Solution of Material Balances for Flow Sheets Modeled with Elementary Modules: The Constrained Case

Flow sheet material balance calculations are greatly simplified if all process input streams, reaction stoichiometry, and conversions, as well as all stream and component split fractions, are specified. Yet in many applications, especially those arising in process design, the available material balance specifications can take on many alternate forms. Each of these additional specifications can readily be expressed as a linear or nonlinear constraint equation involving species or total flow rates.

In this paper, an approach is developed for incorporating such specifications within the computational framework for solving unconstrained material balance problems. The linear as well as the nonlinear constraints are accommodated by generating a parametric solution to the underlying unconstrained problem. The parameters are determined by solving simultaneously first the linear and then the nonlinear constraint equations. Only as many equations are solved iteratively as there are nonlinear constraints.

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SCOPE

The necessity of incorporating specifications other than the natural input parameters of the standard modules employed in modeling a flow sheet has, of course, been recognized for quite some time in the computer aided process design and simulation literature. In the sequential modular approaches, such constraints are typically accommodated by means of additional iteration loops around the module whose normal specifications are undefined provided the constraints involve stream quantities associated with that module. If the constraints involve streams not incident to the underspecified module, then outer loops of iterations involving the entire flow sheet may be required. In the simultaneous approaches, constraints are incorporated by directly adjoining these equations to the remaining flow sheet equations. If these equations and the constraints themselves are linear, then the constraints introduce no particular computational burden. However, if the constraints are nonlinear, then the only alternative is to linearize them and to solve the entire linearized problem iteratively. Both approaches require repetitive solution of the entire material balance problem until satisfactory convergence is attained. Convergence, if it occurs, is by definition a limiting process which often requires a large number of iterations. Yet the underlying unconstrained problem, which constitutes the bulk of the equations, is a linear problem and thus should not require iterative solution.

The goal of this paper is to present a computational strategy which exploits the natural decomposition between material balance and constraint equations. The methodology developed is based on the generation and use of a general parametric solution to the underlying unconstrained problem. The construction of the parametric solution is accomplished by solving the unconstrained problem a finite number of times equal to one plus the number of imposed problem constraints. The parameters of the parametric solution are then determined by separate solution of the constraint equations. The validity of this type of approach is strongly dependent on the structural properties of the model equations. Linear algebraic proofs are used in the paper to confirm the validity in the case of flowsheet material balance problems.

CONCLUSIONS AND SIGNIFICANCE

A methodology for accommodating constraint specifications in computerized flow sheet material balance calculations has been presented. As shown, a properly specified constrained material balance problem with P constraints is equivalent to a set of N-P constant coefficient linear equations, a set of P equations of special structure each involving one of the P unknown natural parameters, and a set of P linear or nonlinear constraints. A simple rule for selecting a set of values of the P unknown natural parameters is given, and it is shown that this rule will lead to a set of linearly independent solutions of the underlying unconstrained material balance problem. These solutions are then used to construct a general parametric solution to the unconstrained problem. The parameters of the general parametric solution are calculated by expressing the constraints in terms of these parameters and solving a set of equations no larger than P. If the constraints are linear, this can be done directly without iteration. If only some of the constraints are linear, they can be partially solved to reduce the number of undetermined parameters. In the presence of nonlinear constraints, the numerical solution of a set of nonlinear equations no larger than the number of nonlinear constraints is required. The use of the parametric solution form also facilitates identification of improper problem specifications.

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The technique presented is general in that it is independent of the strategy used to solve the unconstrained problem, a sequential modular or simultaneous approach could be employed. The methodology could, in principle, be employed with more detailed constrained flow sheet simulation calculations. However, the property that a linearly independent set of natural simulation parameter vectors leads to a linearly independent set of unconstrained problem solutions, although intuitive, is very much problem structure dependent. Cases in which the property does not hold are easily constructed. Hence, the property must be separately verified for applications different from those discussed in the paper. A material balancing program implementing this approach has been developed, and the sample results obtained with several large test problems do indicate that the methodology is practical and robust.

In a predecessor paper (Sood et al., 1979), a calculation approach was developed for solving the material balances associated with process flow sheets expressed in terms of the elementary mixer, splitter, separator, and stoichiometric reactor modules. This approach was based on the key assumption that all process input streams, reaction stoichiometry, and conversions, as well as all stream and component split fractions, are specified. Yet in many applications, especially those arising in process design, the available material balance specifications can take on many alternate forms. Typical examples of these might be specification of the composition of an undesirable species in a recycle stream, product composition and flow rate requirements, ratios of reactant flows to a reactor, ratios of stream compositions in a separator, or required solids to solution ratios in settling operations. Each of these additional specifications can readily be expressed as a linear or nonlinear equation involving species flow rates.

In this paper, we will develop an approach for incorporating such additional specifications within the computational framework developed for unconstrained material balance problems. In particular, we will show that these linear or nonlinear constraint equations can be accommodated by generating a parametric solution to the underlying unconstrained problem. The parameters in the general parametric solution can be determined by solving first the linear and then the remaining nonlinear constraints simultaneously. In this approach, only as many equations need to be solved iteratively as there are nonlinear constraints. The key idea underlying the strategy is derived from the unpublished work of Kneile (1975). The strategy itself has similarities to the work of Ravicz and Norman (1964), but these similarities are only at the conceptual level.

The necessity of incorporating specifications other than the natural input parameters of the standard modules employed in modeling a flow sheet has, of course, been recognized for quite some time in the computer aided process design and simulation literature (Ravicz and Norman, 1964; Henley and Rosen, 1969; Hutchison, 1974). In the sequential modular approaches, such constraints are typically accommodated by means of additional iteration loops around the module whose normal specifications are undefined (Seader et al., 1974) provided the constraints involve stream quantities associated with that module. If the constraints involve streams not incident to the underspecified module, then outer loops of iterations involving the entire flow sheet may be required. In the simultaneous approaches, constraints are incorporated by directly adjoining these equations to the remaining flow sheet equations. If the remaining flow sheet equations are linear and the constraints themselves are linear, then the constraints introduce no particular computational burden (Hutchison, 1974). However, if the constraints are nonlinear, then the only alternative is to linearize them and to solve the entire linearized problem iteratively until satisfactory convergence is attained. The methodology developed in this paper avoids the need for iterating on the complete problem by decomposing the calculation into three separate stages: solution of the underlying unconstrained problem, simultaneous solution of the linear constraints, and iterative solution of the nonlinear constraints. In principle, this strategy for accommodating constraints can be applied both in the sequential as well as the simultaneous approaches, although in the latter case it is only necessary to do so with nonlinear constraints. The only requirement is that solutions of the unconstrained problem be carried out with reasonable efficiency.

THE CONSTRAINED MATERIAL BALANCE PROBLEM

In the previous work, the following elementary module parameters were defined to comprise the set of natural simulation specifications: the species or stream split fractions for each component separator or stream splitter, the stoichiometry and key reactant conversion for all reactors, and the species flow rates in all external process input streams. Following from this definition, a constraint specification (sometimes called control specification) is understood to be any condition imposed on the species flows which is not one of the natural specifications. Furthermore, a constrained material balance problem (CMBP) is a material balance problem involving a flow sheet modeled in terms of elementary modules in which at least one constraint specification is imposed.

A CMBP problem may thus be viewed as an unconstrained problem in which one or more of the natural simulation specifications are unknown and are replaced by constraints. Since it was previously shown that an unconstrained problem always has the correct number of specifications to yield a unique solution (Sood et al., 1979), it follows that a correctly specified CMBP must always have exactly as many independent constraints as there are missing natural specifications. Of course, the fact that the specifications are correct in number does not guarantee that they are proper; that is, the resulting set of equations will have maximum row rank. Hence, as in the unconstrained case, the assumption underlying the subsequent development is that the combined set of specifications are, in fact, proper.

Although constraint specifications can take many forms, in virtually all cases of practical significance they can be reduced to one of four types of specifications: species or total flow rates of internal or output streams, stream compositions, ratios of species flow rates, and ratios of stream compositions.

The first three of these are simply linear equations in the species flow rates. The last is the chief source of non-

linear constraint equations in flow sheet material balance problems. Any relation of the form

$$y_{ij} = m y_{kl}$$

involving mole (or weight) fraction y_{ij} of species i in stream j gives rise to the following equivalent equation in the species flows $N_i^{(j)}$:

$$\frac{N_i^{(j)}}{\sum_{s=1}^{S} N_s^{(j)}} = m \frac{N_k^{(l)}}{\sum_{s=1}^{S} N_s^{(l)}}$$

If the streams j and l are the same, then this equation reduces to one of the third type. Otherwise, it remains a quadratic equation. Typical examples of constraint equations of this type are the equilibrium relations of a flash unit. Even more common are the composition constraints inherent in the definition of a flow splitter. A flow splitter is simply a device which divides a stream flowwise without disturbing the stream composition. If the split fractions are specified, then stream compositions are conserved by assigning the same split fraction to each species in a given output stream. If the split fraction is not known, then in order to insure that stream compositions are conserved, the splitter conditions

$$\frac{N_i^{(j)}}{\sum_s N_s^{(j)}} = \frac{N_i^{(l)}}{\sum_s N_s^{(l)}} \quad i = 1, S-1$$

must be explicitly imposed between each pair of output streams j and l. In general, if there are M splitter output streams, there will be $(S-1)(M-1)$ such conditions. Of course, these quadratic constraints can be reduced to linear constraints if the composition of one of the streams incident to the splitter is known, or, in the case of the flash unit, if the K values and the vapor to liquid total flow ratio are known. However, frequently these quantities are not known, and then such simplifications can not be made.

A properly specified CMBP will thus, in general, consist of an unconstrained material balance problem with a certain number of unknown natural parameters and an equal number of constraint equations, some of which are linear and others of which are nonlinear but typically quadratic. The structure of the underlying unconstrained material balance is further elucidated via the following elementary proposition. To simplify the statement of the proposition, it is assumed that separators and splitters each involve only two output streams. We refer to this assumption as the separator convention. The extension to multiple output streams is obvious.

Proposition 1: suppose each stream vector involves S species. Then:

1. Any reactor module with unspecified conversions can be represented by $S-1$ constant coefficient linear equations plus one equation involving the conversion.

2. Any component separator module with P unspecified species split fractions can be represented by $2S-P$ constant coefficient linear equations and P equations, each involving one of the P split fractions.

3. Any splitter module with unspecified stream split fraction can be represented by S constant coefficient linear equations, $S-1$ quadratic splitter restrictions, and S equations involving the unknown split fraction.

4. Any unspecified species flow rate of a process input stream will give rise to one equation involving that unknown flow rate and will reduce by one the set of constant coefficient linear equations associated with the module to which it is input.

The verification of the proposition is quite straightforward. For illustrative purposes, we will demonstrate statements 1 and 3.

The species balance equations for a reactor expressed in terms of the conversion X_k of key reactant k are

$$N_s^{\text{out}} = N_s^{\text{in}} + \left(\frac{\sigma_{sr}}{-\sigma_{sr}} X_k\right) N_k^{\text{in}} \quad s = 1, \ldots, S,\ s \neq k$$

$$N_k^{\text{out}} = N_k^{\text{in}} (1 - X_k)$$

Eliminating the conversion from the first set of equations by using the second equation, we have

$$N_s^{\text{out}} = N_s^{\text{in}} + \frac{\sigma_{sr}}{-\sigma_{kr}} (N_k^{\text{in}} - N_k^{\text{out}}) \quad s = 1, \ldots, S,\ s \neq k$$

These are constant coefficient linear equations in the unknown species flows. The balance on the key reactant is the only equation involving the unknown natural simulation parameter X_k.

Similarly, if the stream split fraction for a splitter with two output streams is unknown, then the splitter equation

$$N_s^{(1)} = t_s N_s^{(\text{in})} \qquad s = 1, ., S$$

$$N_s^{(2)} = (1 - t_s) N_s^{(\text{in})}$$

and

$$t_s = t_S \qquad s = 1, \ldots, S-1$$

can be written as

$$N_s^{(\text{in})} = N_s^{(1)} + N_s^{(2)} \qquad s = 1, ., S$$

$$\frac{N_s^{(1)}}{\sum_s N_s^{(1)}} = \frac{N_s^{(2)}}{\sum_s N_s^{(2)}} \qquad s = 1, ., S-1$$

and

$$N_s^{(1)} = t_s N_s^{(\text{in})} \qquad s = 1, ., S$$

where the t_s are unspecified natural parameters. Of these three sets of equations, the first S are constant coefficient linear equations, the next $S-1$ are the quadratic splitter constraints, and the last S involve the S unknown natural simulation parameters. Thus, under the separator convention, whenever the stream split fraction is not specified, the splitter can be considered to have S unknown natural specifications and S constraint specifications: the $S-1$ quadratic splitter constraints and one additional constraint specifications which must be imposed to replace the unknown stream split fraction. As an immediate consequence of the above proposition, the following classification of the equations associated with any CMBP can be given. This classification assumes that the separator convention given previously is employed and that all unspecified process feed streams are always introduced into the flow sheet through mixer modules. The latter assumption, which we will call the mixer convention, imposes no loss of generality. If an unknown feed stream is entering directly into a reactor or separator, a dummy mixer whose other input streams are zero can always be introduced without effecting the solution of the CMBP. Of course, the number of streams is increased by one and the number of balance equations by S.

Proposition 2: Under the separator and mixer conventions, any properly specified CMBP consisting of N independent module equations with P constraint specifications is equivalent to an equation set consisting of $N-P$ constant coefficient linear equations, P equations each defining exactly one unknown natural simulation parameter, and P constraint equations.

Since the CMBP is assumed to be properly specified, there must be P unknown natural specifications corresponding to the given P constraint specifications. As shown by proposition 1, each missing natural specification in effect reduces the set of constant coefficient linear equations by one and will introduce one equation involving that natural simulation parameter. Hence, proposition 2 is verified provided that both a species flow rate of a process input stream and a natural parameter associated with that species in the module to which it is input are not both unspecified at the same time. However, that special situation is accommodated by the second assumption underlying proposition 2. Since all unknown feed streams are always introduced through mixers, the above situation can not occur. Each unknown feed stream will simply give rise to a single equation involving this unknown natural parameter; the remaining mixer balances will simply consist of constant coefficient linear equations.

As shown by the next proposition, the equations involving the unspecified ideal parameters have a rather special form. For convenience in notation, we indicate the aggregate of the species flows in all streams except the process input streams by the vector $\mathbf{x}$. That is, $\mathbf{x} = [\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \mathbf{N}^{(3)} \ldots, \mathbf{N}^{(K)}]$.

Proposition 3: Under the mixer convention, each unspecified natural parameter z_i will occur in one and only one equation which will either have the form

$$x_{m(i)} = f_i(z_i)\, x_{n(i)} \tag{1}$$

or the form

$$\sum_{j=1}^{K\times S} a_{ij} x_j = b_i z_i + c_i \tag{2}$$

where $f_i(z_i)$ is a linear or affine function of z_i; the a_{ij}, b_i, and c_i are appropriate constants; and $m(i)$, $n(i)$ are suitable index sets.

From the proof of proposition 1, it is clear that if the module input streams are not process feed streams, then each unspecified conversion or split fraction will give rise to an equation of the first type. If, in addition, the module input stream is a specified feed stream, then the unknown conversions and split fractions will give rise to an equation of the second type. For example, if the module is a reactor, then the unspecified conversion will appear in the equation

$$N_k^{\text{out}} = N_k^{\text{in}} - X_k N_k^{\text{in}}$$

where N_k^{in} is the specified input stream.

As a result of this very elementary analysis, we can conclude that any CMBP must always be viewed as consisting of a set of $N - P$ linear equations

$$\mathbf{G}x = \mathbf{h} \tag{3}$$

a set of P equations of either the first or second type, each involving one of the unknown natural simulation parameters, and a set of P constraints which are either linear or quadratic in the unknown species flow x_i. This classification of the flow sheet module equation suggests that the solution of these equations might well be carried out in stages, beginning with a parametric solution to the $N - P$ constant coefficient linear equations [Equation (3)].

PARAMETRIC SOLUTION OF THE CMBP

It is well known that any system of linear equations $\mathbf{Cx} = \mathbf{d}$ has a solution if and only if $\mathbf{d}$ lies in the range of $\mathbf{C}$, and, if so, then all solutions are given by

$$\mathbf{x} = \mathbf{w}^{(o)} + \sum_i [\mathbf{w}^{(i)} - \mathbf{w}^{(o)}]\lambda_i$$

where $\mathbf{w}^{(o)}$ is any solution to $\mathbf{Cx} = \mathbf{d}$, the $\mathbf{w}^{(i)}$ are any basis of the range of $\mathbf{C}$, and the λ_i are scalar parameters. If $\mathbf{x}$ is N dimensional and $\mathbf{C}$ has rank $N - P$, then it is clear that the $\mathbf{w}^{(i)}$ will correspond to any set of P linearly independent solutions of the system $\mathbf{Cx} = \mathbf{d}$.

This construction suggests that an explicit general solution to the set of $N - P$ constant coefficient linear equations of the CMBP can be developed directly from a suitable set of particular solutions. One merely needs to devise a systematic procedure for generating particular solutions which can insure that these solutions will be linearly independent. A convenient and simple way of generating a particular solution is to arbitrarily assign values to the P simulation parameters z_i in Equations (1) and (2). Assuming that the assigned values will constitute a proper specification, the resulting unconstrained material balance problem can be solved using any available method. The solution obtained will, of course, depend on the values of the z_i selected, and any two solutions generated from two different values of the z_i will be distinct. However, they need not necessarily be linearly independent in general.

As will be verified in proposition 4, the following choice of the parameters z_i can be guaranteed to lead to linearly independent solutions. Specifically, consider a CMBP with P unspecified simulation parameters, the first Q of which are associated with type 1 equations. Let the j^{th} simulation parameter vector be given by

$$z_i^{(j)} \begin{cases} = \alpha_i & \text{if } i = j \\ = \beta_i & \text{otherwise} \end{cases}$$

where the α_i and β_i are selected so that $\alpha_i \neq \beta_i$, $\alpha_i \neq 0$, and, if $Q \neq P$, that

$$\sum_{i=Q+1}^{P} \frac{(c_i + \beta_i b_i)}{b_i(\beta_i - \alpha_i)} \neq 1$$

Denote by $\mathbf{v}^{(j)}$ the solution to Equations (1) through (3) obtained when $\mathbf{z}$ is set equal to $\mathbf{z}^{(j)}$.

Proposition 4: If the specifications $\mathbf{z}^{(j)}$, $j = 1, ., P$ satisfying the conditions given above are proper, then the set of solutions $\mathbf{v}^{(j)}$ obtained will be linearly independent. For proof, see the appendix.

It should be noted that the choice of α_i and β_i in the above construction is quite arbitrary. To keep the solutions generated close to physical reality, it is advisable, but not necessary, to choose values between 0 and 1. Furthermore, the condition $\sum_i q_i/p_{ii} \neq 1$ is not really very restrictive. In practice, it is highly unlikely that any arbitrary choice of α_i and β_i will lead to a violation of this condition. Hence, from our computational experience, a check of the above condition can be quite safely ignored.

By using the above choice of the $z^{(j)}$, we are thus assured that the generated solutions will be linearly independent. Thus, if one further solution $\mathbf{v}^o$ is obtained, say by setting $z_i = \beta_i$ for all i, then the resulting $P + 1$ unconstrained solutions can be assembled to generate a general parametric solution

$$\mathbf{x} = \mathbf{v}^{(0)} + \sum_i [\mathbf{v}^{(i)} - \mathbf{v}^{(0)}]\lambda_i \equiv \mathbf{v}^o + \mathbf{W}\boldsymbol{\lambda} \tag{4}$$

of the CMBP. As shown in the next two sections, this general solution can be inserted into the linear and nonlinear constraints to yield specific values of the λ's. These specific parameter values will, when substituted back into the above parametric solution, in turn, give the desired specific solution to the CMBP.

Before proceeding with that discussion, we digress briefly to point out that the explicit parametric solution can itself be used to extract useful information about the problem

being solved. For instance, it frequently happens in both large and small material balance problems that the stoichiometry of the reactions, the nature of the separations, and the structure of the flow sheet combine to induce flows or ratios of flows which remain invariant of other specifications. Such invariants can be easily recognized from the parametric solution, since those components of $\mathbf{x}$ will be independent of the λ's or will have rows which are simple multiples of each other. These situations can be readily identified and flagged during solutions by examination of the W array. From this information, improper (that is, dependent) specifications in the constraints can frequently be avoided.

SOLUTION IN THE PRESENCE OF LINEAR CONSTRAINTS

Given the explicit parametric solution, Equation (4), to the underlying constrained material balance problem, any set of linear constraints

$$\mathbf{Tx} = \mathbf{u}$$

associated with the CMBP can be accommodated by, in effect, substituting the parametric solution into the constraints and solving the equation

$$\mathbf{TW}\boldsymbol{\lambda} = \mathbf{u} - \mathbf{Tv}^o \equiv \boldsymbol{\gamma} \tag{5}$$

If the CMBP only involves these linear constraints, then assuming the rank of the product matrix TW is equal to P, the substituted Equation (5) will have a unique solution $\boldsymbol{\lambda}^*$. Upon insertion into Equation (4), this λ^* will then yield the required unique solution $\mathbf{x}^*$ of the CMBP. Since TW is a $P \times P$ matrix, simultaneous solution of (5) only involves as many linear equations as there are constraints. Moreover, when any array reduction procedure is used to solve (5), the rank of TW will necessarily be verified, and hence the existence of any improper, that is, dependent specifications, will immediately be recognized. If, in addition, row permutation indexes are saved during the attendant elementary row operations, a set of dependent specifications can be identified so that constructive action can be taken in subsequent problem solution attempts.

If, in addition to the linear constraints, the CMBP also involves nonlinear constraints, then complete solution of (5) is not possible. Instead, an array reduction procedure which involves explicit backward elimination can be employed to generate a partial solution of some components of $\boldsymbol{\lambda}$ in terms of the others. In such cases, the linear constraints, in effect, serve to reduce the dimensionality of $\boldsymbol{\lambda}$.

Suppose the P constraints of L that are linear and $P - L$ that are nonlinear. Reduction of the augmented $L \times (P + 1)$ matrix (TW, $\boldsymbol{\gamma}$) will yield the equivalent array

$$(\mathbf{I}, \mathbf{C}, \mathbf{d})$$

where $\mathbf{I}$ is an $L \times L$ identity matrix, $\mathbf{C}$ is $L \times (P - L)$, and $\mathbf{d}$ is a column vector. Corresponding to this effective partitioning and reduction of TW, the vector $\boldsymbol{\lambda}$ will similarly be partitioned into $\hat{\boldsymbol{\lambda}}$ and $\bar{\boldsymbol{\lambda}}$ such that

$$\hat{\boldsymbol{\lambda}} = \mathbf{C}\bar{\boldsymbol{\lambda}} + \mathbf{d} \tag{6}$$

As a consequence, the parametric solutions to the CMBP become

$$\begin{aligned} \mathbf{x} &= \mathbf{WC}\bar{\boldsymbol{\lambda}} + (\mathbf{w}^o + \mathbf{Wd}) \\ &\equiv \mathbf{D}\bar{\boldsymbol{\lambda}} + \boldsymbol{\delta} \end{aligned} \tag{7}$$

and involve only $P - L$ undetermined parameters.

Note that at this stage, too, the array $\mathbf{D}$ can be examined to determine if any invariants occur which ought not to be subjected to additional specifications.

SOLUTION IN THE PRESENCE OF NONLINEAR CONSTRAINTS

As noted earlier, a CMBP may, in addition to the previously discussed linear constraints, also involve nonlinear constraint equations:

$$g_i(\mathbf{x}) = 0 \quad i = 1, .., P - L$$

If the CMBP is properly specified, then these equations will be sufficient to solve for the unknown parameters $\bar{\boldsymbol{\lambda}}$ in Equations (7). However, since the equations are nonlinear, their solutions will require the use of a suitable iterative equation solving algorithm. For instance, if the Newton-Raphson method is employed, then the following iteration formulas expressed in terms of the variables $\bar{\boldsymbol{\lambda}}$ and the gradients of $g_i(\mathbf{x})$ come into play:

$$[\nabla_x \mathbf{gD}]\,(\Delta\bar{\boldsymbol{\lambda}})^{(k)} = -\,\mathbf{g}\,\{x\,[\bar{\boldsymbol{\lambda}}^{(k)}]\}$$

and

$$\bar{\boldsymbol{\lambda}}^{(k+1)} = \bar{\boldsymbol{\lambda}}^{(k)} + (\Delta\bar{\boldsymbol{\lambda}})^{(k)}$$

where

$$\mathbf{g}[x(\bar{\lambda})] = g(\mathbf{D}\bar{\boldsymbol{\lambda}} + \boldsymbol{\delta})$$

As usual, the iterations must be initiated with an initial estimate $\bar{\boldsymbol{\lambda}}^0$. However, since the $\bar{\boldsymbol{\lambda}}$'s are mathematical conveniences rather than physically identifiable quantities, initial estimates of the $\bar{\lambda}$'s are, in general, not easy to provide. Moreover, because of the nonlinearities, guarantees concerning convergence can not be given, and multiple solutions may well be encountered. Fortunately, most of these difficulties can be overcome in the present application because the functions $g_i(\mathbf{x})$ have a very special structure. As noted earlier, the primary nonlinear constraints occurring in material balance problems are quadratic functions of the form

$$\frac{x_j(\bar{\boldsymbol{\lambda}})}{\sum_l x_l(\boldsymbol{\lambda})} = m_i \frac{x_k(\bar{\boldsymbol{\lambda}})}{\sum_m x_m(\boldsymbol{\lambda})} \tag{8}$$

In this expression, each of the sums in the denominators represents the summation of the species flows associated with a given stream. Hence, it is a sum over only a subset of the x_l.

Since each $x_i(\bar{\boldsymbol{\lambda}})$ in the above functions is a known linear function of the $\bar{\boldsymbol{\lambda}}$'s, the derivatives are easily calculated in general form. In particular if we let

$$g_i[\mathbf{x}(\bar{\boldsymbol{\lambda}})] = x_j(\bar{\mathbf{x}})\,[\sum_m x_m(\bar{\lambda})] - m_i x_k(\bar{\boldsymbol{\lambda}})\,[\sum_l x_l(\bar{\boldsymbol{\lambda}})] \tag{9}$$

then, from Equation (7)

$$\begin{aligned} \frac{\partial g_i(\bar{\boldsymbol{\lambda}})}{\partial \lambda_n} &= (\sum_m d_{mn})\, x_j(\bar{\boldsymbol{\lambda}}) + [\sum_m x_m(\bar{\boldsymbol{\lambda}})]\, d_{jn} \\ &\quad - m_i\,\{(\sum_l d_{ln}) + x_k(\bar{\boldsymbol{\lambda}}) + [\sum_l x_l(\bar{\boldsymbol{\lambda}})]\, d_{kn}\} \end{aligned} \tag{10}$$

Since the ratios on each side of Equation (8) are mole or weight fractions of certain species in selected streams, their values must always lie between 0 and 1. Thus, if by convention, Equation (8) is always formulated so that $m_i \leq 1$, then reasonable initial ratio estimates y_i^0 can always be obtained by selecting values in the range $0 \leq y_i^0 \leq m_i$. From these estimates, it is easy to calculate initial

TABLE 1. TEST PROBLEM CHARACTERISTICS

Problem No.	Application	Source	Number of Mixers	Reactors	Separators	Streams	Species
1	Chlorobenzene	Thatcher, 1962	3	2	5	17	5
2	Ammonia/nitric acid	Reklaitis, 1973	4	5	4	21	9
3	Cracking gas	Nagiev, 1964	3	5	6	21	6
4	Natural gasoline	Motard et al., 1969	6	1	9	28	10
5	Coal conversion process	Parsons, 1974 Kneile, 1975	18	13	32	105	17

estimates of the $\bar{\lambda}$'s by simply setting each side of Equation (8) equal to its respective y_i^0. This leads to $2(P-L)$ linear equations in the $P-L$ variables $\bar{\lambda}_n$ which can be solved in normal form (Forsythe and Moler, 1967) to give a minimum norm initial estimate of the $\bar{\lambda}_n$'s. Alternately, one can simply use only the right-hand ratio in Equation (8) and obtain $\bar{\lambda}^0$ by solving the linear system

$$x_k(\bar{\lambda}) = y_i^0 m_i[\sum_m x_m(\bar{\lambda})] \quad i = 1, \ldots, P-L$$

or

$$\sum_{n=1}^{P-L} d_{kn}\bar{\lambda}_n + \delta_k = y_i^0 m_i \left[\sum_m \left[\sum_{n=1}^{P-L} d_{mn}\bar{\lambda}_n + \delta_m \right] \right]$$
$$i = 1, \ldots, P-L$$

In either case, the initial estimates of the $\bar{\lambda}_n$'s obtained in this manner are, in our experience, sufficient so that problems of divergence or convergence to fictitious solutions are avoided. In fact, in all of the test cases run to date, even the choice $y_i^0 = 0$ has proven to be satisfactory when used in conjunction with the normal form of the equations for estimating $\bar{\lambda}^0$.

Once the initial $\bar{\lambda}^0$ vector is calculated, Equations (7) can be evaluated to obtain $\mathbf{x}(\bar{\lambda}^0)$. With this known, the $g_i(\lambda)$ and partial derivatives $\partial g_i/\partial \lambda_n$ can be evaluated from Equations (9) and (10), respectively, and the usual Newton-Raphson iterations initiated. The key point to be again noted is that in the Newton iterations only as many equations are solved as there are nonlinear constraints.

SUMMARY OF THE CALCULATION STRATEGY

The algorithm for the solution of CMBP's with P undefined natural specifications thus can be decomposed into four separate phases:

1. Solution of the underlying unconstrained material balance problem $P+1$ times to generate the general parametric solution, Equation (4).
2. Simultaneous (partial) solution of the L linear constraints to generate the reduced parametric solution, Equation (7).
3. Iterative solution of the $P-L$ nonlinear constraints to determine the parameter vector $\bar{\lambda}$.
4. Recovery of the vector of stream flows via Equations (7) or (6) and (4).

In this algorithm, the iterative calculations are clearly isolated from those calculations which involve solution of linear equations. This decomposition is obtained at the price of having to carry out $P+1$ unconstrained solutions, simultaneous solution of L linear constraint equations, and solution of $P-L$ linear equations to determine initial estimates of the $\bar{\lambda}$. Of these calculations, the unconstrained solutions are clearly the most costly. However, providing adequate care is taken to save a calculation map for the unconstrained solution, the remaining P unconstrained solutions can be obtained quite expeditiously. As shown in our previous work (Sood et al., 1979), such a calculation map can readily be retained by saving the symbolic form of the mixer equations and the precedence order for the mixer equation calculations.

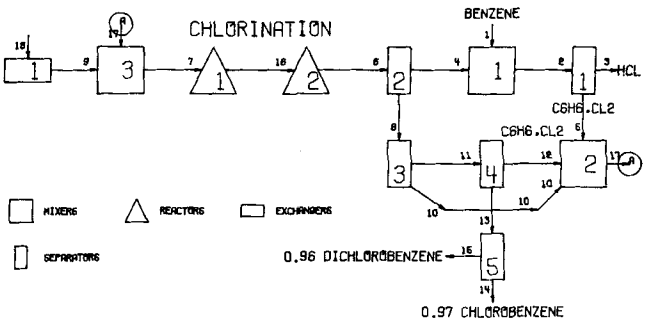

Fig. 1. Chlorobenzene flow sheet.

COMPUTER CODE AND RESULTS

A program called MBPI implementing this calculation strategy has been coded. The program solves the unconstrained subproblem using the mixer equation methodology of Sood et al. (1979). Provisions have been made in the program for three types of constraints:

1. Species or total flow = constant.
2. Species or total flow = species or total flow × constant.
3. Mass Fraction of species i in stream k − mass fraction of species j in stream m × constant.

The last of these is the only source of nonlinear constraints. Constraints of this type always occur when the split fraction of a flow splitter or an equilibrium flash unit are not specified.

In implementing the above algorithm, there is some choice as to how step 4 is to be carried out. If the complete set of $P+1$ unconstrained solutions generated in step 1 are saved, then once the λ's are known, the final solution can be determined from Equation (4). However, for purposes of steps 2 and 3, the complete set of solutions is really not required. Hence, considerable storage savings can be achieved by only storing the solution corresponding to the x_i actually involved in the constraints. In that case, however, once the λ's are determined, the $P+1$ material balance solutions must be regenerated so that the complete final flows can be recovered. Hence, the storage savings is achieved by about doubling the computation time. This latter calculation mode was implemented in MBP-I.

The program was tested on a number of flow sheet case problems. The general characteristics of the problems are listed in Table 1. The smallest problem is a textbook application (Figure 1), while the largest represents a solvent refined coal synthetic fuels complex, a flow sheet of which

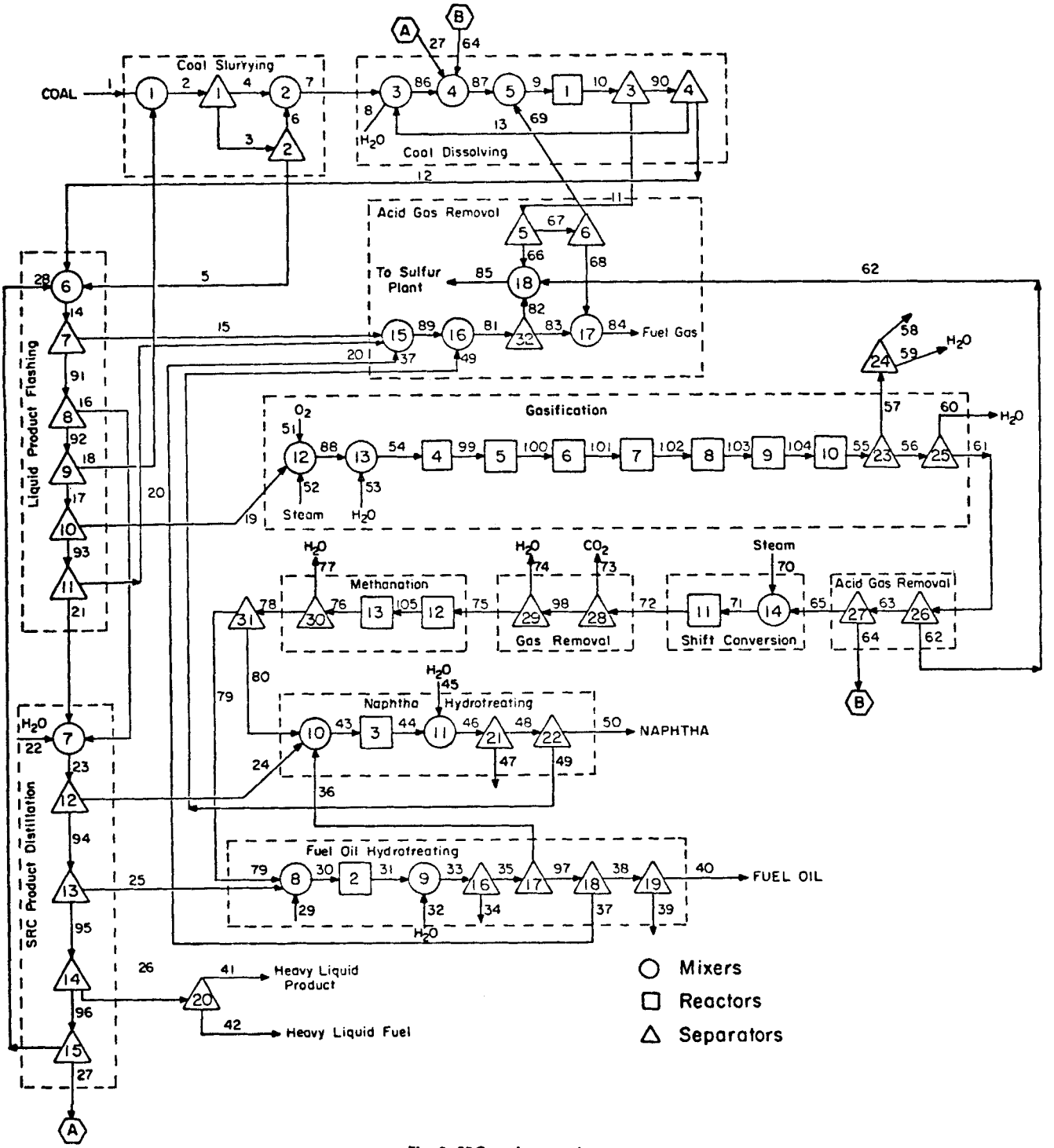

Fig. 2. SRC coal conversion process.

TABLE 2. CORE AND EXECUTION TIME REQUIREMENTS FOR CONSTRAINED PROBLEM SOLUTIONS

Problem No.	Number of equivalent linear equations	Number of constraints		Core requirements (K words) octal	Execution time* (CPU s)	Ratio of constrained to unconstrained CPU time
		Linear	Nonlinear			
1	75	2	1	42	1.37	4.2
2	153	13	—	47	10.2	14.6
3	120	—	2	43	1.1	2.8
4	250	1	9	46	10.6	11.5
5	1 615	10	—	105	140	14.3

*CDC 6500.

is shown in Figure 2. Further details of the problems can be found in the program user's manual (Sood and Reklaitis, 1977) which is available from the authors upon request. Computational statistics for the solution of the constrained form of these problems are summarized in Table 2. The number of equivalent linear equations given in the table refers to the total number of species balance equations associated with the flow sheet elementary modules. This number is only intended to suggest the problem size if a simultaneous approach was used.

The CPU times reported were those required by the Purdue Universaity CDC 6500 and include normal program input and output overheads. The ratio of the constrained to unconstrained CPU times confirms that the computation time is essentially proportional to the number of constraints. The computation time for nonlinear constraints does not appear to be substantially larger than that for linear constraints. Moreover, the choice of initial estimates does not appear to be critical; the three nonlinearly constrained problems were all successfully solved with zero initial estimates.

The main alternative to the strategy proposed in this paper is the strategy conventionally used in conjunction with the sequential modular method for solving material balance problems, namely, repetitive solution of the entire flow sheet problem with iterative adjustment of the unknown natural specifications until constraint satisfaction is achieved. Since the parametric solution strategy requires a fixed, finite number of unconstrained flow sheet solutions, while the conventional approach requires a sequence of solutions that is only limited by an imposed relative error criterion, the former strategy appears to enjoy an inherent computational advantage. Detailed computational experiments to confirm this superiority are tedious to carry out because of the number of influencing factors: effects of initial estimates, choice of convergence promotion method, etc. Fortunately, as shown by the results obtained in attempting to solve problem 1 using the conventional strategy, such detailed comparisons are, in fact, unnecessary.

Problem 1, the flow sheet for which is shown in Figure 1, involves three unknown natural parameters: the flow of benzene in stream (1), the conversion in reactor 1, and the split fraction of chlorine in separator 2. Three constraints are imposed: the product flow, [stream (14)], is specified, the chlorobenzene composition of the product is specified, and the ratio of the chlorine mass fractions in streams (4) and (11) are specified. The problem thus has two linear and one nonlinear constraint. This constrained problem was solved by using the conventional modular approach with bounded Wegstein convergence promotion on stream (7). Iterative adjustment of the three unspecified natural parameters was carried out using Brown's algorithm (Brown, 1969; Brown and Dennis, 1971), as implemented in subroutine ZSYSTM of the IMSL library (see references). This algorithm is an efficient Newton analogue for solving simultaneous nonlinear equations which only require function values. Starting with initial estimates of 2 000, 0.2, and 0.5 for the feed, conversion, and split fraction, ninety unconstrained solutions were required to reach the actual values of 1 919.205, 0.23048, 0.6283 within a relative error tolerance of 10^{-7}. CPU time on the Purdue CDC 6500 was 44.5 s. Using the same tolerance, MBP-I required 1.37 s. Of course, different times will be obtained with different initial estimates. Good estimates had to be provided to avoid divergence. The problem could be solved with either four or eight unconstrained solutions, depending upon the storage strategy used, if the parametric solution construction was used in conjunction with the sequential modular method for solving the unconstrained problem.

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NOTATION

$\mathbf{A}$ = (a_{ij}) } coefficients of the module equation of type
$\mathbf{b}$ = (b_i) } 2 containing unspecified natural parameters
$\mathbf{c}$ = (c_i) } z_i
$\mathbf{C}$ = reduction remainder of the array W
$\mathbf{D}$ = WC, coefficient matrix of the reduced parametric solution of the CMBP
$\mathbf{d}$ = the vector $\boldsymbol{\delta}$ after array reduction
$\mathbf{e}$ = vector with unit components
$f_i(\ )$ = affine function involving the unspecified natural parameter z_i
$\mathbf{F}$ = array of coefficients of module equation of type 1
$\mathbf{G}$ = array of coefficients of the $N - P$ constant coefficient linear module equations associated with the CMBP
$g(\ )$ = nonlinear constraint functions
$\mathbf{h}$ = right-hand side vector associated with $\mathbf{G}$
K = number of unknown streams
L = number of linear constraints
M = number of splitter output streams
m_i = proportionality constant in the i^{th} nonlinear constraint
$m(i)$, $n(i)$ = indexes of unknown stream variables associated with unknown natural parameters
$\mathbf{N}^{(j)}$ = vector of species flow in stream j
N = total number of flow sheet module balance equations
P = number of unspecified natural parameters
$\mathbf{P}$ = (p_{ii}) = diagonal matrix with elements $p_{ii} = b_i(\alpha_i - \beta_i)$
$\mathbf{q}$ = vector with elements $q_i = c_i + \beta_i b_i$
Q = number of module equations of type 1 involving unspecified natural parameters
S = number of species
$\mathbf{T}$ = coefficient matrix of the linear constraints
t_s = split fraction of component s
$\mathbf{u}$ = right-hand side vector of the linear constraints
$\mathbf{V}$ = $(\mathbf{v}^{(j)})$ = matrix of unconstrained solution vectors
$\mathbf{W}$ = matrix of homogeneous unconstrained solutions with columns $\mathbf{v}^{(j)} - \mathbf{v}^{(o)}$
X_k = conversion of species k
$\mathbf{x}$ = aggregate vector of all species flows in all streams
y_{ij} = mole or weight fraction of species i in stream j
$\mathbf{z}$ = vector of unspecified natural parameters

Greek Letters

α_i = } arbitrary nonzero choices of values for the
β_i = } natural parameter z_i
$\boldsymbol{\delta}$ = constant vector in the reduced parametric solution of $\mathbf{x}$
$\boldsymbol{\lambda}$ = vector of unknown parameters in the parametric solution of the CMBP
$\boldsymbol{\theta}$ = vector of scalar multipliers θ_i
σ_{sr} = stoichiometric coefficient of species s in reactor r

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APPENDIX: PROOF OF PROPOSITION 4

Proof: Consider the system of equations

$$\mathbf{Gx} = \mathbf{h}$$
$$x_{m(i)} = f_i(z_i)x_{n(i)} \qquad i = 1, .., Q$$
$$\sum_j a_{ij}x_j = b_i z_i + c_i \qquad i = Q+1, .., P$$

Note that for the first Q solutions $v^{(j)}$, the right-hand sides of the last set of equations will be constants equal to $b_i\beta_i + c_i$. For the remaining $P - Q$ solutions, the second set of equations will have constant coefficients $f_i(\beta_i)$. Linear independence of the P solutions $\mathbf{v}^{(j)}$ can thus be proved in two parts: first by showing that each of the first Q solutions cannot be linearly dependent on the remaining solutions, and second, by showing that the other $P - Q$ solutions are themselves linearly independent.

To prove the first part, suppose that any one of the first Q solutions, say $\mathbf{v}^{(l)}$, can be written as a linear combination of the others. If so, then there must exist a set of scalars $\theta^{(k)}$, $k = 1, .., P$, and $k \neq l$ such that

$$\mathbf{v}^{(l)} = \sum_{k\neq l} \theta^{(k)}\mathbf{v}^{(k)}$$

Consider the equation containing the l^{th} parameter

$$x_{m(l)} = f_l(z_l)z_{n(l)}$$

By construction

$$v^{(k)}_{m(l)} = f_l(\beta_l)v^{(k)}_{n(l)} \qquad k = 1, .., P, k \neq 1 \qquad \text{(A1)}$$

while the l^{th} solution must satisfy

$$v^{(l)}_{m(l)} = f_l(\alpha_l)v^{(l)}_{n(l)} \qquad \text{(A2)}$$

Multiplying both sides of each of Equations (A1) by $\theta^{(k)}$ and summing, we have

$$\sum_{k\neq l} \theta^{(k)}v^{(k)}_{m(l)} = f_l(\beta_l)\sum_{k\neq l} \theta^{(k)}v^{(k)}_{n(l)}$$

From this it follows that both

$$v^{(l)}_{m(l)} = f_l(\beta_l)v^{(l)}_{n(l)}$$

and Equation (A2) must be satisfied simultaneously. But this is a contradiction since it is assumed that $\alpha_i \neq \beta_i$ and since the f_l are bijections by construction. Hence, the first part is proved. To prove the linear independence of the solution vectors $v^{(j)}$, $j = Q + 1, .., P$, recall that for these cases $z_i^{(j)} = \beta_i$ for $i = 1, .., Q$. Thus, the set of equations which the $P - Q$ solutions must all satisfy contains a set of constant coefficient linear equations

$$\mathbf{Gx} = \mathbf{h}$$

and

$$\mathbf{Fx} = \mathbf{0}$$

where the latter Q homogeneous equations are those of type 1. In addition, each of these solutions must satisfy the equation

$$\mathbf{Ax} = \mathbf{bz} + \mathbf{c}$$

for its corresponding value $\mathbf{z}^{(j)}$. The complete set of $P - Q$ solutions must thus satisfy the matrix equations

$$\begin{bmatrix} \mathbf{G} \\ \mathbf{F} \\ \mathbf{A} \end{bmatrix} \mathbf{V} = \left[\begin{bmatrix} \mathbf{0} \\ \mathbf{0} \\ \mathbf{P} \end{bmatrix} + \begin{bmatrix} \mathbf{h} \\ \mathbf{0} \\ \mathbf{q} \end{bmatrix} \mathbf{e}^T \right]$$

where the elements of the diagonal matrix $\mathbf{P}$ are

$$p_{ii} = b_i(\alpha_i - \beta_i) \qquad i = Q+1, .., P,$$

the vector $\mathbf{q}$ has elements

$$q_i = c_i + \beta_i b_i \qquad i = Q+1, .., P,$$

and the $P - Q$ component vector $\mathbf{e}$ has components unity. The matrix $(\mathbf{P} + \mathbf{qe}^T)$ has the same rank as a symmetric matrix consisting of off diagonal elements equal to 1 and diagonal elements $(q_i + p_{ii})/q_i$. To verify that under the assumption

$$\sum_i q_i/p_{ii} \neq 1$$

the matrix has full rank, we proceed by contradiction. Suppose the matrix does not have maximal rank. Then, for some k, there must exist scalars $\theta^{(j)} \neq 0$, $j = Q + 1, .., P$, and $j \neq k$ such that

$$\frac{q_k + p_{kk}}{q_k} = \sum_{j\neq k} 1 \cdot \theta^{(j)}$$

and

$$1 = \left(\frac{q_i + p_{ii}}{q_i}\right)\theta^{(i)} + \sum_{\substack{j\neq i \\ j\neq k}} 1 \cdot \theta^{(j)},$$

$$Q + 1 \leq i \leq P \quad \text{and} \quad i \neq k$$

Subtracting the first equation from each of the others, we obtain

$$\frac{q_k - (q_k + p_{kk})}{q_k} = \left[\frac{(q_i + p_{ii}) - q_i}{q_i}\right]\theta^{(i)}$$

or

$$\theta^{(i)} = \frac{-p_{kk}/q_k}{p_{ii}/q_i} \qquad Q + 1 \leq i \leq P \quad \text{and} \quad i \neq k$$

But this implies that

$$\frac{q_k + p_{kk}}{q_k} = \sum_{i\neq k}\left(\frac{-p_{kk}/q_k}{p_{ii}/q_i}\right)$$

or, upon simplification, that

$$\sum_i (q_i/p_{ii}) = 1$$

which clearly contradicts the initial assumption. Thus, the right-hand side of the matrix equation must have rank equal to $P - Q$. Since the module equations themselves have full rank, by hypothesis, that is

$$\begin{bmatrix} G \\ F \\ A \end{bmatrix} \text{ has rank } N$$

it follows that the matrix of solutions V must have rank $P - Q$. Thus, the solutions generated from the $z^{(J)}$ must be linearly independent, and the proposition is verified.

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Use of a Finite-Stage Transport Concept for Analyzing Residence Time Distributions of Continuous Processes

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This study is concerned with the derivation and application of the finite-stage transport concept for modeling residence time distributions (RTD's) originally proposed by Adler and Hovorka (1961). This six-parameter model is shown to be more versatile and accurate than the common two-parameter tanks-in-series or axial dispersion models. Radioactive tracer results are given for a number of particulate unit processes with special emphasis on wet-discharge ball mills.

SCOPE

The residence time distribution (RTD) concept is becoming more and more important to chemical engineers in the modeling of continuous, first-order processes by the segregated flow approach (Himmelblau and Bischoff, 1968; Levenspiel, 1962). It is very advantageous to have analytical functions for the RTD's encountered as evidenced by interest in the simple two-parameter tanks-in-series and axial dispersion models. These simple models often do not offer sufficient versatility or accuracy. Therefore, the present paper reexamines a previously proposed six-parameter, finite-stage transport concept for increased versatility and accuracy.

To accomplish this objective, a complete derivation of the model is included, along with an accurate and efficient parameter estimation method for it. In addition, the model is incorporated into the segregated flow concept to model a general first-order process. Finally, radioactive tracer results for a number of particulate unit processes with emphasis on wet-discharge ball mills are given which indicate the increased versatility and accuracy of this model over the simple two-parameter models.

CONCLUSIONS AND SIGNIFICANCE

In this study, the finite-stage transport concept of Adler and Hovorka (1961) is investigated as a general transfer function for industrial process analysis. Application of the model is demonstrated experimentally on several continuous particulate mineral processes. The study indicates that the parameter estimation method proposed can provide a high degree of accuracy for fitting the finite-stage model to actual data and that it is possible to obtain explicit, closed-form analytical solutions to a wide class of steady state first-order processes by the use of the segregated flow concept with this model. Extensions of the model and experimental methods that are often necessary or desirable when using radioactive tracers have also been derived and demonstrated.

The finite-stage transport concept has the advantages over the simpler tanks-in-series and axial dispersion models of greater versatility and improved accuracy. It provides these advantages while still yielding analytical models for first-order process phenomena when the segregated flow concept is used. The axial dispersion model does not

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