Solving Reaction Models for the Systems with Particulate Solids

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A relatively simple method has been developed for the integration of highly stiff sets of differential equations. The method is based on the semi-implicit Euler scheme which makes it possible to solve the resulting algebraic equations separately with the aid of always converging procedures such as the interval halving or "regula falsi". An alternative algorithm has been presented for the size control of variable time step in the course of the computation. The developed semi-implicit Euler method has been extensively tested and compared to some implicit and semi-implicit techniques. Problems have been discussed with the convergence of the iterative solutions of the nonlinear, algebraic systems resulting from the implicit schemes. Behaviour of various methods is also examined when they are applied to a practical problem in reaction engineering. Computed break-through curves have been confronted with the experimental measurements.

Mathematical models of the dynamic behaviour of the chemical reactors with multiphase and multicomponent systems are mostly embodied by sets of the ordinary differential equations (ODE) or by systems of the partial differential equations (PDE) with the time derivative. Various combinations of the ordinary and partial differential equations frequently occur in modelling. In general, the systems of model equations are nonlinear. The reaction terms or the terms describing mass transfer between different phases are usually found as the sources of nonlinearities. In addition to chemical reaction and interfacial mass transfer, the conservation equations include convection, accumulation and, quite frequently, also dispersion.

A characteristic feature of the noncatalytic, gas—solid reaction systems is the simple fact that a more or less pure solid particle reacts quite rapidly with a very lean gas phase. Contacting the hot flue gas with limestone or lime can serve as an illustrative example [1]. Elementary arithmetic predicts that a volume of 1 cm³ of the solid CaO is stoichiometrically equivalent at 850 °C to an enormous volume of about 1.5 m³ of flue gas containing 0.1 vol. % SO_2. As we found [2, 3], the sulfation reaction is quite rapid at high temperature. This is the case particularly in early stages of the reaction even though the partial pressure of sulfur dioxide is very low.

It is the combination of the considerable rapidity of reaction and the very large reaction (sorption) capacity of the solids which is the principal cause of the high stiffness of such systems in the physicochemical sense. The character of stiff systems necessitates the use of an extremely small increment of time when common difference schemes are employed for the integration. Since the large reaction times are usually of practical interest, such computation can hardly be feasible with the use of conventional methods. It should be noted that the problems associated with solving the stiff systems do not only reside in approximating the true solution or in the stability of the employed difference scheme. There are also difficulties involved in determining the roots of simultaneous sets of the nonlinear algebraic equations that result from the implicit schemes. It appears that convergence of the iteration procedures can be conditioned by the use of very small increments of time or an initial estimate must be very close to the true solution.

Development of computational methods to solve the stiff ordinary differential equations has reached a certain level [4—14]. However, the situation as regards the numerical techniques for solving the partial differential equations is less satisfactory (*e.g.* [15, 16]), even though such systems frequently occur in reactor engineering. In more or less standard situations, codes and packages (*e.g.* GEAR, GEARB, EPISODE or ODE-PACK) can often ease the computational difficulties.

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Practice shows that a diversified approach is usually needed in which previous experience and intuition still play an important role.

In a recent study of ours [17] we reported results on sorption of sulfur dioxide from flue gas in a fluidized bed of inert particles containing magnesium oxide. The measured transient curves of sulfur dioxide were employed for determining the kinetics of this high-temperature, sulfation reaction. At that time, strict space limitations did not make it possible to present the numerical solution of the model equations. The technique was later further improved, tested and successfully applied also to notably different systems.

In this paper, we demonstrate this simple method and compare it to the procedures of other authors.

Outline of the Problem

We assume that the model is embodied by a system of highly stiff ordinary (ODE) or partial differential equations (PDE). Such set describes the states of the gas concentrations and the solids conversions as a function of time and position within the reactor. We refer to the concept of stiffness as defined for ODE systems, e.g. in [7]. In the case of PDE sets, this character can be ascribed to such equations the approximation of which in the spatial variable leads to the stiff ODE systems.

The explicit difference schemes seem to be attractive for their simplicity. Unfortunately, they are known to be mostly unstable or to have extremely limited stability regions of the time.

The implicit schemes are usually stable or have considerably wider stability regions. But the implicit methods require the solution of nonlinear systems of algebraic equations (NAE) the number of which can be large, particularly with PDE. In such a case the problems occur how to find a successful iteration method. The conditions of convergence of the iteration techniques depend on the employed time and spatial steps $(\Delta t, \Delta w)$. Common experience shows that the resulting sets of nonlinear equations can converge only for very small Δt. If the time step is larger, then the initial guess of an iteration process must be assigned extremely close to the sought solution which poses a problem again. As an illustration, the Newton—Raphson method can be mentioned as a widely recommended iteration technique. The fundamental condition concerning convergence requires an initial guess to be "near" the true solution of the set of equations (e.g. [18]). In solving of NAE resulting from the difference approximation of the differential equations, such an ambiguously defined condition can generally be met only if the time step tends to zero ($\Delta t \to 0$).

Standard semi-implicit methods that do not necessitate a NAE solution may lead in some cases to the results falling outside of the definition region of the sought quantities.

In search of an adequate numerical procedure, our aims are as follows:

To find a difference scheme which can be solved at every time step by some always converging techniques and with a tolerance which can be reliably estimated.

Choosing a variable time step, Δt, the number of integration steps at preserving a realistic tolerance of the overall error of the solution is minimized. Effort to find an effective procedure is of particular importance when the integration of the model (stiff) equations becomes a subproblem of some often repeated process as e.g. in evaluating the model parameters from the experimental data. It is a well-established fact that most of the iteration techniques have a defect which resides in the initial estimate.

If a proper choice of the initial estimate is not made, the convergence is not ensured. There are only two, always converging procedures for solving the nonlinear equations: the method known as "interval halving" and the "regula-falsi" iteration. Both of them can be employed for solving an equation in the form $f(x) = 0$, where $f(x)$ is a continuous, real function of the real variable, x. Both algorithms assume that the function has one and the only one root on a certain, initial interval $x \in \langle a, b \rangle$. When using either method we know the maximum error quite accurately. No other criteria for stopping the iteration process are needed. In fact, such criteria do not guarantee that the approximation is reliably close to the true solution.

Both the above methods cannot be generally applied to the systems of NAE. This fact makes it impossible to consider the implicit scheme in search of a feasible, finite difference pattern. The only possibility is to resort to a suitable "semi-implicit" scheme, chosen in such a way that the resulting system will be the set of real equations always with one unknown variable. Some procedures in formulating the semi-implicit schemes are shown in solving a real illustrative model in the next paragraphs.

In choosing the variable time step, different procedures can be used in dependence on the fulfilment of certain criteria. Apart from a strategy for optimizing the time step as described below, the strategies proposed in [19] and [20] are also employed in this work. To examine how accurately the numerical results approximate the models, an overall mass balance was computed simultaneously with the solution. In its way, this procedure provides the total sum of all possible errors of the solution coming from a variety of sources. As shown, this checking can serve as the basis for controlling the variable time step.

The model solutions provided by the proposed, semi-implicit method with the different strategies for the control of Δt are compared with the solutions obtained by five different procedures. The computed break-through curves were also verified by the measured concentrations in the gas phase at the exit of reactor.

Mathematical Model

Three mathematical models were developed for the sorption of sulfur dioxide by magnesium oxide in a semi-batch reactor with fluidized bed [17]. The conservation equations have been formulated for different combinations of the limiting flow conditions, *i.e.* for ideal mixing and plug flow regimes. The models refer to the batch operations, in which no sorbent particles enter or leave the bed. The reactor is of continuous-flow character from the standpoint of the gas phase. One of the models (V2) is given below.

This model assumes that the gas phase occurs in plug flow and the solids are ideally mixed. Then, $C = C(w,t)$, $X = X(t)$ for $w \in (0,1\rangle$ and $t \geq 0$. This situation is described by

$$\frac{\partial C}{\partial t} = -\frac{1}{\bar{t}_g} \cdot \frac{\partial C}{\partial w} - \frac{t_s}{\bar{t}_g} \cdot C_0 \cdot R(C,X) \qquad (1)$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \int_0^1 R(C,X)\mathrm{d}w \qquad (2)$$

The initial conditions are

$$C(w,0) = C_0, \quad X(0) = 0 \quad \text{for } w \in \langle 0,1\rangle \qquad (3)$$

and the boundary condition is

$$C(0,t) = C_0 \quad \text{for } t \in \langle 0,\infty) \qquad (4)$$

The reaction term $R(C,X)$ in eqns (1) and (2) is defined by the nonlinear, empirical relationship

$$R(C,X) = 0.3653\, C^{0.873} \cdot (0.4 - X)^{1.70} \qquad (5)$$

deduced from the experimental measurements given in [17].

The quantities t_s and $\bar{t}_g$ in the model equations are the stoichiometric time and the mean residence time of gas in the bed, respectively. Their values widely differ in the orders of magnitude. While the mean residence time of gas is usually of the order of magnitude, $\bar{t}_g \approx 10^{-1}$, the stoichiometric time is mostly in the region $t \approx 10^6$—10^8. The illustrative problems presented in this work were solved with $\bar{t}_g = 0.23$, $t_s = 20003$, and $C_0 = 0.0033$.

With such values of t_s and $\bar{t}_g$, the model systems have the high stiff character as defined in the preceding paragraphs. Experience shows that the conventional integration methods can proceed only if the step size is as small as 10^{-2}—10^{-3}. Practical needs require the operational time of the sorption over a wide range of 10^4—10^5. In some cases, the step size, Δt, can be somewhat enlarged as the solution is approaching the steady state and/or the exhaustion of sorbent. In general, the classical integration methods are forced to take very small steps on a considerably large interval of time the size of which is not known in advance. Due to this fact, the conventional integration procedures become extremely inefficient.

Integral Conservation Equations

Having in mind an integral balance of the active gas component in the bed, we introduce a variable

$$\overline{\overline{X}}(t) = \frac{1}{t_s} \int_0^t \left(1 - \frac{C_w(t)}{C_0}\right) \mathrm{d}t \qquad (6)$$

where $C_w(t)$ is the concentration of gas at the exit of the bed in a given time t. On integrating the model equations over the variable t and the variable w in the interval $\langle 0,1\rangle$, we alternatively express the same quantity $X(t)$ for the chosen model V2

$$\overline{\overline{X}}(t) = X(t) + \frac{\bar{t}_g}{t_s} \int_0^1 \frac{C(w,t)}{C_0} \mathrm{d}w \qquad (7)$$

It is apparent that the exact solution will provide the same values of $\overline{\overline{X}}(t)$. Possible differences in $X(t)$ computed from eqns (6) and (7) can be attributed to the numerical procedure as a whole. These differences reflect all conceivable errors which can result from the use of a chosen difference scheme and time step strategy. They also follow from the approximate solutions of NAE systems that have to be iteratively solved in each time step.

The above integral relationships offer an engineering means of assessing the quality of the numerical results obtained with the aid of a chosen difference scheme and applied strategy for the control of step size. It can be viewed as a "cross reference" of the computations. Since the integrals in eqns (6) and (7) are numerically evaluated on the same mesh as the model solution, a possible effect of the grid density is greatly reduced, if not entirely eliminated, in this respect.

Solving the Model

The above-mentioned model V2 is solved by the method which is the main subject of this work and that is described below. It is denoted in the text as SIMEL (semi-implicit Euler scheme). For the comparison, the model V2 is also integrated by a number of other numerical techniques.

The model was solved with a variable time step controlled by one of the following strategies. One of these strategies is that proposed in [19] which compares in each step the computed result with the "backward Euler" value (BE). The second technique, "step halving" (HV) was proposed in [20]. The "balance corridor" procedure (BC) was developed and also employed in this work. The SIMEL difference scheme, its solution as well as the optimization strategies BE, HV, and BC are described in the next paragraphs.

SIMEL Difference Scheme

In constructing the finite difference scheme, the time and the spatial derivatives of the variables C and

X are approximated with the backward differences. The integral of the function R is evaluated with the aid of the trapezoidal rule. In order that the resulting system of the nonlinear equations could be solved step-by-step by the method of interval halving, the reaction term is replaced in the respective equations as follows

$$\text{in eqn } (1) \quad R = R[C(w,t), X(t - \Delta t)] \qquad (8)$$

$$\text{in eqn } (2) \quad R = R[C(w, t - \Delta t), X(t)] \qquad (9)$$

We discretize the spatial variable w by an increment of $\Delta w = 1/n$ and write

$$w = i \cdot \Delta w \quad w_0 = 0 \qquad (10)$$

$$C_i(t) = C(w_i, t) \quad \text{for } i = 1, 2, \ldots, n \quad C_0(t) = C_0 \qquad (11)$$

$$X_i(t) = X(w_i, t) \equiv X(t) \qquad (12)$$

Then, the resulting finite difference scheme of the model reads

$$\frac{C_i(t) - C_i(t - \Delta t)}{\Delta t} = -\frac{1}{\overline{t_g}} \frac{C_i(t) - C_{i-1}(t - \Delta t)}{\Delta w} - \frac{t_s}{\overline{t_g}} C_0 R(C_i(t), X(t - \Delta t)) \qquad (13)$$

for $i = 1, 2, \ldots, n$

$$\frac{X(t) - X(t - \Delta t)}{\Delta t} = \frac{1}{2} \sum_{i=1}^{n} [R(C_i(t - \Delta t), X(t)) + R(C_{i-1}(t - \Delta t), X(t))] \cdot \Delta w \qquad (14)$$

The nonlinear equations resulting from the respective schemes can be solved with respect to $C(t)$ and $X(t)$ by the procedure of interval halving with the initial intervals $\langle 0, C \rangle$ and $\langle 0, X = 0.4 \rangle$, respectively. The number of these iterations is chosen with respect to the error term given by

$$|x_N - x^*| = \frac{|b - a|}{2^N} \qquad (15)$$

Aside from the convergence of the finite difference procedure for PDE, the aspect of "consistency" of this scheme must also be examined as pointed out in [18] and illustrated on the approximation of the heat-conduction equation as proposed by DuFort and Frankel.

The scheme SIMEL, as applied to the original PDE, is not consistent with the original eqn (1) for $\Delta t / \Delta w = $ const when $\Delta t, \Delta w \to 0$. We work with the ODE system at a spatial step $\Delta w = $ const that is a substitute for the PDE. Thus, the question of the consistency loses its sense and the point is reduced to a problem of the approximations of ODE given by eqns (13) and (14).

Further details on the approximation as well as the discussion of the SIMEL scheme stability are given in the Appendix.

Control of the Time Step

Three following procedures were employed to control the time step.

Step Halving (HV)

The idea of this approach is based on the estimation of local error by evaluating a difference in solutions obtained when a full-step and half-step is used. The choice of a new time step is then given by a procedure described in [20]. This strategy can generally be applied to the control of various schemes.

Backward Euler Strategy (BE)

Choice of a new integration step results from comparison of the solution provided by a given method and the solution obtained by the Back Euler formula. Such a procedure is described in [19]. In the case of the SIMEL scheme, the procedure minimizes the error of this method with respect to the fully implicit scheme of Euler.

Balance Corridor Strategy (BC)

Philosophy of this procedure rests upon the need to work with Δt as large as possible and on the simultaneous requirement to fulfil the integral conservation eqns (6) and (7) within the pre-set interval of errors (balance corridor). With an in advance prescribed corridor $\langle \alpha, \beta \rangle$, we choose Δt_{new} as

$$\Delta t_{\text{new}} = \Delta t \quad \text{if } \alpha < E_b < \beta \qquad (16)$$

$$\Delta t_{\text{new}} = 2\Delta t \quad \text{if } E_b \leq \alpha \qquad (17)$$

or

$$\Delta t_{\text{new}} = \Delta t/2 \quad \text{if } E_b \geq \beta \qquad (18)$$

where

$$E_b = \left| \frac{\Delta r(t) - \Delta l(t)}{\Delta r(t) + \text{EPS}} \right| \qquad (19)$$

$$\Delta r(t) = r(t) - r(t - \Delta t) \qquad (20)$$

$$\Delta l(t) = l(t) - l(t - \Delta t) \qquad (21)$$

$r(t)$ is the right-hand side of eqn (6) and $l(t)$ is the right-hand side of eqn (7). EPS is a small positive parameter that makes it possible to choose whether the relative or the absolute error is controlled. The obtained value is tested again if it does not exceed the prescribed Δt_{max}.

Table 1. Numerical Results with Different Methods

	RRSTIFF	CMR	BMR	MICH3	SIMEL	IMEL
$C(1, t_{max}) \cdot 10^3$	3.152	3.151	3.151	3.152	3.146	3.150
$C_{min} \cdot 10^3$	–	4.7×10^{-4}	4.9×10^{-4}	4.8×10^{-4}	4.4×10^{-4}	5.4×10^{-4}
t-break	–	–	–	–	–	–
Δt-final	–	3.7×10^2	5.0×10^2	1.6×10^3	1.2×10^2	1.2×10^2
Δt-min	–	1.0×10^{-3}	3.8×10^{-40}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
RE relative to RRSTIFF	–	7.7×10^{-5}	4.4×10^{-5}	7.9×10^{-6}	2.8×10^{-3}	5.2×10^{-4}
Error in balance/%	–	0.016	0.021	0.050	0.345	0.147
Comput. time/s	30.0	44.1	300.5	20.0	804.4	162.4
Comput. steps	636	83	304	57	935	282
Reject	–	0	598	0	0	0
Error	–	–	–	–	–	–

Model V2, $n = 5$, $r = 0.87$, Δt control: HV, relative error tolerance: 10^{-4}, $t_{max} = 14760$.

Table 2. Numerical Results with Different Methods

	RRSTIFF	CMR	BMR	MICH3	SIMEL	IMEL
$C(1, t_{max}) \cdot 10^3$	3.152	3.152	3.151	3.152	3.141	3.147
$C_{min} \cdot 10^3$	–	2.3×10^{-4}	4.9×10^{-4}	4.7×10^{-4}	1.5×10^{-4}	9.7×10^{-4}
t-break	–	–	–	–	–	–
Δt-final	–	1.0×10^2	5.0×10^2	1.0×10^2	6.2×10^1	1.0×10^2
Δt-min	–	1.0×10^{-3}	3.8×10^{-40}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
RE relative to RRSTIFF	–	7.6×10^{-5}	4.4×10^{-5}	6.1×10^{-6}	3.5×10^{-3}	1.3×10^{-3}
Error in balance/%	–	0.000	0.021	0.001	0.844	0.452
Comput. time/s	30.0	44.5	300.5	34.0	300.7	61.9
Comput. steps	636	174	304	174	794	217
Reject	–	0	598	0	0	0
Error	–	–	–	–	–	–

Model V2, $n = 5$, $r = 0.87$, Δt control: BC (corridor $\langle 0.5, 1\ \% \rangle$, $t_{max} = 14760$).

RESULTS AND COMPARISON WITH OTHER METHODS

The model V2 was systematically solved with the semi-implicit Euler scheme (SIMEL) developed in this work. For comparison, these model equations were also integrated by a number of the following, more or less classical methods:

IMEL (Implicit Euler Method), L-stable, the 1st order

Rosenbrock method, A-stable, the 3rd order

CMR, implicit, A-stable, the 2nd order [19]

BMR, implicit, L-stable, the 3rd order [19]

ISI3, semi-implicit Runge—Kutta method, A-stable, the 3rd order [6]

MICH3, Michelson's modification of ISI3, A-stable, the 3rd order [20]

The strategies HV, BE, and BC were employed in all the above procedures to control the size of time step.

RRSTIFF is a code developed at the Department of Chemical Engineering, Technical University Delft (the Netherlands). It works with automatic control of the integration step and is suitable for the stiff as well as nonstiff systems.

The results of testing are summarized in Tables 1—5. Since the Rosenbrock method and the procedure ISI3 behave similarly, their results are not mentioned in these tables.

As it might be expected, this comparative study shows that all the above methods are very effective (i.e. rapid and accurate), provided they do not cease to function. This comparison also indicates that with certain values of the model parameters, these current methods lose their efficiency or they do not work at all. Such a situation can occur due to the reaction term $R[C^r, (X_{max} - X)^s]$ when the power r or s is less than unity (i.e. $r < 1$ and/or $s < 1$). For $C \to 0+$, such models have singularities of the elements in Jacobian of the ODE system. The reaction terms are not defined for $C < 0$ or $X_{max} - X < 0$. This fact can lead to considerable difficulties associated with the common numerical procedures:

1. Though always stable, the implicit schemes are considerably restricted by the convergence radius of a given iteration method, particularly for appreciable values of Δt. Moreover, there is a real possibility that the values of C can become negative in the course of iteration.

2. Semi-implicit, always stable methods, using the

Table 3. Numerical Results with Different Methods

	RRSTIFF	CMR	BMR	MICH3	SIMEL	IMEL
$C(1, t_{\max}) \cdot 10^3$	3.152	3.152	3.148	3.152	3.149	3.147
$C_{\min} \cdot 10^3$	–	4.5×10^{-4}	5.3×10^{-4}	4.8×10^{-4}	2.1×10^{-4}	9.7×10^{-4}
t-break	–	–	–	–	–	–
Δt-final	–	7.1×10^1	1.5×10^2	4.4×10^2	1.6	8.4×10^1
Δt-min	–	1.0×10^{-3}	3.8×10^{-40}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
RE relative to RRSTIFF	–	4.1×10^{-6}	9.9×10^{-4}	7.3×10^{-6}	6.8×10^{-4}	1.4×10^{-3}
Error in balance/%	–	0.000	0.173	0.006	0.384	0.332
Comput. time/s	30.0	146.2	199.1	42.5	1407.3	63.0
Comput. steps	636	654	447	207	3864	305
Reject	–	0	622	0	0	0
Error	–	–	–	–	–	–

Model V2, $n = 5$, $r = 0.87$, Δt control: BE, TOL = 0.001, ATOL = 0.001, $t_{\max} = 14760$.

Table 4. Numerical Results with Different Methods

	CMR	BMR	MICH3	SIMEL	IMEL
$C(1, t_{\max}) \cdot 10^3$	3.273	$3.8 \times 10^{-30}*$	3.273	3.272	3.273
$C_{\min} \cdot 10^3$	4.5×10^{-31}	$3.8 \times 10^{-30}*$	4.1×10^{-31}	1.8×10^{-30}	7.0×10^{-31}
t-break	–	1.1×10^{-3}	–	–	–
Δt-final	7.6×10^2	3.2×10^{-8}	1.4×10^3	1.1×10^2	2.0×10^2
Δt-min	9.6×10^{-13}	1.2×10^{-41}	2.0×10^{-13}	9.9×10^{-4}	8.1×10^{-13}
RE relative to SIMEL	9.0×10^{-4}	–	9.1×10^{-4}	0.0	6.9×10^{-4}
Error in balance/%	0.008	–	0.066	0.160	0.097
Comput. time/s	103.9	726.1	48.2	1128.6	122.5
Comput. steps	194	1001	101	1305	234
Reject	254	2927	314	0	140
Error	–	–	–	–	–

Model V2, $n = 5$, $r = 0.6$, Δt control: HV, relative error tolerance: 10^{-4}, $t_{\max} = 14760$.
* Computations terminated prematurely.

Table 5. Numerical Results with Different Methods

	CMR	BMR	MICH3	SIMEL	IMEL
$C(1, t_{\max}) \cdot 10^3$	$1.0 \times 10^{-39}*$	$1.7 \times 10^{-34}*$	$1.0 \times 10^{-39}*$	3.285	$1.0 \times 10^{-39}*$
$C_{\min} \cdot 10^3$	$1.0 \times 10^{-39}*$	$1.7 \times 10^{-34}*$	$1.0 \times 10^{-39}*$	0.0	$1.0 \times 10^{-39}*$
t-break	2.8×10^{-4}	2.8×10^{-4}	3.3×10^{-4}	–	3.4×10^{-4}
Δt-final	1.8×10^{-19}	1.0×10^{-19}	5.4×10^{-23}	6.5×10^1	3.2×10^{-19}
Δt-min	2.2×10^{-21}	2.9×10^{-42}	5.4×10^{-23}	1.0×10^{-3}	6.4×10^{-22}
RE relative to SIMEL	–	–	–	0.0	–
Error in balance/%	–	–	–	0.138	–
Comput. time/s	612.0	115.7	221.5	1575.3	610.1
Comput. steps	1001	135	1001	1436	1001
Reject	6040	533	1298	0	6101
Error	–	OWERFL	–	–	–

Model V2, $n = 5$, $r = 0.5$, Δt control: HV, relative error tolerance: 10^{-4}, $t_{\max} = 14760$.
* Computations terminated prematurely.

values of the ODE Jacobian in the vicinity of the singular values, can also be employed only with a very restricted integration step. Otherwise, they usually lead to the negative values of C.

In both cases, there is a real possibility of overflow of the power in operations with the elements of the Jacobian.

Such problems occurred in the use of all the above methods, including the code RRSTIFF. The value of the power r appeared as the most important factor in this respect. For $r = 0.873$, the mentioned methods are still more efficient than SIMEL. However, when $r = 0.625$ SIMEL works more effectively than the current methods. This value is also a limit at which the code RRSTIFF failed. When $r < 0.625$, all the algorithms, except SIMEL, provide negative values of C or converge extremely slowly by the Newton iteration.

Figs. 1 and 2 show the computed model solutions along with the experimentally determined breakthrough curve [17]. The computations were performed
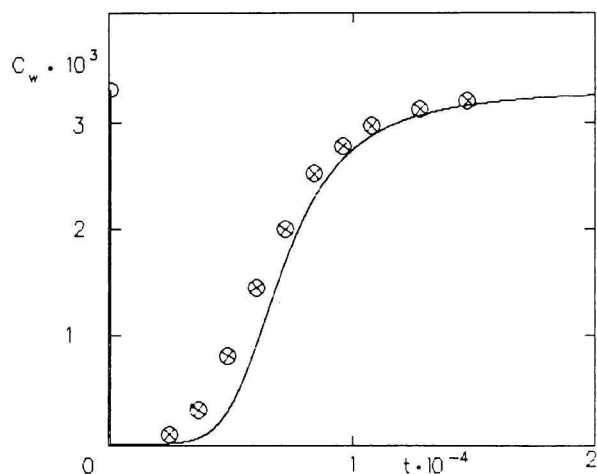
Fig. 1. Comparison of the predictions of the model V2 with the experimental break-through curve: $\otimes$ measured values. The solid line shows the model predictions. The model equations were solved by SIMEL for $\bar{t}_g = 0.23$ s, $t_s = 20003$ s, and $C_0 = 0.0033$.
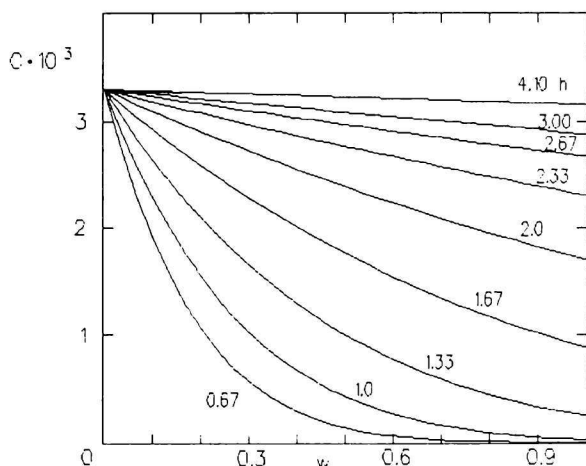
Fig. 2. Transient gaseous concentration profiles within the bed as predicted by the model V2. The values of the model parameters and the other conditions are the same as in Fig. 1.

on an AT personal computer. It is apparent that the computer time is considerably overestimated as the respective routines were carried out in "QUICK BASIC" (except for RRSTIFF). Moreover, a number of additional procedures were included for testing.

It was necessary to test the transition of the concentrations to negative values. At this moment, the computation is terminated (the code RRSTIFF) or the run can be repeated with a smaller integration step. However, this implies that the step size has to be controlled also with respect to this phenomenon, in addition to the local approximation error and the scheme stability. For the sake of objectivity of the comparison, this procedure was also employed. Some information

is also given in Tables 1—5 on the behaviour of the respective methods in the course of computations. Aside from the values of C at $w = 1$ for $t_{\max} = 14760$, relative error, balance error, computation time, and the number of the integration steps, the tables also provide information on $C_{\min}$, number of step reductions when $C < 0$, and an indication of "error". A moment of time is also mentioned when a given method failed.

Tables 1—3 show the results for the power $r = 0.87$ and the different strategies of control of the integration step. As apparent, all the tested algorithms are more effective and more accurate than the method SIMEL in this case. The line "reject" indicates that at the method BMR, the time step has to be controlled also with respect to possible occurrence of the negative values of C. The relative error, RE, is related to the results provided by the code RRSTIFF.

Table 4 gives solutions for $r = 0.6$. Since the code RRSTIFF failed in this situation, the relative error, RE, is given with respect to the values computed by the scheme SIMEL. All the other schemes require repeated reductions of the time step. The method BMR was not continued after 1000 steps, as the needed integration step was extremely small and the integration process practically ceased. Table 5 illustrates the situation for $r = 0.5$. All the methods had to be terminated for the necessity of an extremely small step at which the integration was not feasible. The scheme BMR ends with overflow during evaluations of one of the Jacobians that are employed in this method.

A possibility to substitute a very small, positive value of C when the Newton iteration method provides negative concentrations was also considered. Such a more or less incorrect intervention may be sometimes used, but it cannot be generally recommended. The process can converge very slowly, it can lead to the values very distant from the true solution or even oscillates.

CONCLUSION

Needs for the integration of stiff ODE and PDE systems eventually lead to the problems with the iteration solutions of simultaneous sets of the nonlinear, algebraic equations. This occurs even when a sufficiently stable difference scheme is chosen. The stability and the good approximation of a given difference representation, constitute a necessary but not sufficient condition for the successful numerical solving of the stiff differential equations.

The relatively simple, semi-implicit method SIMEL has been developed for ODE and PDE systems at which the integration step has to be chosen with respect not only to the stability and the approximation of a given scheme, but also to a possibility that the results can fall outside of the definition region. Such situations can occur during the iteration solutions of nonlinear systems resulting from the most of schemes.

The scheme SIMEL is based on the implicitness of the variables occurring separately in the respective equations of a system. Then, the resulting nonlinear algebraic equations can simply be solved by interval halving. The implicitness of the respective ODE equations in combination with interval halving ensures that the computed results lie within a given definition region.

The scheme SIMEL is a method of the first order the accuracy of which is generally less and the number of integration steps is larger than with the tested schemes of other authors. However, in some situations ($r < 1$), quite common in reaction engineering, the overall effectiveness of SIMEL can be better than that of the current schemes.

With respect to the accuracy of results, the step control strategy HV appears as correct. The BE strategy affects only the local error with respect to the solution provided by the implicit Euler scheme. The BC procedure controls the overall balance of the modelled process. Good balance agreement is a necessary condition, but, in a rigorous sense, it does not have to be a sufficient condition for good approximation. However, our experience indicates that this strategy usually provides good results as for example in parameter searching.

Intermediate accuracy of the SIMEL scheme is given by the lower-order approximation and by an error committed by replacing the normal implicit scheme with the semi-implicit pattern. Relatively less efficiency in the instance of a small ODE system is given by the fact that the interval halving is less effective than the Newton iterations provided that the Newton method converges.

The method SIMEL in combination with different strategies for the integration step control solved satisfactorily the reaction models. The use of the standard methods often led to difficulties that could not practically be removed. The authors believe that this scheme can be employed in a number of similarly oriented problems.

APPENDIX

Analysis of the Problem

The models of unsteady-state reaction of a gas with solids involve the reaction term in the form $R(C, X) = k \cdot C^r \cdot (X_{\max} - X)^s$. The models are represented by highly stiff ODE or PDE systems that might apparently be solved with the use of some efficient conventional method or code. However, the source of difficulties is a fact that the power of C or $(X_{\max} - X)$ is less than unity (*i.e.* r or $s < 1$). Values of the sought reactive concentrations C lie in the interval $(0, 1)$ and for $C \rightarrow 0+$, the elements of Jacobian of the right-hand side of ODE with terms C^{r-1} are not limited in their absolute value and norm of the Jacobian increases without any limitation. This results in very

serious consequences for the use of the conventional methods that are based on evaluating the Jacobian regardless of their high stability. Iterative solutions of the nonlinear algebraic equations resulting from the implicit difference schemes converge extremely slowly in the vicinity of a singularity. Moreover, the transition can occur outside of the definition region of a variable. Conventional semi-implicit methods based on the local linearization of the corresponding ODE in the vicinity of singularities of the Jacobian elements require the use of a very small time step Δt. Otherwise, they lead again to values out of the definition region. This fact is particularly serious at the pseudosteady states when the system is close to the singular values and the computational process is very sensitive to round-off errors.

In light of the above arguments, an effort is justified to employ somewhat unconventional methods of the SIMEL type. It should be noted that these methods are of the first order with respect to the approximation and the analysis of stability of their schemes can be considerably complicated.

It is a well-documented fact that the orders of reaction less than unity occur very frequently in reaction engineering. In other words, there is a good reason for an alternative approach to the solving of models in the vicinity of the singularities of the Jacobian elements for the corresponding ODE.

Approximation by the SIMEL Scheme

Let the ODE system be

$$y'(t) = f[y_1(t), \ldots, y_n(t)], \ i = 1, \ldots, n; \ t \in \langle 0, \infty)$$

with an initial condition $y(0) = y_{0i}$ or in the vector form

$$\mathbf{y}'(t) = \mathbf{f(y)} \quad \mathbf{y}(0) = \mathbf{y}_0 \tag{A1}$$

where $\mathbf{y} = (y_1, \ldots, y_n)^T$.

In case of the linear ODE system we have

$$\mathbf{y}'(t) = \mathbf{A} \cdot \mathbf{y} + \mathbf{b} \quad \mathbf{A} = (a_{i,j}); \ i, j = 1, \ldots, n$$

Let us denote the Jacobian of the right-hand side of ODE as $\mathbf{J(f)}$, *i.e.* the matrix $\mathbf{J(f)} = (\partial f_i / \partial y_j); \ i, j = 1, \ldots, n$ and $\lambda(\mathbf{A})$ are the eigenvalues of the matrix $\mathbf{A}$. Furthermore, $\mathbf{I}$ is the unit matrix, $\mathbf{N}$ is a matrix the elements of which are units and $\mathbf{o}(x)$ is the column vector constituted by the symbols $0(x)$. We will deal with the systems for which the real components of the numbers $\lambda[\mathbf{J(f)}]$ are negative, *i.e.* $\text{Re}(\lambda) < 0$. It is assumed that the elements of the Jacobian $\mathbf{J(f)}$ do not have singular points within the region of solution.

Difference scheme

If we introduce a vector function $\mathbf{g}[\mathbf{y}(t), h]$ by

$$g_i[\mathbf{y}(t), h] = f_i[y_1(t), \ldots, y_i(t+h), \ldots, y_n(t)]$$

then, the scheme SIMEL is given as

$$\mathbf{y}(t+h) = \mathbf{y}(t) + h \cdot \mathbf{g}[\mathbf{y}(t), h] \qquad (A2)$$

where h is the chosen integration step.

For the linear ODE system, the scheme can be written in the vector form as

$$\mathbf{y}(t+h) = \mathbf{y}(t) + h \cdot \mathbf{A}_0 \cdot \mathbf{y}(t) + h \cdot \mathbf{A}_1 \cdot \mathbf{y}(t+h) + \\ + \mathbf{b} \qquad (A3)$$

where $\mathbf{A}_1$ is the diagonal matrix with the elements $a_{i,i}$ and the matrix $\mathbf{A}$ is defined by

$$\mathbf{A}_0 = \mathbf{A} - \mathbf{A}_1$$

By the first-order expansion of the vector function $\mathbf{y}(t)$ at the point $t+h$ we get after arrangement

$$\mathbf{y}(t+h) = \mathbf{y}(t) + h \cdot \mathbf{y}'(t+h) + \mathbf{o}(h^2)$$

Since the function $\mathbf{y}$ is the solution of the system (A1), we can write

$$\mathbf{y}(t+h) = \mathbf{y}(t) + h \cdot \mathbf{f}[\mathbf{y}(t+h)] + \mathbf{o}(h^2) \qquad (A4)$$

If we denote $\Delta \mathbf{y}(t) = \mathbf{y}(t+h) - \mathbf{y}(t)$, then it follows from eqn (A4): $\Delta \mathbf{y}(t) = \mathbf{o}(h)$. Then, with the use of the theorem on the increment of a function of more independent variables we have

$$\mathbf{f}[\mathbf{y}(t+h)] = \mathbf{g}[\mathbf{y}(t), h] + (\mathbf{N} - \mathbf{I}) \cdot \mathbf{J}[\mathbf{f}(t)] \cdot \Delta \mathbf{y}(t) + \\ + \mathbf{o}(h^2)$$

On substituting in eqn (A4) and with respect to the property of the increment $\Delta \mathbf{y}(t)$ we finally get

$$\mathbf{y}(t+h) = \mathbf{y}(t) + h \cdot \mathbf{g}[\mathbf{y}(t), h] + \mathbf{o}(h^2)$$

It follows from the comparison with eqn (A2) that SIMEL is a scheme of the first order.

Stability

Stability analysis will be performed for the testing linear system

$$\mathbf{y}' = \mathbf{A} \cdot \mathbf{y}$$

For further consideration the matrix $\mathbf{C}(h)$ is defined as

$$\mathbf{C}(h) = (\mathbf{I} - h \cdot \mathbf{A}_1)^{-1} \cdot (\mathbf{I} + h \cdot \mathbf{A}_0)$$

The matrix $\mathbf{C}$ is defined for all $h > 0$ provided that all the eigenvalues $\lambda(\mathbf{A}_1) < 0$. This requirement will be considered as a condition necessary for the application of the SIMEL scheme to a given problem. From eqn (A3) we get

$$\mathbf{y}(t+h) = \mathbf{C}(h) \cdot \mathbf{y}(t)$$

The condition for scheme stability is then $|\lambda[\mathbf{C}(h)]| \leq 1$.

From the standpoint of the scheme usefulness, it is desirable to estimate the conditions necessary for the scheme to be A-stable or even L-stable.

When $h \to \infty$, $\mathbf{C}(h) \to \mathbf{C}_\infty = -\mathbf{A}^{-1} \cdot \mathbf{A}_0$. On discussing the situation when $n = 2$, we can get the combinations of results such as follows:

a) Provided that the matrix $\mathbf{A}$ has only the real eigenvalues and all $\lambda(\mathbf{A}_0)$ are real, then the scheme is A-stable.

b) If either of the above conditions is not met, the scheme can still be A-stable. It is always at least locally stable.

In other words, the A-stability of SIMEL is guaranteed for the ODE systems for which "residue of the system" defined by the matrix $\mathbf{A}_0$ does not contain the oscillating components.

The authors realize that the general analysis of the scheme stability should include situations when $n > 2$. Our numerical experiments with SIMEL suggest that the above conditions of stability can also be applied in such cases.

SYMBOLS

a	left-hand point of interval
$\mathbf{A}$	matrix with elements $a_{i,j}$
b	right-hand point of interval
$\mathbf{b}$	column vector of elements b_j
BC	control of time step by "balance corridor"
BE	control of time step by "backward Euler"
BMR	difference scheme "backward mid-point rule"
C	mole fraction of SO_2 in gas phase
C_0	inlet gas mole fraction
C_{min}	minimum mole fraction during computations
C_w	exit gas mole fraction
CMR	difference scheme "classical implicit mid-point rule"
$C(1, t_{max})$	exit gas mole fraction at t_{max}
error	indication of possible overflow of values of Jacobian
$\mathbf{f}(\mathbf{y})$	vector of functions of vector $\mathbf{y}$, $\mathbf{f} = (f_1, f_2, \ldots, f_n)$; $f_i(y) = f_i(y_1, \ldots, y_n)^T$; $i = 1, \ldots, n$
F	cross-section of reactor/cm^2
H	distance above gas distributor/cm
H_1	height of expanded bed/cm

HV	Δt control by step halving
h	integration step
$\mathbf{I}$	unit matrix
IMEL	difference scheme "implicit Euler"
$\mathbf{J(f)}$	Jacobian of the ODE system, matrix $\mathbf{J(f)} = (\partial f_i/\partial y_j)$, $i, j = 1, \ldots, n$
MICH3	semi-implicit Runge—Kutta method
$\mathbf{N}$	matrix of units, $n_{i,j} = 1$ for $i, j = 1, \ldots, n$
N	number of interval halving
n	number of division of interval $w \in \langle 0, 1 \rangle$
n_s	amount of substance of sorbent/mol
NAE	nonlinear algebraic equation(s)
NC	noncontrolled time step
ODE	ordinary differential equation(s)
$O(h)$	function for which it holds $\lim_{h \to 0} O(h)/h = 0$
$\mathbf{o}(x)$	column vector of symbols $O(x)$
PDE	partial differential equation(s)
$R(C, X)$	reaction rate/s^{-1}
Re(λ)	real component of complex number λ
RE	relative error
reject	number of Δt shortening forced by transition of C to negative values
RRSTIFF	computational code developed at the Department of Chemical Engineering, Technical University Delft, the Netherlands
r	power to which C is raised in the reaction rate equation
s	power to which $(X_{max} - X)$ is raised in the reaction rate equation
SIMEL	semi-implicit Euler scheme, this paper
t	time/s
t-break	time of interruption of computation on external intervention or on "error"/s
Δt	time step/s
Δt_{max}	maximum time step/s
$\bar{t}_g$	mean residence time of gas in bed/s
$t_s = n_s/(FU\rho_G C_0)$	stoichiometric time/s
U	superficial gas velocity/(cm s^{-1})
$w = H/H_1$	relative distance above the distributor
$\Delta w = 1/n$	spatial step
X	conversion of sorbent
X_{max}	maximum conversion of sorbent
x_n	n-th approximation of root
x^*	true value of root
$\overline{X}$	balance integral given by eqn (3)
$\mathbf{y}_0$	column vector of initial conditions for ODE
$y(t)$	real function of real variable
$\mathbf{y}(t)$	column vector of solution of the ODE system

$\lambda(\mathbf{A})$	eigenvalue of matrix $\mathbf{A}$
ρ_G	density of gas phase/(mol cm^{-3})

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