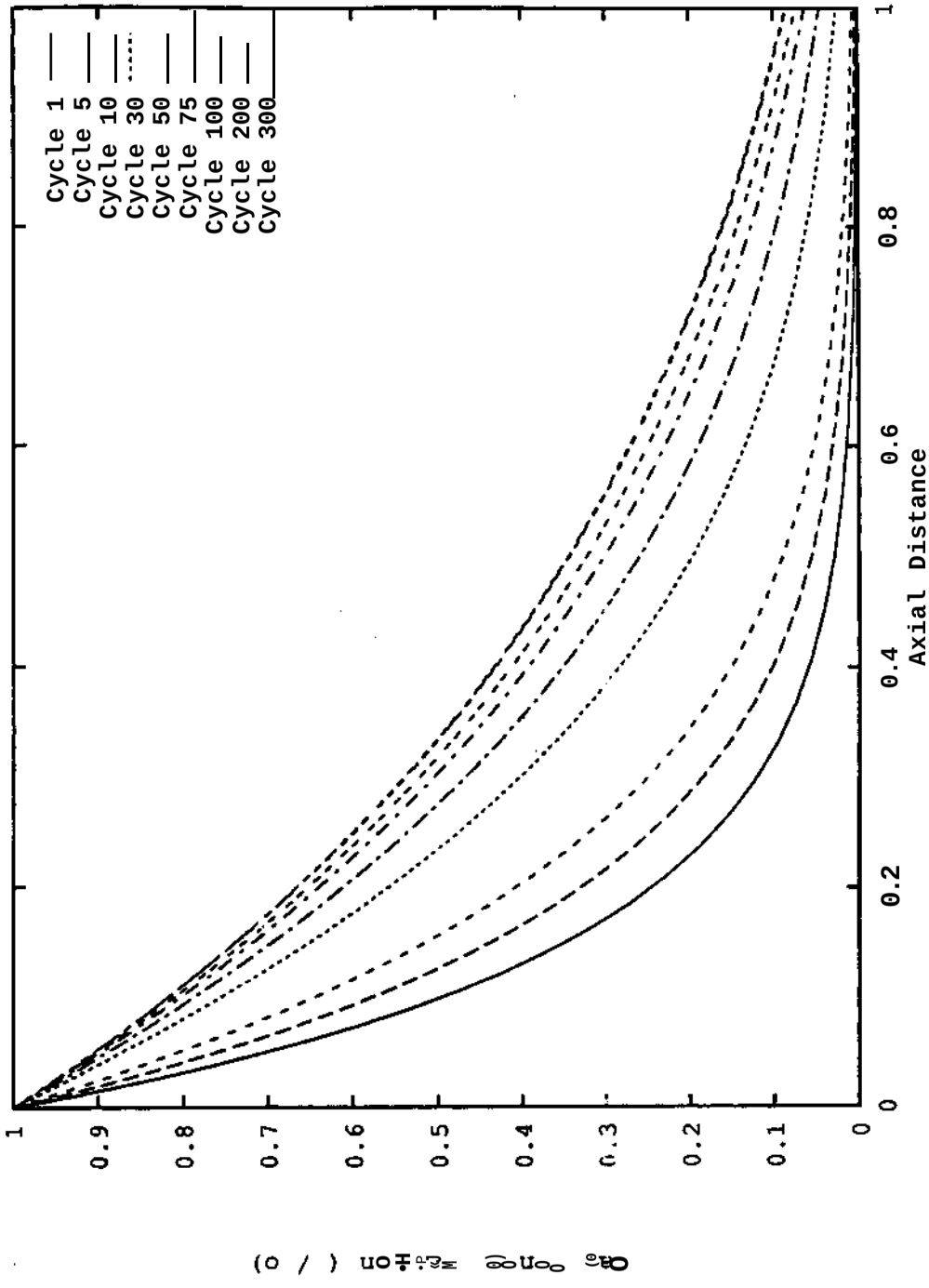
## Acceleration of Cyclic Steady State Convergence

Since some PSA models require a large number of simulation cycles to achieve a CSS, it is desirable to develop a method that could increase the convergence rates of these models and achieve CSS in many fewer cycles. Convergence methods which add significantly to the computational effort of the problem become possible since the simulation of just one PSA cycle can be very time consuming.




Solid Concentration (q/q*)

3 [illegible]2: [illegible]d Phase Profiles after [illegible]




Figur 3: Oas Phase Pro ·⊢r A 8 ◎p on O℘ on

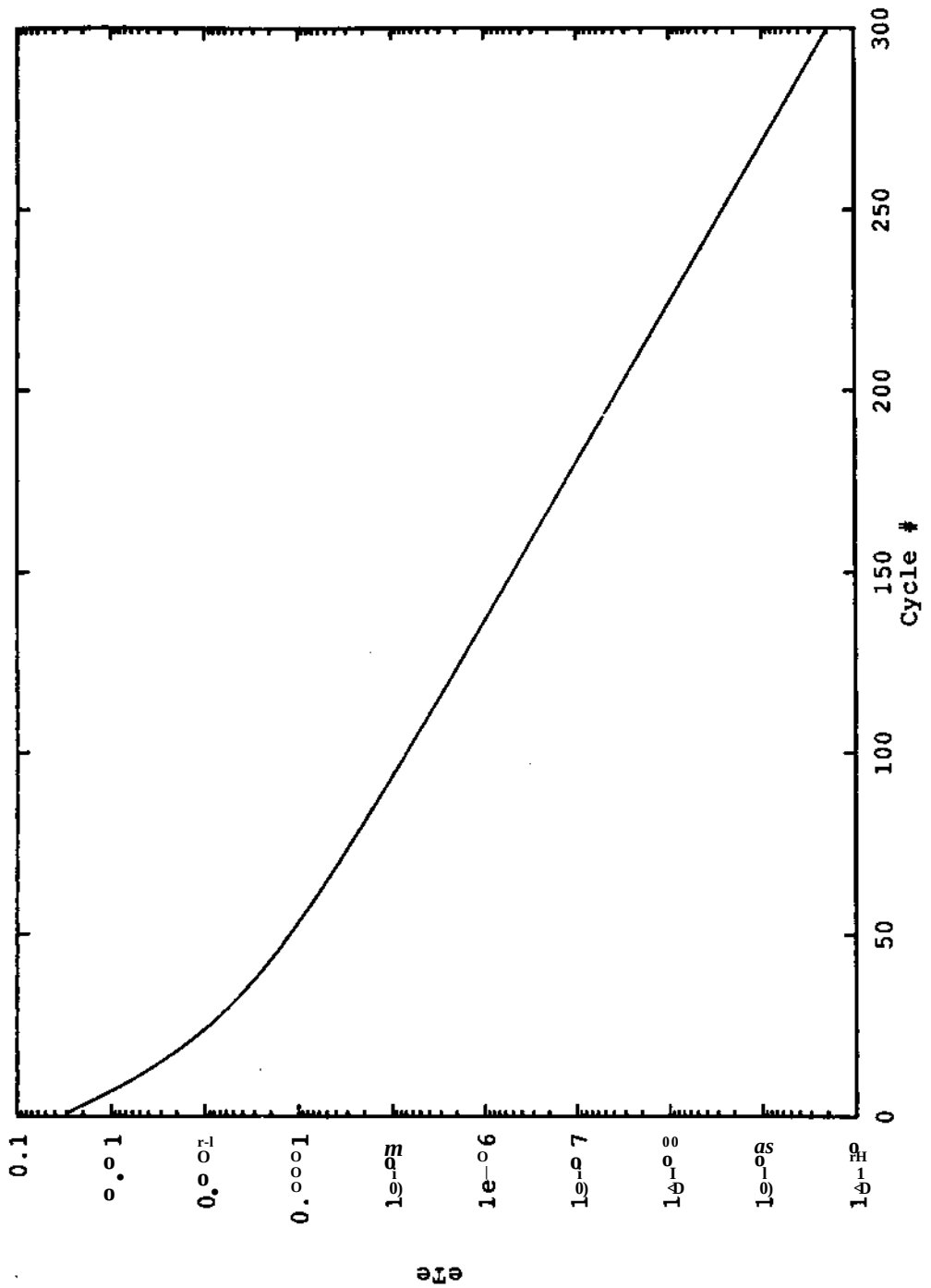



**Figure 4: Error of Approach to CSS**

Advanced convergence methods may be considered because the decrease in the number of cycles simulated can more than compensate for the additional effort expended. The formulation of the convergence equations and method for the CSS problem can be written in many different ways, a few of which will be discussed further below.

## Problem Formulation

Suppose that at a given time, $t_0$, the entire state of a PSA model can be given by the vector of states, $X(t_o)$. $X(t_o)$ would include variables such as the gas and solid phase concentration profiles for each component, the temperature profile, the pressure profile, the velocity profile, and any other variables that are necessary to define the state of the system. If we have a model that simulates the performance of the PSA system, such as a MOL model as given above, then the state of the system at a new time, $y$, can be written as a function of the state of the system at the old time, $t_{o\%}$ and the system design parameters, $d$, which are constant during the time interval:

$$X(t_f) = O[X(t_o)_9 d] \tag{10}$$

The method of determining the CSS of a MOL model, as discussed above, is to simulate the system for a number of cycles, using as the initial conditions for an operation the final conditions of the previous operation. For equation 10, this is when $tj - t_o + T$, where $T$ is the system cycle time, and thus a complete operation cycle has been simulated This method of converging equation 10 can be called the successive (or direct) substitution method since we are simply using the newly calculated states as our next guess, i.e.:

$$X^{k+l} = <P[X^k{}_9 d] \tag{11}$$

where it is assumed that the time between $X^k$ and $X^{k+l}$ is $T$.

This method of calculating the CSS is of course inspired by the operation of an actual unit which when started from an initial state will reach the CSS after a number of cycles. Thus, for a model that describes an actual system, we know that the successive substitution method must always converge to a CSS which implies:

$$\|V_X \circledR^T\| < 1 \tag{12}$$

Thus the convergence of equations 11 is at best linear. A linear convergence rate can become

unacceptable. Many solution methods exist that have convergence rates larger than linear when close to the solution. By reformulating equation 10, it can be shown how these methods can be exploited.

## Different Solution Techniques

As the work of Young (Young, 1971) indicated, the rate of convergence of a successive substitution method depends on the maximum eigenvalue of V^ <&$^T$. Several acceleration methods have been proposed that attempt to reduce the maximum eigenvalue to a minimal value (Young, 1971) (Orbach and Crowe, 1971), but they apply the same acceleration factor to all iterate variables. The secant or Wegstein method (Wegstein, 1958) applies separate acceleration factors to each variable. For all of these methods, though, it is essential that the iterate variables are uncoupled or only weakly coupled. This conditions may not be true for a PSA model.

The above acceleration techniques take a "black-box" approach to the problem without making use of the model O. Other acceleration methods can be formulated using the fact that *O* is a dynamic model and usually is a set of ODEs. In fact if O is a purely ODE model, then with the additional CSS constraints, equations 1, the CSS *czn* be found by the solution of a two-point boundary value problem. Equations 1 for the gas phase can be expressed as:

$$f/LY_x(t_o)_9 \bullet \bullet \bullet {}_9Y\hat{}t_o), Y_x(t_f), \ \ldots \ , Y_N(t_f)) \ \sim \ 0 \qquad (13)$$

The boundary conditions for the TPBVP are thus implicit and are nonlinear functions of both the initial and terminal conditions. This type of TPBVP can be solved by the method of adjoints (Roberts and Shipman, 1972), but to solve the problem numerically involves the forward evaluation of the equations and *N* backward evaluations of the adjoints for each iteration which would be too intensive (where *N* is the dimension of the state vector *X).*

A recent article (Toftegard and Jorgensen, 1989) presents a modification of a method due to Petzold (Petzold, 1978) for dynamic simulation of nonsingular periodically cycled chemical processes. In this method, direct integration of the transients is performed for only the first few starting cycles. A value of the state vector at a specific point then may be followed in order to track the slow changes from cycle to cycle. This approach can be very time saving since only a small number of cycles needs to be evaluated in detail before the prediction of several cycles ahead becomes quite accurate. A predictor-corrector integration method is used with a Newton method to increase the convergence. However, the calculation of the necessary Jacobian will involve *N* simulation cycles which could be large for our problems.

## Quasi-Newton Methods

Instead of using a successive substitution method to converge equation 10, a higher order method, such as a Newton method, is desirable. If we define the function f as:

$$f(X,d) \equiv X(t_f) - X(t_o) \tag{14}$$

and rewriting using 10:

$$f(X,d) = <!>[X(t_o)_t d] - X(t_o) \tag{15}$$

and at the CSS of the model we know that:

$$f(X,d) = 0 \tag{16}$$

which defines a set of $N$ nonlinear equations in $N$ unknowns (where again $N$ is the dimension of the state vector X).

Thus, we could solve equatio:I 16 by any of the standard nonlinear equation methods to determine the CSS of the PSA model, keeping the following limitations in mind:

1. The evaluation of the functions, f, for a given $X$ can be computationally very expensive since it involves the simulation of an entire PSA cycle.
2. In general the Jacobian matrix, J with elements $\frac{df_i}{}$, cannot be obtained analytically.

The class of quasi-Newton methods proposed by Broyden (Broyden, 1965) addresses both of these limitations directly. For these methods, an approximation of the Ja:obian matrix, A, is updated so that the change in f predicted by $A^{l+1}$ in a direction $z$ orthogonal to $AX^{l}$ is the same as would be predicted by A*.

$$A^{k+1}z - A^{i}z \tag{17}$$

$$z^T A X^l = 0 \tag{18}$$

Another form of Broyden's formula allows the direct update of the inverse of $A^{1}$ by the use of Householder's formula.

$$H^{1'} - (A^{1'})^{*''1} \tag{19}$$

By updating the inverse directly we eliminate the need to solve a set of linear equations to obtain the next iterate but instead must perform a simple matrix multiplication. The Broyden update formula for updating the inverse of the approximate Jacobian is:

$$H^{I+1} = H^{1'} - (H'Af - AX^{1}) \frac{K \quad J}{'(AX')^{r}H'Af} \tag{20}$$

where:

$$Af - P - f^{1'-1} \tag{21}$$

$$AX^{1'} = X^{1} - X^{1''-1} \tag{22}$$

The use of a Broyden method directly addresses limitation 2 above since only an approximate estimate for the Jacobian matrix need be supplied. The Broyden method, though, may fail on limitation 1 above since there is no guarantee, as there is for successive substitution, that the method will ever converge. It is thus desirable to formulate a mixed solution strategy that exploits the strong points of each method; that is, take the Broyden step when possible but, when it would result in an increase in error, revert to a successive substitution step.

The Broyden step is thus first calculated, and one PSA cycle is simulated to determine if by taking this step the error is reduced. If the error is reduced, the step is accepted, the matrix is updated, and a new Broyden step is calculated. If the error is not reduced, the Broyden step is rejected and a successive substitution step is taken. Since to check if the Broyden step is possible requires one full function evaluation, if the Broyden step is always rejected and a successive substitution step is taken, this method would result in the use of twice as many cycle evaluations as a straight successive substitution method would. For this reason, if a certain number of successive Broyden steps have been rejected (which indicates the estimate of the Jacobian is in error), it is desirable to reevaluate the approximation of the Jacobian matrix and restart the algorithm.

The suggested algorithm for the use of a mixed Broyden and .iuccessive substitution method is:

1. Supply **a close** initial guess to the CSS, $X°$ (this could be obtained from a few successive substitution steps) and determine $t°$.
2. Estimate the Jacobian matrix and evaluate its inverse, $H^1$.
3. Calculate the Broyden step, $AX^1 = -H^1 f^*$. Let $i = 1$.
4. Let $JC = X^{1+1} - AX^1$ and determine if this step results in a reduction of $(f)^T f$, if it does go to step 5 if not go to step 10. If $(f)^T f$ small enough, exit.
5. Evaluate $Af$ and $AX^T$ also set $y = 0$.
6. Evaluate the denominator of the last term in equation 20. If the denominator is too small (less than $lOr^4$ times any element in $H^1$), skip to step 8.
7. Evaluate $H^{1+1}$ using equation 20.
8. Estimate next $AX^{U\,l} = -H^{I+1} f$.
9. Set $i = i + 1$ and repeat from step 4.
10. Take a successive substitution step $X^{l+1} = X^i + f$.
11. Set $y = j + 1$. If $j \geq 5$ restart from step 2.
12. Set $i = i + 1$ and repeat from step 4.

The estimation of the Jacobian matrix in step 2 is an important part of the algorithm. If a good estimate for the full Jacobian is calculated (order of $N$ cycles of simulation), convergence may be accelerated greatly, but $N$ cycles have already been simulated. If successive substitution converges in order $N$ cycles, the calculation of the full Jacobian in the above algorithm is not possible. Only an estimate to the Jacobian that takes significantly fewer than $N$ simulation cycles can be used.

The structure of the Jacobian thus becomes very important., since it can be taken advantage of to lessen the amount of calculations. For the above formulation, ths elements of the vector of functions f are:

$$f_i = X_i(t_f) - X_i(t_o) \tag{23}$$

and the elements of the Jacobian are:

$$J_{i,j} = \frac{\partial f_i}{\partial X_j} \tag{24,}$$

One would expect each $f_L$ to be influenced more from its corresponding state $X_i$ than any other state variable. The influence of this on the structure of the Jacobian and its calculation is shown below.

**For a single component isothermal system, the Jacobian may thus be predicted to be dominant on the main diagonal and could be approximated closely by:**

$$J = cI \tag{25}$$

where *c* is a constant, and thus only one cycle of simulation is necessary to determine it. For an isothermal system with two adsorbable components, the interactions between the components may become important since they are competing for adsorbent; thus, as the concentration of one component increases at a certain position, the concentration of the other component would be expected to decrease about the same amount. The structure of the Jacobian may have the structure shown in Figure 5.

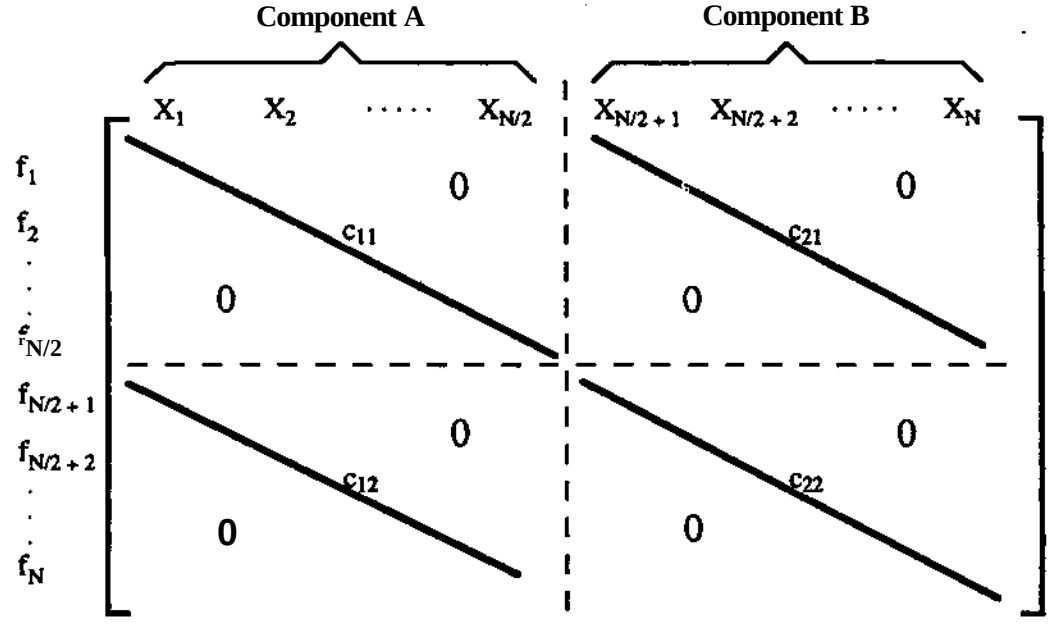



**Figure 5:** Possible Structure of a Two Component System Jacobian

Determination of the four constants on the diagonals ($c_u$, $c_{12}$, $c_{21}$, $c_{22}$) involves the calculation of only two columns of the Jacobian which takes two cycles of simulatioa

If this structure continues for a *n* component system, only *n* cycles need be simulated to obtain a good approximation of the Jacobian. Even if the structure is much different than that proposed, the algorithm does update the Jacobian and a large amount of acceleration can still be observed.

## Results

Consider the example problem above for which the CSS was calculated using a MOL or successive substitution approach. This is a single component isothermal system and thus the initial Jacobian will be approximated by equation 25. The constant, which was calculated using the middle column of the matrix, allows a good approximation of the inverse of the Jacobian to be:

$$Hi - \frac{1}{c}1 \tag{26}$$

The number of cycles simulated to calculate the CSS using the above algorithm as well as successive substitution is given in Table 2. The model was that given for the previous example problem with different values for the adsorption and desorption mass transfer coefficients. The termination criteria was $(f)^r f \wedge 1 \times 10^{-9}$. A significant decrease in the number of cycles necessary to achieve the CSS

| LDF Coefficient | Cycles above Algorithm | Cycles S. S. |
|---|---|---|
| $*\ll* = {}^{k}des - 2.78 \times 10^{\sim 5}$ | 8 | 493 |
| $k_{ads} = k_{des} - 2.78 \times 10^{-4}$ | 13 | 269 |
| $\wedge ads = k_{des} - 2.78 \times 10\text{-}^{3}$ | 51 | 130 |

Table 2: Comparison of Cycles for Convergence

using the above algorithm over successive substitution was observed for all the examples. As the LDF mass transfer coefficient increases (mass transfer resistance decreases) though, the number of cycles for the above algorithm increases while for successive substitution it is decreasing. If there is no mass transfer resistance (equilibrium adsorption), successive substitution should take one cycle to converge. When the fronts are moving slowly towards the CSS, successive substitution converges slowly while the above algorithm converges quickly. Therefore, the new algorithm is a viable alternative method to determine the CSS if successive substitution converges slowly.

# Nomenclature

| | |
|---|---|
| $A$ | **approximate jacobian matrix** |
| $d$ | **design variable** |
| $e$ | **error** |
| **f** | generic function |
| / | Jacobian matrix |
| $H$ | inverse of Jacobian matrix |
| $k_f$ | linear driving force coefficient - $sec^{-1}$ |
| $K^{eq}$ | adsorption equilibrium constant - $\frac{n?}{kgmole}$ |
| $L$ | bed length - $m$ |
| $P$ | pressure - $Pa$ |
| $q_L$ | amount adsorbed on solid phase - $\frac{T}{kg_{id}\_s}$ |
| $q_i^*$ | equilibrium amount adsorbed on solid phase - $T\frac{kg_i}{kg_{id}\_s}$ |
| $\overline{q}_i$ | dimensionless amount adsorbed on solid phase |
| $R$ | gas constant - $\frac{g}{K}\ \frac{J}{g}\ \frac{g}{K}$ |
| $t$ | time - $sec$ |
| $T$ | temperature - $K$ |
| $u$ | velocity - ^ |
| $V$ | volume - $m^3$ |
| $X$ | state variable **vector** |
| $Y$ | **mole** fraction - dimensionless |
| $z$ | axial distance - $n:$ |
| F | dimensionless axial distance |

*Greek letters*

| | |
|---|---|
| **e** | void fraction - dimensionless |

| | |
|---|---|
| $\Phi$ | **PSA model** |
| x | **dimensionless time** |

***Subscripts***

| | |
|---|---|
| ***end*** | **operation end** |
| ***op*** | **operation** |

# References


Broyden, C. G. (196S). A *Class* of Methods for Solving Nonlinear Simultaneous Equations. *Mathematics of Computation,* 79, 577-593.

Carver, M B. and W. E. Schiessei[1]. (November 1980). Biased Upwind Difference Approximation for First-Order Hyperbolic (Convective) Partial Differential Equations . Paper presented at the 73rd Annual Meeting meeting of the AIChE.

Hindmarsh, A. C. (1980). Two New Initial Value Ordinary Differential Equation Solvers. *ACM-Signum Newsletters,* 75(4), 10-11.

Orbach, O. and C. M. Crowe. (1971). Convergence Promotion in the Simulation of Chemical Processes with Recycle - The Dominant Eigenvalue Method. *Can. J. Chem. Eng.,9 49,*509.

Petzold, L. R. (August 1978). *An Efficient Numerical Method for Highly Oscillatory Differential Equations.* Doctoral dissertation, University of Illinois at Urbana-Champaign.

Pirkle Jr., J. C. and W. E. Schiesser. (July 1987). DSS/2: A Transportable Fortran 77 Code For Systems of Ordinary and One, Two and Three-Dimensional Partial Differential Equations . Paper presented at the 1987 Summer Computer Simulation Conference meeting of the Society for Computer Simulation.

Raghavan, N. S., M. M. Hassan, and D. M. Ruthven. (1985). Numerical Simulation of a PSA System. *AIChE J.,* 57(3), 385-392.

Roberts, S. M. and J. S. Shipman. (1972). *Two-Point Boundary Value Problems: Shooting Methods.* New York, NY: American Elsevier.

Toftegard, B. and S. B. Jorgensen. (1989). An Integration Method for Dynamic Simulation of Cycled Processes. *Comp. Chem. Engng.,* 75(8), 927-930.

Wegstein, J. H. (1958). Commun. Assoc. Comput., 1(9).

Young, D. M. (1971). *Iterative Solution of Large Linear Systems.* New York, NY: Academic Press.