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MODELING AND SIMULATION OF MULTISPECIES REACTION/DIFFUSION TRANSIENTS *

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Abstract

Prior to the work described here, numerical dynamic simulation of reactions and diffusive transport of fluid species in porous solids was confined to diffusion-limited cases, rate-limited cases and a few reduced complexity, nondimensionalized, isothermal models with equimolar counter-diffusion and relatively small values of reaction modulus. In 1983-1985, the authors showed that reformulation and discretization by the numerical method of lines for solution by a general-purpose ODE solver permitted economical simulations over the full range of behavior. In 1988, the authors published a study of the forms the model could take and the appropriate solution techniques for the temperature dependent, nonzero net flux, reversible, dimensional systems and released a code, MSRS, for such multispecies problems.

In this paper, the authors summarize the studies of formulation/solver tradeoffs and discuss the issues of ODE versus DAE systems, equation set index, consistency of initial conditions, occurrence of fast initial numerical transients and numerical error suppression. Examples include a nine fluid/ten solid/fifteen reaction simulation of a spherical oil-shale particle undergoing in-situ retorting. Features include time-dependent boundary conditions and Arrhenius rates of reaction. Comparisons with EMCD and isothermal simulations are included.

1 Introduction

Over the past eight years the authors have worked together to develop appropriate model forms and numerical techniques for the simulation of transients in reacting and diffusing flows in porous media. The work originated in the need for a dynamic simulation of in-situ oil shale retorting for control system design and validation. Progress has been reported in the literature [1,2,3,4] and technical reports obtainable from the Lawrence Livermore National Laboratory [5,6]. The latest publications [4,5] describe a computer code, MSRS (Multispecies Shale Retorting Simulator), that is now available to DOE agencies and contractors. The code solves spherically symmetric reaction/diffusion problems involving multiple diffusing species, multiple stationary species and multiple reactions. An energy equation accommodates nonisothermality. This paper is a summary of the single-pellet work with a brief description of the code and sample results.

The starting point for this effort was an attempt to assist R.L. Braun of LLNL obtain economical numerical solutions of the partial differential equation (PDE) models of in-situ retorting of oil shale developed by Braun and the Earth Sciences Dept. Oil Shale Project with the assistance of H.Y. Sohn of the University of Utah Dept. of Met. and Metallurgical Eng. and Dept. of Mining and Fuels Eng. The models are described in papers by Sohn and Braun [7,8] and several Oil Shale Project reports. Sohn's work is prominent in the literature of such problems and he described the state of the art in 1979 as being confined to the analytical treatment of limiting cases, e.g., shrinking-core and diffusion-controlled cases, and pointed out the desirability of being able to treat the situation when, "...the controlling mechanism can often shift from the intrinsic chemical kinetics to mixed kinetics to diffusion." This more general case requires numerical solution of the rigorous governing equations [7].

The early models consisted of one or two conservation equations for the fluid reactants in the porous solid and two or one mass balances for the solid reactants. By applying the pseudosteady-state approximation and the assumptions of equimolar counter-diffusion (EMCD), constant pseudobinary effective diffusivities and isothermality, and assuming that the reactions are irreversible, then the governing equations can be nondimensionalized to

$$\nabla^2 p_A - 6\sigma_A^2(1-w)p_A = 0$$

$$\nabla^2 p_C - 6\sigma_C^2(1-w)p_C = 0,$$

and

$$\partial w/\partial t = (1-w)(p_A + p_C)$$

for a two fluid/one solid model where the p's are fluid concentrations and w is solid concentration. For a one fluid/two solid model

$$\nabla^2 p - 6\sigma^2[(1-w_B) + \gamma\beta(1-w_D)]p = 0$$

$$\partial w_B/\partial t = (1-w_B)p \quad \text{and} \quad \partial w_D/\partial t = \beta(1-w_D)p.$$

The σ's represent dimensionless ratios of capacities for chemical reaction and internal diffusion. These moduli, σ, are small when diffusion is rapid and the conversion is controlled by chemical kinetics and large when the overall rate is controlled by diffusion.

The boundary conditions for the fluid equations when the solid(s) form(s) a spherically symmetric pellet are

$$\text{smoothness condition at the center:} \quad \partial p/\partial\eta = 0$$

and

$$\text{convection condition at the outer surface:} \quad \partial p/\partial\eta = Sh^*(p_{bulk} - p)$$

where η is a dimensionless position and the same modified Sherwood number, Sh^* , is used for both fluid species. This implies that the ratio of external mass transfer to internal mass transfer is assumed to be the same for both species.

The purpose of this paper is not to duplicate the presentations in earlier papers, but to provide an overview and summary of previous work. Therefore many steps will be described rather than demonstrated and the interested reader is encouraged to seek the details in the references. The isothermal, EMCD models above warranted a lengthy description since they provided the basis for the subsequent work, all of which consists of variations on the originating models, extensive though those variations may be, and some features of the later models are as they are simply because they are retained from the models above.

2 Method of Lines Reformulation

The fluid conservation equations above, with the pseudosteady-state assumption invoked, constitute a spatial ODE two-point boundary-value problem which depends on the instantaneous solid concentration profile(s). The solid mass balance equation(s) are temporal ODEs which depend on the local fluid concentration(s). Rather than maintain this difference and separate the solution procedures for the fluid and solid equations, as had been the practice, considerable numerical efficiency would result from being able to treat both equations the same way *and* to so formulate the problem as to bring to bear a proven, general-purpose software package. If the pseudosteady-state assumption is not invoked, the fluid equations regain explicit temporal first partial derivative terms multiplied by small coefficients. The greater the validity of the pseudosteady assumption, the smaller the coefficients and the greater the stiffness of the combined fluid and solid equations, or, more precisely, the greater the stiffness of the set of temporal ODEs resulting from a method of lines (MOL) reformulation in which the spatial derivatives are replaced by finite-difference, algebraic approximations. For large values of the reaction modulus the MOL reformulation produces a very stiff set of ODEs for which the initial value problem (IVP) is posed, therefore the selection of a suitable solution method is crucial. In our treatments, the LSODE [9] software package which solves stiff and nonstiff ODE systems is used exclusively whenever an ODE-IVP arises. For stiff problems, LSODE makes explicit use of the ODE-system Jacobian matrix, storing either a full or banded form of the Jacobian. In all of the cases studied, with one exception noted below, with suitable ordering of the unknowns the Jacobians have been rather tightly banded and the associated computations are quite efficient.

In [1], the authors describe, in considerable detail, the MOL reformulation of the explicitly time-dependent governing equations and the numerical solution of the resulting ODE-IVP by application of LSODE. The one fluid/two solid case was investigated more fully than the two fluid case above. For the one fluid case, system behavior is governed by the product, $\sigma^2\gamma\beta$. In [1], solutions are presented for values of this product ranging from 10^{-2} to 10^8 with extremely steep fronts developing in the spatial profiles at large $\sigma^2\gamma\beta$. It is the steepness of these fronts which had prevented obtaining solutions by previously applied numerical approaches.

All of the simulations described here and in the references assume spherical symmetry (the work in [2] applies equally well to cylindrical and slablike pellets although only spherical pellets were used in the examples). All of the numerical work has been performed on fixed grids, with one exception, and fixed mesh-point spacing based on concentric, equal-volume increments proved to be a better choice than radially equal grid increments. The exception to fixed-grid solutions is described in [1] in which an application of adaptive regridding is presented. The virtual shrinking-core behavior at large $\sigma^2\gamma\beta$ was difficult to resolve when a coarse grid was used. On a finer grid, resolution of the fronts improved but more computer time and memory were comsumed solving the larger number of equations. In [1] it is shown that, with little additional effort, an adaptive regridding routine, like ANUGB [10], can be combined with LSODE to achieve detailed front resolution at a fraction of the computer time and memory penalty of an equivalent, fine-mesh fixed grid.

3 Pellet-Grain Models

The dependent variables in the models above are fluid concentrations or mole fractions and densities or extents of conversion for solids. The physical model is one of fluids diffusing and reacting within a porous matrix, the porosity of which changes as solid reactants are consumed and/or solid products formed. At the completion of the process a porous solid product matrix or inert porous substructure remains. In contrast, a competing physical model consists of a pellet composed of grains where the amount of the single solid reactant present is measured by the location of the reaction zone within a grain. The particular models studied originated in Sohn and Szekely[11]. See also the book, *Gas-Solid Reactions*, by Szekeley, Evans and Sohn [12].

As with the continuum models above, the pellet-grain models consist of a pseudosteady-state fluid conservation PDE, that is, without explicit time dependence, and a first-order differential equation in time which determines the local reaction front position within the grain

$$\nabla^2 p = 2F_g F_p \sigma^2 \xi^{F_g-1} p \quad \text{if} \quad \xi \geq 0,$$

$$\text{otherwise} \quad \nabla^2 p = 0$$

and

$$\partial\xi/\partial t = -p \quad \text{if} \quad \xi \geq 0; \quad \text{otherwise} \quad \partial\xi/\partial t = 0.$$

In general these equations had to be solved numerically and several numerical techniques were applied. As above, these numerical methods encountered difficulties when a steep front would develop in the spatial profiles. Once again the pseudosteady-state assumption was dropped, in which case the fluid equation reverted to being explicitly time dependent. This permitted an MOL reformulation and discretization into a set of first-order ODEs for solution by LSODE. The quantities F_p and F_g are geometrical shape factors ($1, 2$ or 3 for slab, cylinder or sphere, respectively) for the pellet and the grains.

Since the location of the reaction zone within the grain cannot be negative, $\xi \geq 0$, the righthand side of the grain front ODE is discontinuous (and so is that of the fluid equation for slablike grains, $F_g = 1$). The anticipated numerical inefficiency associated with such jump discontinuities in the temporal derivatives can be avoided by allowing the front position dependent variable, ξ, to continue decreasing through zero to negative values and then replacing the unrealistic negative values by zeros for output only. The model remains valid because this modification does not alter the ODEs for fluid concentration, p. While solutions had been obtained from code which immediately reset negative-going local values for ξ, the solution process was inefficient. The above modification improved performance considerably, a factor of three in execution time reduction for a particular set of parameters, for example.

The development and solution of the pellet-grain models are described in detail in [2]. A code, ROFOS, for simulating the transient behavior of simple pellet-grain models was written, which uses LSODE as the ODE-IVP solver, and is available from the National Energy Software Center (Johnson and Hindmarsh, 1982).

4 Stefan-Maxwell Diffusion

Armed with the above experience, an attempt was made to write a code which extended the above to multiple species and multiple reactions and reverted to a form of the governing equations in which neither the assumption of isothermality nor equimolar counter-diffusion need be invoked for solutions to be obtained. The attempt was not successful and it was decided to postpone the extension to multiple species, and instead incorporate an energy equation and the Stefan-Maxwell equations for diffusion according to Fick's first law into an otherwise simplest possible reacting/diffusing system. This allowed investigation of the numerical behavior of a system with all of the features desired but of a tractable size. The following binary fluid system, with equations taken directly from Bird, Stewart and Lightfoot [13], became the test case

$$\varepsilon C \partial x_A / \partial t + \nabla \cdot N_A = R_A$$

$$\varepsilon C \partial x_P / \partial t + \nabla \cdot N_P = R_P$$

for the fluid species where fluid A is the fluid reactant and B the fluid product. For the solid species

$$\alpha \rho_B \partial w_B / \partial t = R_B$$

$$\alpha \rho_Q \partial w_Q / \partial t = R_Q$$

where solid B is the reactant and Q the product. The Stefan-Maxwell equations for binary bulk diffusion are

$$N_A = x_A(N_A + N_P) - C D_{AP} \nabla x_A$$

$$N_P = x_P(N_A + N_P) - CD_{PA}\nabla x_P$$

in terms of vector molar fluxes, N. Here $D_{AP} = D_{PA} = D$, the binary diffusivity. The energy equation was added subsequently. The source terms, R, were all rewritten in terms of a single, reversible reaction rate expression

$$v = ksC(x_A - x_P/K)\alpha\rho_B w_B$$

using notation from Bird, et al., and Sohn and Braun. The smoothness boundary conditions and external surface convective boundary conditions were carried forward from the earlier models. In [3] the authors show that if $N_A + N_P = 0$ is postulated, the new nonEMCD or explicit flux model reduces to the EMCD model forms above analytically, and the code for the explicit flux model reproduces the EMCD numerical results.

Since the product solid fraction, w_Q , does not appear on the righthand sides of the other equations, the differential equation for w_Q need not be solved. The remaining five equations together with the rate expression above constitute an isothermal explicit flux model in which the EMCD assumption has not been invoked. This explicit flux model is straightforward to obtain, coming as it does directly from Birdfoot. However, the discretized MOL equations which result form a mixed set of differential equations arising from the fluid and solid conservation equations and algebraic equations resulting from the discretization of the Stefan-Maxwell equations.

The continuous isothermal, EMCD models and the pellet-grain models above could have been cast as differential/algebraic equation (DAE) sets after discretization simply by retaining the pseudosteady-state assumption. Then a DAE solver like LSODI or DASSL [14] would have been employed. Instead the explicit time dependence was restored to the fluid conservation equations in order to achieve a set of temporal differential equations after MOL discretization. This permitted solution by ODE-IVP solvers like GEAR or LSODE. In as much as there was physical justification for restoring time dependence and because ODE solvers are generally more robust than DAE solvers, that was the preferred course of action. The explicit flux model differs in that there is no physical justification for adding temporal derivatives to the Stefan-Maxwell equations, the singular character of the S-M equations makes adding time derivatives problematical anyway, and other experiences with DASSL and LSODI improved the outlook for getting solutions to DAE sets dependably and economicallly.

Differential/algebraic systems are different from ODE systems in that, while DAE systems include ODE systems as a special case, they also encompass traits and behavior that are quite different and make quite different demands on a solver code. Some DAE systems can cause severe difficulties for existing numerical methods. Roughly speaking, the more singular a DAE system is, the more difficult it is to solve numerically [15]. The index of a DAE system is a measure of the degree of singularity present. An ODE system is a DAE system of index = 0. Semi-explicit DAE systems, that is systems which can be written

$$dy/dt = f(y,z) \quad \text{and} \quad 0 = g(y,z)$$

have an index of 1 if the algebraic equations, $g = 0$, can be inverted. If the Jacobian of g with respect to z is nonsingular, at least in principle z could be obtained in terms of y and substituted into f to produce an index zero set of equations. If $J = \partial g/\partial z$ is singular, the index is higher than one. Much of the literature of nonlinear DAE numerics is due to L. Petzold and includes a recent book [16]. The index of a DAE system is important because, as it has turned out, LSODI has proven to be an effective solver for index one semi-explicit DAE systems and DASSL solves index one problems and remains reasonably effective for index two versions of the reaction/diffusion problems in question.

The MOL isothermal explicit flux model discretizes into an index two DAE set. In light of the above, a search for other forms of the model which might have lower indices was advisable. An alternate, implicit flux model can be obtained by adding the fluid conservation equations together and substituting the following total quantities

$$x_A + x_P = 1, \quad R = R_A + R_P \quad \text{and} \quad N = N_A + N_P$$

yields a new relationship

$$\nabla \cdot N = R$$

which replaces the Stefan-Maxwell equations. The fluxes in the fluid equations can be reconstructed from N by the following relationships

$$N_A = x_A N - CD\nabla x_A \quad \text{and} \quad N_P = x_P N - CD\nabla x_P.$$

The implicit flux model consists of two fluid equations, one solid equation, and either

$$\nabla \cdot N = R$$

for an index one DAE problem, or the latter equation can be integrated numerically

$$N = [\text{Inverse-Divergence}](R)$$

as a step separate from the operation of the solver for an index zero problem.

5 Nonisothermal Systems

To permit simulation of pellet dynamics which are significantly affected by temperature effects, an energy equation from Bird, et al.,

$$\alpha \rho_B C_p \partial T/\partial t = K\nabla^2 T + Q$$

must become part of the model along with an equation of state for the fluid species. If the equation of state is such that changes in temperature dictate changes in total molar concentration, then the fluid conservation equations of the previous section are no longer valid. They depend on C being constant so that

$$\partial(Cx_A)/\partial t = C\partial x_A/\partial t \quad \text{and} \quad \partial(Cx_P)/\partial t = C\partial x_P/\partial t.$$

If C is allowed to vary then

$$\partial(Cx_A)/\partial t = C\partial x_A/\partial t + x\partial C/\partial t$$

and differentiating the equation of state produces an expression for the derivative of C in terms of system dependent variables. In the case of the ideal gas equation of state, C and $\partial C/\partial t$ are functions of T and $\partial T/\partial t$. If the reaction rate is temperature dependent, all of the model equations are altered, becoming more complicated and interconnected. See [3].

The energy equation chosen assumes that conduction is the only transport mechanism operating. The particular form of the energy equation is not constrained by the solution methods, and energy storage and energy transport by the diffusing species could just as well been included. Similarly, nonisobaric systems with significant pressure dependence could be accommodated also.

6 System Index and Solver Selection

In the early work, DAE systems were converted to ODE systems in order to apply a general-purpose ODE-IVP solver like LSODE. From the perspective of DAE indices, the conversion was from a problem with index greater than zero to an index zero problem in order to apply an index zero solver. When problems of index greater than zero are to be solved, one must turn to solvers for DAE systems like DASSL which is intended for the solution of index one problems. Another widely available solver, LSODI, was originally intended for the solution of linearly implicit index zero problems, but employs solution methods which are suitable also for index one problems.

Semi-explicit DAE systems of index greater than one can often be converted into equivalent systems of low index by a formal process of repeatedly differentiating the algebraic equation subset with respect to time and doing some manipulation of the result. The number of times this process must be repeated to reach index zero is the index of the original system of equations. Strictly speaking, these remarks apply to the discretized, MOL formulation and not to the continuous PDEs. See the discussion in [3]. The index of a DAE system is an important indicator of the performance that one can expect from a given problem/solver combination. It also warns the analyst that special care must be taken with the initialization of a simulation.

The dependent variables of semi-explicit DAE systems fall into two groups: those governed by temporal ODEs and those governed by the algebraic equations. Index zero systems have temporal ODEs only and the initial values must be specified to complete a well-posed problem. For an index one problem the initial values of the variables governed by the temporal ODEs must be specified and then the initial values of the remaining variables can be computed by inverting the algebraic equations. The nonsingularity of the algebraic equations is the condition that assures that the system is of index one. For index two systems, the initial conditions must also satisfy the algebraic equations of the equivalent, index one problem. Such initial conditions are called consistent initial conditions, that is, consistent initial conditions satisfy the temporal ODEs of the original index two problem, the algebraic equations of the original index two problem (which does not complete the specification of the initial state of the system), and the algebraic equations of the equivalent index one problem (arrived at by a differentiation), which provides the additional constraints to complete uniquely the problem statement. The generation of consistent initial conditions can be as formidable a task as obtaining the subsequent solution.

Consistency of initial conditions has to do with the computation of initial values for the dependent variables governed by the algebraic equations in semi-explicit DAE sets once the initial values of the dependent variables governed by the temporal ODEs have been specified. When the DAE set has resulted from an MOL formulation of a mixed (with and without explicit time dependence) set of continuous PDEs, the task of specifying initial values for the dependent variables governed by the temporal ODEs can be just as challenging. Selecting realistic initial profiles, from which can evolve realistic solutions, is another case of having to solve the problem in order to solve the problem. The task is simplified considerably if the system is able to move rapidly from unrealistic initial profiles to realistic profiles from which the sebsequent solution can proceed. If these early-time realistic profiles are largely unaffected by the particular unrealistic initial-time profiles, the system of equations is said to exhibit "fast-transient" recovery from arbitrary initial profiles. In relatively simple cases, it may be possible to establish analytically that fast transient behavior is likely, as was done in [3]. In more complicated cases, it may be necessary to demonstrate numerically that any use made of an assumption of fast transient behavior is justified.

7 Discretization and Error Control

When formulating an MOL problem from a set of PDEs, the most pressing discretization issue for hyperbolic problems is usually the selection of appropriate approximations for the spatial derivatives. By contrast, that question has never arisen in the context of the parabolic systems representing these reacting/diffusing models. Three-point, centered, finite-differences have been adequate for all of the work described herein, with two-point algorithms at the boundaries. However other discretization issues have needed to be addressed. A crucial detail that prevented obtaining credible solutions until it was recognized is that the mole fractions sum to one in the continuous models but that careless discretization, particularly at and near the boundaries, produced discrete models in which the local mole fractions did not necesarily sum to one for all times. A well-posed model is such that the conservation of the mole-fraction sum can be recovered from the discrete equations and the discrete boundary conditions, just as it can be from the continuous governing equations and boundary conditions.

The fluxless forms of the models contain another opportunity for careless discretization. The equation for the total flux contains a divergence operator which must be replaced by a numerical approximation in the course of discretization. The computation of consistent initial profiles depends on a numerical inverse divergence operator. If the two numerical algorithms are not precise numerical inverses, the initial residues computed by the solver are not sufficiently small for the solution process to continue. This kind of obstacle can be a subtlety that is hard to find while trying to get the first successful execution of a complicated PDE simulation.

Once errors in the models are corrected, one turns to error control by the solver. LSODI and DASSL are variable-order, variable- stepsize solvers under user-specified error control. Considerable experimentation with the relative and absolute error specifications has failed to demonstrate much sensitivity to the particular values chosen. Tolerances of 10^{-5} or 10^{-6} have proven to be suit-

	Explicit Flux Models		Implicit Flux Models	
Isothermal Case	A A′	(Index 2) (Index 1)	B B′	(Index 0) (Index 1)
Nonisothermal Case	EA′	(Index 1)	EB′	(Index 1)

Table 1. Summary of the binary model codes used for formulation testing and solver matching. Each entry represents one application program in two closely related versions, one using LSODI and the other using DASSL for DAE solution. Model B uses only LSODE.

able compromises. Considerably smaller numbers slow execution, while considerably larger choices degrade the solution profiles. Values from 10^{-4} to 10^{-8} yield about the same solver performance.

8 Prototype Flux Model Results

The basic physical system consists of one reversible reaction between one fluid reactant and one solid reactant which yields one fluid product and one solid product within a homogeneous, spherical, porous pellet. Six different simulations and three solvers – DASSL, LSODI and LSODE – have been investigated. The models are summarized in Table 1, which is adapted from [3].

Model A is the most straightforward model for the pellet. It consists of conservation equations and the Stefan-Maxwell equations. Unfortunately, it is index 2, which makes it a poor match with available solvers. Model A′ is an equivalent index one problem obtained by differentiating and reorganizing the original algebraic equations. This matches the problem to the strengths of DASSL and LSODI, but the systems analysis burden of reducing the index by one and generating consistent initial profiles is considerable. Model EA′ is the nonisothermal version of A′ with the same reformulation burden.

The models in the A, or explicit flux, family contain the Stefan- Maxwell equations explicitly. Fluxes are treated implicitly in the B family which contains explicit references to the total flux only. If the total flux is obtained from a numerical inverse divergence operation on the net rate of production, an index zero problem results which can be solved by a robust ODE-IVP solver like

LSODE. The quadrature algorithm for computing the inverse divergence has the unfortunate effect on the system Jacobian of converting it from being rather tightly banded in structure to being lower triangular full. This requires storing most of the Jacobian or attempting solution with only a central band of the Jacobian. Neither choice is competitive with other family B model/solver combinations. Model B$'$ is identical to Model B except that the total flux is the solution of

$$\nabla \cdot N = R$$

and, after discretization, an index one DAE set results. Model EB$'$ is the nonisothermal version of B$'$ which means that the B$'$ equations have been rewritten to include the effects of nonconstant total concentration and temperature dependences and the B$'$ equations are augmented by an energy equation.

Simulations were run with stoichiometric coefficient ratios ranging from 1/3 to 3 and the square of the reaction modulus varying from one to 1000. A total of 125 simulations is reported in [3]. Both LSODI and DASSL were successful in solving the index 2 problem for most parameter combinations, with DASSL failing to get started once and LSODI failing at the larger values of reaction modulus. Both solvers succeeded in completing simulations using Model A$'$ except for LSODI in the cases of $\sigma^2 = 1000$. When both solvers were successful, LSODI was generally 25% faster. Tests with Model B$'$, the other index one model, produced similar results. DASSL completed all runs and LSODI failed for $\sigma^2 = 100$. When both solvers succeeded, LSODI, on average, consumed 25% less CPU time. Model B$'$ seemed the obvious choice for subsequent development. Index one forms better match the capabilities of available solvers than the index zero form or the index two form. The B$'$ index one model was obtained straightforwardly from first principles, although some informed choices had to be made, while the index one form of the A, or explicit flux, model required considerable manipulation and pretreatment, besides executing slower and requiring more memory.

Thus the small flux models, explicit in the fluxes and implicit, served the purposes of clarifying the choices to made among possible continuous models, guiding the development of the discretized equations, and selecting the most advantageous model/solver combination.

9 Multispecies Reaction/Diffusion Simulator

The formulation and solution of the small, implicit-flux model comsumed substantial time, effort and resources while being brought to the conclusion described above. However, in retrospect, no strategy of large model development which bypasses that small-model step could have been as successful, at least for these authors during that time. The extension of the single-reaction, binary fluid model to a model of multiple fluid and solid species undergoing multiple reactions remained, but the small model had provided an opportunity to focus on the impact of incorporating diffusive transport and the matching of formulation to solver. In [4], the authors describe the considerable generalization of the small model to problems of practical size and complexity.

The extension of model EB$'$ to handle multiple species and reactions is relatively straightforward. The principal difficulty comes from the reconstruction of the divergences of the fluxes for use in the fluid equations, from the total flux at every spatial location and timestep. What had been relatively simple in the binary system above, becomes a challenging task of creating a robust algorithm for the inversion of the singular Stefan-Maxwell equations. The literature treats this problem but the technique in [4] seems to differ from existing approaches.

The treatment of the outer boundary conditions for the multispecies case required considerable development also. In fact, [4] contains a discussion and correction of an oversight in [2]. Under assumptions carried forward from the earliest forms of the dimensionless, isothermal, EMCD models, the modified Sherwood number, which specifies the boundary convection of fluid species, and the modified Nusselt number, which describes the boundary convection of heat, are not independent and cannot both be constant.

With the experience gained from the small model, the discretization and initialization of the multispecies model were worked out without serious obstacle and a general-purpose code written for the simulation of reactions and diffusion in symmetric porous spheres. The code, Multispecies Shale Retorting Simulator (MSRS), and a user's manual [5] are available from the DOE National Energy Software Center, with distribution presently limited to DOE agencies and contractors.

The code, written in Fortran 77, consists of a main program and several subprograms and calls DASSL, a general-purpose differential/algebraic equation solver, to produce single-pellet simulations based upon specific models defined in six user-supplied subroutines. The pellet is assumed to be a symmetric, porous, solid sphere of unchanging overall size in a spatially uniform environment. The code contains generic output routines but the user is encouraged to substitute problem-specific output routines. Users are strongly discouraged from changing the MSRS solution routines, however. Experienced DASSL users may want to change solver parameters, but restructuring of the equations requires care and should not be undertaken without a full understanding of the implied model, the preservation of fluid species conservation, the operation of the solver and the incorporation of boundary conditions.

The examples are presented in [4] in sufficient detail to permit their resimulation by interested readers. The smaller is a three fluid (one inert)/two solid (one inert)/one reaction, simplified version of the larger model. The larger model is a nine fluid/ten solid/fifteen reaction simulation of in situ oil shale retorting [17]. The discretized smaller model on the coarsest grid (11 solution points) consists of 77 equations, eleven algebraic equations and the remainder are temporal differential equations. A typical execution time for the small model on a CRAY-1 is 11.83 seconds. The larger model on the finest grid (41 solution points) consists of 861 equations, 41 algebraic and 820 ODEs. A typical execution time for the simulations reported in [4] is 593 seconds on a CRAY-1.

10 Model Development

In [4] the authors describe the nine fluid/ten solid/fifteen reaction model in considerable detail and present eight plots of mole-fraction and solid density profiles showing temporal evolution. The purpose of that example in that paper is to demonstrate the capabilities of the underlying methods and the code, MSRS. The code has survived two years of use at LLNL without changes. No errors have been found nor need for algorithm redesign arisen. With confidence gained in the simulation code and solver, attention has turned to the model, that is, the details in the six subroutines which define the particular pellet, fluids, solids, reactions and properties being simulated. In particular, a point has been reached where one can investigate such questions as: Are the assumptions valid? Is the effort justified?

One crucial assumption that must be validated is that there is an initial period of fast transient recovery from unrealistic, flat profiles, followed by a period of physically meaningful transient response. Moreover, it is assumed that the physical transient is insensitive to the particular choices of unrealistic, flat initial profiles, by virtue of the fast transient.

In the case of isothermal simulations with a small number of species and reactions, it may be possible to establish the existence of an initial period of fast transient response, a priori. See [3]. As models become larger and more complicated, it becomes more difficult to make that determination analytically. A fast transient is not important itself, but the presence of a fast transient ensures that the subsequent, physically meaningful transients are unaffected by the use of arbitrary initial conditions.

The usual situation is to observe, a posteriori, that a fast transient existed and deduce that the use of arbitrary initial profiles was harmless. Unfortunately, the nine fluid/ten solid/fifteen reaction model sends mixed signals. A better test of solution insensitivity to initial profiles is to vary the initial profiles. Two quite different initial configurations of flat initial profiles were applied to the 9/10/15 model without significant differences appearing in the slow transients after about 20000 seconds. See Table 2.

The solutions resulting from the two sets of initial profiles given in Table 2 were in close agreement after 20000 s. of a simulation which runs for 50000 s. There were significant differences initially that were still in evidence at 10000 s. The fast transient is not particularly fast and clearly overlaps the physical transient. If arbitrary initial profiles are going to be used to start a DAE simulation like this, it seems the prudent thing to do to demonstrate solution insensitivity directly by varying the initial profiles.

The question of justification of the effort required to create and execute a model of the com-

Fluid Species Mole Fractions Flat Initial Profile Levels

Species	First Set	Second Set of Initial Interior Values
N_2	1.000	0.502
O_2	0.000	0.000
CO_2	0.000	0.170
CO	0.000	0.050
H_2	0.000	0.060
CH_4	0.000	0.008
CH_x	0.000	0.008
H_2O	0.000	0.200
Oil Vapor	0.000	0.002

Table 2. Two sets of values for the flat initial fluid species profiles used to demonstrate solution insensitivity. The second set of values for the interior initial mole fractions matches the initial exterior or bulk initial values used for both simulations.

plexity of this one must be left to the users ultimately. Perhaps part of an answer comes from the plots in [4] and below. The profiles demonstrate that no limiting case, simplified model could portray the rich and diverse behavior that seems to exist within the pellet, at least according to this model. In [3] there are plots in which the thermal effects have been isolated and they show that an isothermal model would miss significant steepening of the reaction fronts and slowing of the overall conversion, at least in particular cases.

A major justification for this work was the perceived need to eliminate having to invoke the EMCD assumption in order to get economical numerical solutions. Reasonably economical solutions are now possible but there remains the question of whether or not the perceived need existed. In [3] there is a comparison of a flux model conversion history and the same for an equivalent model in which EMCD is assumed. In that simple binary case, the difference is not impressive.

A comparison of an MSRS simulation of the 9/10/15 model and an equivalent EMCD simulation was attempted. A modified version of MSRS was created which would approximate an EMCD simulation by imposing the requirement that total $N = 0$ everywhere, for all times. While total N is usually small in magnitude, 10^{-7} moles/m^{2}s is typical, imposing total $N = 0$ has a drastic effect on the sum of the fluid species mole fractions. The additional constraint, $N = 0$, prevents

Model Time (s.)	Radial Variation in z
0	0
500	0.0000346 - 0.143
5000	0.270 - 0.373
10000	0.576 - 0.605
15000	0.839 - 5.333
20000	6.598 - 982.7
22500	67.55 - 2461.

Table 3. Radial variation of the error in conservation of fluid species as a function of time when equimolar counter-diffusion transport is imposed on the 9/10/15 model.

the simulator from holding the sum of the fluid species mole fractions minus one close to zero. If

$$\Sigma x_i - 1 = z$$

then z ranges from zero to 6.66×10^{-10} during a typical 9/10/15 simulation with MSRS. In fact, z is used as a code performance indicator. With the imposition of total $N = 0$, the simulator is no longer able to keep z small. The radial variations of z during an EMCD simulation with the modified MSRS are listed in Table 3.

An EMCD model could be formulated in a way that would impose $z = 0$, as well as total $N = 0$, by omitting one fluid continuity equation, for example. But Table 3 indicates that some aspect of the solution will have to suffer rather drastic consequences when EMCD is imposed.

11 Example Simulation Results

The methods and algorithms above and the code, MSRS, have been developed to permit simulation of realistic, first-principle models like the 9/10/15 model of an oil-shale pellet. The plots in [4] show the detailed information that can be obtained from such a simulation. There is a question of whether or not the results are sensitive to the internal details of the model.

In [4] there is a discussion of some simplifications made to the reaction rate expressions in order to eliminate potential numerical problems. In one case, the rate expression for a reaction between residual organic carbon and carbon dioxide was to have been dependent on the ratio of two fluid mole fractions

$$v = kw/(1 + x_{CO}/Kx_{CO2})$$

where the CO_2 concentration can become very small and even change sign due to numerical effects or model inconsistencies. Anticipating that the impact on v would be unacceptable, the rate expression was simplified to $v = kw$. The resulting transient behavior of the CO_2 is shown in Figure 1, which is taken from [4]. Figure 2 shows the CO_2 profiles that result from replacing the above rate expression by

$$v = kwx_{CO2}/(x_{CO2} + x_{CO}/K + 0.001)$$

which is closer to the original rate and free of apparent numerical anomalies. The effects are quite evident. The carbon dioxide profiles once went negative, but after the change, seem well behaved. The residual organic carbon profiles are altered and the sulfur consumption is reduced to about half of what it had been. The point is not so much that the model has been improved as it is that the simulator portrays the effects of changing a rate expression and that the simulator is a sensitive tool that can be used for design, development, identification and sensitivity studies.

12 Conclusion

The authors have tried to summarize several years work which has been reported in several papers. As a consequence of trying to limit the length and avoid repetition, this paper gives an overview if read alone, but must be read with the references for a comprehensive view. The inconvenience is compounded by the fact that a crucial reference [4] has not appeared in print yet. The authors apologize, but wanted to take this opportunity to describe the simulator and perhaps attract some future users.

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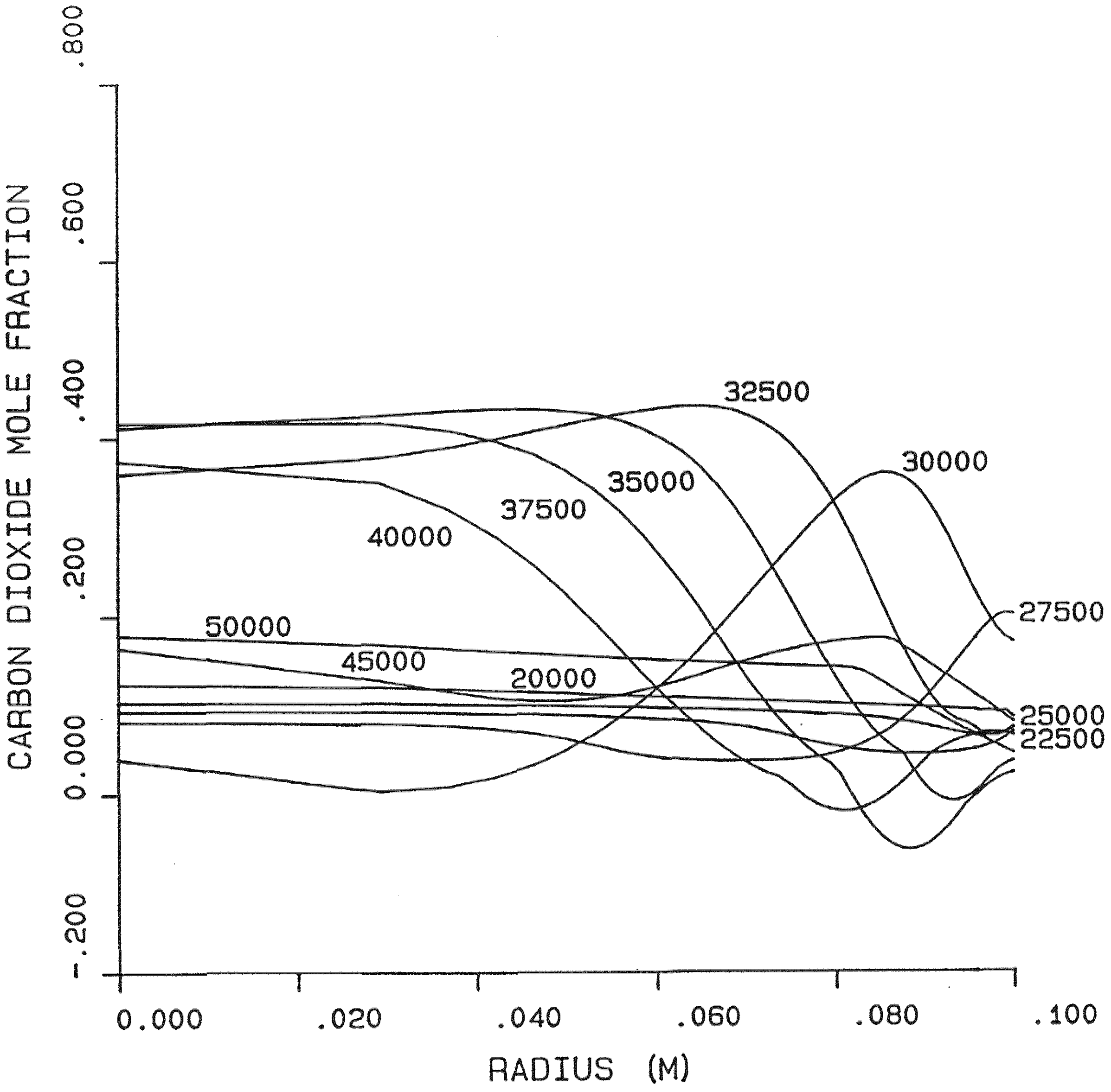

Figure 1. Carbon Dioxide Mole Fraction Profiles. In an attempt to avoid numerical difficulties, a reaction rate expression was simplified. As a consequence, model difficulties arose, leading to negative mole fraction values at some spatial locations and some times. Profile labels are times of occurence in seconds.

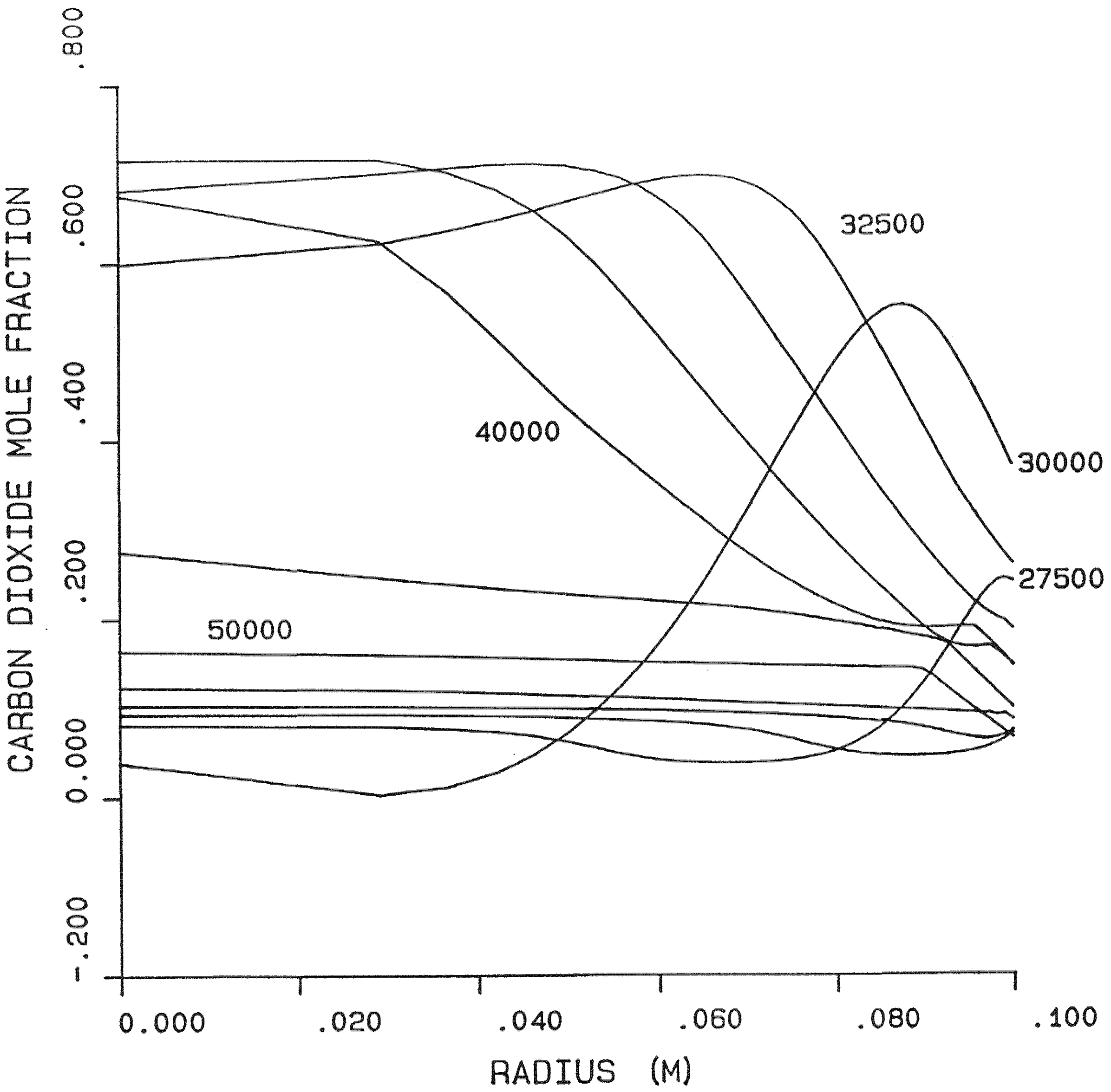

Figure 2. Carbon Dioxide Mole Fraction Profiles. In an attempt to overcome the model difficulties shown in Figure 1, a new rate expression, closer to the original, with a less drastic modification to circumvent numerical difficulties was substituted and these profiles obtained. Profile labels are times of occurence in seconds. The set of output times for Figure 2 is the same as for Figure 1.