An Analysis of Techniques for Reactor Problems with Simultaneous Slow and Fast Reactions

K. J. ANSELMO,
R. S. UPADHYE, and
T. C. YOUNG

Air Products and Chemicals, Inc.
Allentown, PA 18105

INTRODUCTION

One often encounters simultaneous slow, kinetic and fast, equilibrium reactions during the simulation of chemical reactors. In coal gasification the reactions of carbon with carbon dioxide and steam are slow:

$$C + CO_2 \rightleftharpoons 2CO \tag{1}$$

$$C + H_2O \rightleftharpoons CO + H_2 \tag{2}$$

On the other hand, as mentioned by Walker et al. (1959) the water gas shift reaction, catalyzed by the ash in coal, is about 10^5 times faster, and is at equilibrium almost everywhere in the gasifier:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$

Another industrially important example is the formation of alkylamines from alkyl alcohol and ammonia, where two different types of reactions are observed:

Amines formation reactions:

$$R - OH + NH_3 \rightleftharpoons R - NH_2 + H_2O \tag{4}$$

$$R - OH + R - NH_2 \rightleftharpoons R_2NH + H_2O \tag{5}$$

$$R - OH + R_2NH \rightleftharpoons R_3N + H_2O \tag{6}$$

Amines reformation reactions:

$$2\ RNH_2 \rightleftharpoons R_2 - NH + NH_3 \tag{7}$$

$$2\ R_2NH \rightleftharpoons R - NH_2 + R_3 - N \tag{8}$$

With different catalysts, one or more of the above reactions may be suppressed and made very slow, and some others may be accelerated and made very fast to the extent that they appear to be in equilibrium at all points in the reactor (Weigert, 1980; Costa-Novella and Vasquez-Una, 1969a,b; Ramioulle and David, 1981).

We have considered two approaches to formulating and solving the problem involving simultaneous occurrences of slow and fast reactions. We call the first approach the mixed differential and algebraic equations (MDA) approach in which we set up differential equations for the slow reactions and algebraic equations, based on the law of mass action, for the fast equilibrium reactions. The two types of equations are solved separately. We have called the second approach the stiff differential equation system (SDS) approach, where we treat the equilibrium reactions and set up differential equations for these, in the same way as for the slow reactions. The resulting set of equations consists of differential equations only. The system of equations thus obtained tends to be stiff due to the largely differing reaction rates.

There are many methods for solving the algebraic equations generated in MDA (Hiebert, 1982). We have chosen one of them and implemented it on our computer using commercially available software (Moré et al., 1980). To implement MDA, we include the procedure for solving the algebraic equations in the subroutine that calculates the spatial derivatives. This method ensures that thermodynamic consistency is maintained at each derivative calculation and also that the results are independent of the particular integrator and the step size used.

In order to maintain chemical equilibrium (or a very close approach to it) in SDS, the rate coefficients must be chosen as large as possible such that thermodynamic consistency is maintained. However, the larger the rates of the fast reactions, the stiffer the differential equations systems will be. One is thus faced with the conflicting requirements of setting the rate coefficients as large as possible to approach equilibrium *and* as small as possible to avoid stiffness.

The next section develops the formulations for the two approaches discussed. The section following that contains a discussion of the numerical methods used. The final sections present the results of the computations and comparisons among the various approaches and the details of the implementation of SDS.

PROBLEM FORMULATION

Consider a chemical system comprising S chemical species, denoted by $S_1, S_2, \ldots S_s$. Let there be R-independent chemical reactions between the S molecular species, denoted by $r_1, r_2, \ldots r_R$. Let $[A]$ be the stoichiometric matrix of size $S \times R$, such that a_{ij} represents the number of moles of component S_i in the reaction r_j. We shall follow the convention that a_{ij} is positive if S_i is on the righthand side in reaction r_j, negative if S_i is on the lefthand side, and zero if S_i does not appear in reaction r_j. Let the first R_1 reactions be either slow, kinetically controlled or irreversible, and let

---

Correspondence concerning this paper should be addressed to R. S. Upadhye, at the Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550 the remaining R_2 reactions be fast, reversible, and equilibrium controlled. Let X be a column vector, of size R, denoting the extents of reactions, such that X_j equals the extent of the reaction r_j, defined by the relationships

$$n = n_o + [A] \cdot X \tag{9}$$

where $\boldsymbol{n}$ and n_o represent the component flows at point z and at the reactor entrance, respectively. Let f be a column vector of functions $f_{j,z}$ such that $f_{j,z}$ represents the rate of reaction r_j at a point denoted by z in the reactor. In general, $f_{j,z}$ is a function of the temperature, catalyst activity, and partial pressures of the species at point z, denoted by p_z.

For the first R_1 reactions, a material balance on a differential element of the tubular reactor yields

$$\frac{dX_j}{dz} = f_{j,z}\,(\boldsymbol{p}_z,\ T,\ \text{catalyst activity}) \tag{10}$$

$$j = 1,2, \ldots R_1$$

For the remaining R_2 reactions, which are in equilibrium at any point z in the reactor, application of the law of mass action yields

$$\phi_{j,z}(\boldsymbol{p}_z) = Kj\,(T_z) \quad j = R_1 + 1, R_1 + 2, \ldots R_2 \tag{11}$$

where

$$\phi_{j,z}(\boldsymbol{p}_z) \equiv \prod_{i=1}^{S} P_i^{a_{ij}} \tag{12}$$

and K_j is the equilibrium constant for the jth reaction, always assumed to be at equilibrium, at temperature T_z. At conditions far from ideality, the component partial pressures may be replaced by component activities.

For an adiabatic reactor, an energy balance for a differential reactor element yields

$$F \cdot cp \frac{dT}{dz} = (-\Delta H) \cdot \left([A] \cdot \frac{dX}{dz}\right) \tag{13}$$

where $F{\cdot}cp$ denotes the heat capacity of the material entering the differential element and the vector ΔH represents the heats of reactions.

Equations 9 through 13—coupled with standard equations defining partial pressures (or activities), Arrhenius law expressions relating the rate coefficients to temperature, well-known thermodynamic equations relating the equilibrium K values to the temperature of reactions, and empirical equations relating the rates of reactions to temperature and partial pressures of the components—constitute the definition of the problem. Solution of these equations will yield the desired temperature and concentration profiles along the length of the reactor.

DISCUSSION OF SOLUTION TECHNIQUES

We have considered two approaches to solving Eqs. 10, 11, and 13 (Eqs. 9 and 12 are merely definitions of the terms involved in the other three sets). In the first, which we call the mixed differential and algebraic (MDA) equations approach, we solve the algebraic equations simultaneously with the calculation of the derivative (i.e., evaluation of the right-hand sides of Eqs. 10 and 13). This keeps Eq. 11 satisfied at all points in the reactor.

The second approach we call the stiff differential equations system approach. Here we treat the fast, equilibrium reactions the same way as the kinetic reactions, and the algebraic Eq. 11 is replaced by differential equations similar to Eq. 10:

$$\frac{dX_j}{dz} = k_j \prod_{a_{ij}^i<0} p_i^{-a_{ij}} - k_j' \prod_{a_{ij}^i>0} p_i^{a_{ij}} \tag{14}$$

$$j = R_1 + 1, \ldots R2$$
$$i = 1,2, \quad \ldots S$$

The values of k_j and k_j' are chosen such that (1)

$$\frac{k_j}{k_j'} = K_j \tag{15}$$

and (2) both k_j and k_j' are reasonably large.

Criterion 1 is necessary to maintain thermodynamic consistency. Criterion 2 is rather vague, but implies that the larger the k_j and k_j' are, the closer the approach to equilibrium. This, however, presents a computational dilemma. If the k_j and k_j' are not large enough, Eq. 11 may not be satisfied within the given tolerance. On the other hand, if k_j and k_j' are made very large, the resulting differential equation system consisting of Eqs. 10, 13, and 15 may be unacceptably stiff and may lead to numerical difficulty.

Our studies indicate that it is possible to choose the values of k_j and k_j' so that Eq. 11 is satisfied within acceptable tolerance, while maintaining the stiffness of the differential equation system sufficiently low to avoid numerical problems.

The next section describes the numerical techniques used, followed by a detailed discussion of our numerical results.

DISCUSSION OF NUMERICAL TECHNIQUES

The computer programs used in this work are constructed from widely available quality software. We consider this an important point and wish to stress that by using quality software we easily and quickly explored the solution schemes reported in this paper. The major fundamental software parts include temporal integrators, a nonlinear algebraic equation solver, and an eigenvalue routine. All of these routines are available to the general public at nominal cost.

The temporal integrators we used are LSODE and RFK45. LSODE is used to integrate the stiff model equations; RKF45 is used for the nonstiff model. Subroutine LSODE, written by A. C. Hindmarsh, is based on the GEAR and GEARB packages (Hindmarsh, 1972). The stiff option used in this work is based on the stiffly stable Gear backward differentiation formulas. LSODE is available from the National Energy Software Center (NESC) in Argonne, IL. RKF45, used to integrate the nonstiff systems, is based on Runge-Kutta formulas developed by E. Fehlberg. It is described by Forsythe et al. (1977), where there are also directions for obtaining the code. We found both packages to be very efficient and noted that the stiff problems were handled as easily as the nonstiff ones.

The nonlinear algebraic equation solver used in this work, HYBRD1, is part of the MINPACK-1 package (Moré et al., 1980). It is used to solve for the equilibrium reaction extents in the nonstiff model. HYBRD1 uses Powell's hybrid method, which combines the quasi-Newton with the gradient method. The Jacobian is initially calculated by forward differences and then approximated by a Broyden update. MINPACK-1 is available from IMSL and NESC.

IMSL subroutine EIGRF is used to calculate the eigenvalues of the linearized differential system in the stiff case. The ratio of the maximum to the minimum eigenvalue then measures the stiffness of the system. Linearization is accomplished by the slightly modified MINPACK-1 subroutine FDJAC.

COMPARISON OF THE TWO TECHNIQUES

We shall now compare the two approaches discussed above, namely, the mixed differential and algebraic equations (MDA)

TABLE 1. COMPARISON BETWEEN SDS AND MDA (SCALE FACTOR FOR SDS = 10^8)

Criterion	SDS	MDA
Final Normalized Equilibrium Residuals	6.61×10^{-10}, 4.18×10^{-10}	9.71×10^{-17}, 4.30×10^{-16}
Simplicity of Coding	Easy, straightforward	Complicated, arbitrary logic
Maintainability of Coding	Easy to change and maintain	Difficult to change and maintain
Flexibility	Applicable to moderately fast reactions as well	Applicable to slow and very fast reactions only
No. of Derivative Calls	1,269	1,206
CPU, s	0.648	3.708

approach and the stiff differential equations system (SDS) approach, on the basis of the following criteria:

- Accuracy
- Computer time requirements
- Simplicity and maintainability of the resultant software
- Reliability
- Flexibility

The importance of accuracy is, of course, obvious, and need not be stressed here. Computer time requirements are important, but the weight placed on this criterion is fast diminishing, since faster and cheaper computers are being developed. We feel that the relevance of the remaining criteria is increasing, as costs of quality software keep escalating much faster than the cost of hardware is coming down. Table 1 summarizes the comparison between the two approaches.

The accuracy of implementing the equilibrium relationships is measured by the normalized residuals, defined by

$$\begin{matrix}\text{Residual for equilibrium} \\ \text{reaction } j\end{matrix} = 1 - \frac{\phi_{j,z}(\mathbf{p}_z)}{K_j(T_z)} \tag{16}$$

Table 1 shows the final residuals for comparison purposes only; in fact, the residuals are checked at every integration step in SDS. The table clearly shows that, at least for the particular scale factor chosen, both SDS and MDA yield acceptable accuracy.

The time requirements for MDA are over five times larger than those for SDS, even though the number of derivative cells is slightly smaller for MDA. The major reason for this is the necessity of frequently solving a set of nonlinear algebraic equations. Since the equations given by equation set 11 are solved each time a derivative call is made, the cost of one derivative call in MDA is much larger than that in SDS.

In our experience, the formulation and coding of SDS are far simpler than for MDA. Given reliable stiff integrators, such as LSODE (Hindmarsh, 1972), the programming and implementation of SDS were relatively easy and straightforward. On the other hand, although conceptually equally simple, MDA required complicated logic and lengthy and difficult programming for its implementation. Special care had to be taken to mimimize the effect of singularities and discontinuities caused by the algebraic equation solver routines during integration. Because of the simplicity of SDS, we find it to be much easier to maintain and change as compared to MDA. The simplicity of the formulations of SDS contributes to simple computer code.

The criterion of flexibility deserves special attention for the problem we are considering. The assumption of equilibrium is often made for reversible reactions that are so fast that measurement of their rates is either impossible or impractical. However, the constant improvement in analytical techniques and instruments, coupled with microprocessors, may make it possible to measure some of these rates in the future. Since SDS is always dealing with rates, such a situation poses no problem. Instead of assuming equilibrium, the measured kinetics are used. The same, however, is not true of MDA, which has to be restructured when the assumption of equilibrium is replaced by fast kinetics. Thus, SDS is much more flexible, and requires fewer changes once programmed than MDA.

On the basis of the above discussion, we feel that the stiff differential equations system approach is superior to the mixed differential and algebraic equations approach for simulating tubular reactors with simultaneous slow and fast reactions.
mik

IMPLEMENTATION OF SDS

In SDS, we convert the algebraic Eq. 11 by the differential Eq. 14, which may be rewritten as

$$\frac{dX_j}{dz} = k_j \left(\prod_{a^i_{ij}<0} p_i^{-a_{ij}} - \frac{1}{K_j} \prod_{a^i_{ij}>0} p_i^{-a_{ij}} \right) \tag{17}$$

For small values of k_j in Eq. 17, one gets reactions limited by kinetics. As k_j gets larger, the reactions gradually tend to equilibrium. For a sufficiently large value of k_j, one can get a sufficiently close approach to equilibrium. Let J denote the value of j such that

$$k_J = \max_j (k_j) \qquad j = 1,2,\ldots \tag{18}$$

We then rewrite Eq. 17 as

TABLE 2. COMPARISON BETWEEN DIFFERENT SCALE FACTORS FOR SDS

Log, Scale Factor	Log, Stiffness Ratio*	Derivative Calls	CPU, s	Final Temp., R	Equilibrium Residuals	
1	0.11	267	0.166	1303.6	1.37×10^{-1}	1.35×10^{-1}
2	2.02	305	0.189	1311.9	5.51×10^{-3}	3.61×10^{-3}
3	3.06	495	0.277	1305.4	1.26×10^{-3}	8.06×10^{-4}
4	4.03	886	0.465	1310.1	7.36×10^{-5}	4.59×10^{-5}
5	5.03	1047	0.541	1310.7	6.77×10^{-6}	4.21×10^{-6}
6	6.03	1074	0.548	1310.7	6.70×10^{-7}	4.17×10^{-7}
7	7.03	1217	0.613	1310.7	6.64×10^{-8}	4.20×10^{-8}
8	8.03	1269	0.627	1310.7	7.67×10^{-9}	3.96×10^{-9}
9	9.03	1333	0.648	1310.7	6.61×10^{-10}	4.18×10^{-10}
10	10.03	1279	0.629	1310.7	8.12×10^{-11}	3.96×10^{-11}

* Defined as the absolute value of the ratio between the largest and smallest eigenvalues of the differential equation system.

TABLE 3. PROBLEM DEFINITION

Stoichiometry:

$CH_3OH + NH_3 \rightleftharpoons CH_3NH_2 + H_2O$ (1)
$2\ CH_3NH_2 \rightleftharpoons (CH_3)_2NH + NH_3$ (2)
$2\ (CH_3)_2NH \rightleftharpoons (CH_3)_3N + CH_3NH_2$ (3)

Kinetics:

Reaction 1 is slow, kinetically controlled
Reactions 2 and 3 are at equilibrium

$K_1 = 1.2251 \times 10^9 \exp(-2{,}726/T)$ gmol/h·L·atm^2

$K_1 = 1.225 \times \exp(3{,}571/T)$
$K_2 = 1.32 \times \exp(2{,}156/T)$
$K_3 = 0.568 \times \exp(1{,}395/T)$

Reactor Feed:

30 mol/h CH_3OH
60 mol/h NH_3

Feed Temperature:

1,059.7 R

Reactor Volume:

15 L

$$\frac{dX_j}{dz} = \text{SF} \cdot k_J \left(\prod_{a^i_{ij}<0} p_i^{-a_{ij}} - \frac{1}{K_j} \prod_{a^i_{ij}>0} p_i^{a_{ij}} \right) \tag{19}$$

where SF is the scale factor.

By changing SF, one can get as close an approach to equilibrium as desired. Table 2 shows the results of varying the SF from 10^1 to 10^{10}.

As expected, at low values of the scale factor, reactions 2 and 3 of Table 3 are far from equilibrium. As the SF is increased, a closer approach to equilibrium is observed. For values larger than and equal to 10^6, a close approach is observed. This is accomplished at the cost of increased number of derivative calls and computer time. Initially, both the number of derivative calls and CPU time increase rapidly. Both these stabilize, though, at values of SF nearing 10^7. Beyond 10^7, any increase in SF does not significantly change either the computer time or the number of derivative calls. It can also be seen from Table 2 that the stiffness ratio increases in proportion to the SF.

Thus, by increasing SF, one gets increasingly stiffer systems of differential equations. The main points that emerge from the Table 2 are

1. It is possible to get a scale factor that will lead to a close approach to equilibrium without making the system excessively stiff, or without using a lot of computer time.
2. Beyond a certain value of the SF (10^7, in our case), neither the number of derivative calls nor the amount of computer time required changes significantly.

These two observations lead us to the following heuristic for choosing the scale factor:

1. Select the length of the initial interval in the reactor at the end of which equilibrium will be approached to within the specified tolerence. This is necessary to give the reactions sufficient time to get to equilibrium. We suggest a value of 0.1% of the reactor length for the initial interval for this purpose, since it is probably not significant from the process point of view, yet is large enough for the computer.
2. Select 10^4 as an initial value of SF.
3. Integrate to the end of the interval set in step 1. Check the residuals for the equilibrium reactions.
4. If the residuals are not smaller than the set tolerence, increase SF by one order of magnitude and return to step 3.

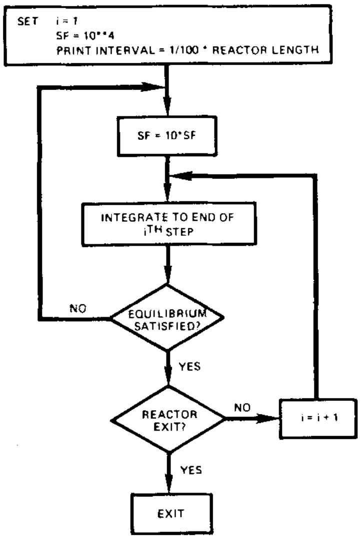

Figure 1. Algorithm.

5. If the residuals are smaller than the set tolerence, keep the SF and continue. Monitor the residuals periodically. If they get larger than the set tolerence at any step, increase SF by an order of magnitude and continue. This should rarely be needed, since the reaction that reached equilibrium at the end of the first interval should normally stay close to equilibrium throughout the reactor.

The algorithm is shown in Figure 1.

Since the amount of computer time required is rather insensitive to the value of SF, beyond a certain value, there is little incentive to search for the minimum value of the SF that will yield acceptably close approaches to equilibrium. Thus, the simple algorithm presented above should lead one to an acceptable value of the SF.

ACKNOWLEDGMENT

The authors wish to thank A. R. Garcia for providing many literature references and helpful discussions, and Air Products and Chemicals, Inc., for granting permission to publish this work.

NOTATION

a_{ij} = stoichiometric coefficient of component i in reaction j
$[A]$ = stoichiometric coefficient matrix
c_p = specific heat, cal/gmol/°C
f = vector of rates of reaction
F = total molar flow rate, mol/h
k_j, k_j' = forward and backward rate coefficients for reaction j
K_j = reaction equilibrium coefficient for reaction j
n = vector of molar component flows, mol/h
n_o = vector of molar component flows in the feed, mol/h
p = vector of component partial pressures
R = number of independent reactions
S = number of components
T = temperature, °C
X = vector of extents of reaction
z = variable density position along the reactor axis, m

Greek Letters

ϕ = vector of the lefthand side of Eq. 11
ΔH = vector of the heats of reaction

LITERATURE CITED

Costa-Nevella, E., and G. Vasquez-Una, "Production of Methylamines. I. Selection of Catalysts and Influence of the Several Variables," *Anal. Quim. Madrid*, **65**(7), (1969).

———, "Production of Methylamines. II. Mechanism and Kinetics of the Process," *Anal. Quim. Madrid*, **65**(8), (1969).

Forsythe, G. E., M. A. Malcolm, and C. B. Moler, *Computer Methods for Mathematical Computations*, Prentice-Hall, Englewood Cliffs, NJ (1977).

Hiebert, K. L., "An Evaluation of Mathematical Software That Solves Systems of Nonlinear Equations," *ACM Trans. Math. Soft.* **8**, 5 (1982).

Hindmarsh, A. C., "GEAR: Ordinary Differential Equation System Solver," UCID-3001, Rev. 2, Lawrence Livermore Lab, Univ. of California, Livermore (1972).

Moré, J. J., B. S. Garbow, and K. E. Hillstrom, "User Guide for MINPACK-1," Argonne National Lab. ANL-80-74 (1980).

Ramioulle, J., and A. David, "Improved Methylamines Process," *Hydrocarbon Processing*, July (1981).

Walker, P. L., F. Rusinko, and L. G. Austin, *Advan. Catalysis*, **11**, 133 (1959).

Weigert, F. J., "Preparation of Mono-Methylamines from Ammonia and Methanol, Using a Zeolite Catalyst," European Pat. Application, EP 0025G93A1, March (1981).

Yoon, H., J. Wei, and M. M. Denn, "A Model for Moving-Bed Coal Gasification Reactors," *AIChE J.*, **24**, 885 (1978).

Manuscript received Apr. 4, 1984, and accepted Apr. 30.