A comparative study of flux-limiting methods for numerical simulation of gas-solid reactions with Arrhenius type reaction kinetics

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Abstract

Heterogeneous gas-solid reactions play an important role in a wide variety of engineering problems. Accurate numerical modeling is essential in order to correctly interpret experimental measurements, leading to developing a better understanding and design of industrial scale processes. The exothermic nature of gas-solid reactions results in large concentration and temperature gradients, leading to steep reaction fronts. Such sharp reaction fronts are difficult to capture using traditional numerical schemes unless by means of very fine grid numerical simulations. However, fine grid simulations of gas-solid reactions at large scale are computationally expensive. On the other hand, using coarse grid block simulations leads to excessive front dissipation/smearing and inaccurate results. In this study, we investigate the application of higher-order and flux-limiting methods for numerically modeling one-dimensional coupled heat and mass transfer accompanied with a gas-solid reaction. A comparative study of different numerical schemes is presented. Numerical simulations of gas-solid reactions show that at low grid resolution which is of practical importance Superbee, MC, and van Albada-2 flux limiters are superior as compared to other schemes. Results of this study will find application in numerical modeling of gas-solid reactions with Arrhenius type reaction kinetics involved in various industrial operations.

Keywords: gas-solid reactions; higher-order methods; flux limiter; numerical modeling

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1. Introduction

Heterogeneous gas-solid reactions play a significant role in many industrial applications. These processes include but are not limited to heavy oil recovery, the roasting and reduction of ores, the pyrolysis of biomass and coal, the combustion of solids, waste incineration, the absorption of acid gases by lime, reactive vapor phase deposition, producing ceramic materials, extractive metallurgy, coal gasification, and catalyst manufacture (Ramachandran & Doraiswamy, 1982; Rajaiah et al., 1988; Hastaoglu & Berruti, 1989; Patisson & Ablitzer, 2000; Marias et al., 2001). Analytical solutions of the governing partial differential equations of gas–solid reactions are usually impossible or extremely difficult to obtain. Numerical modelling of gas-solid reactions is therefore the approach one must pursue, and such has been widely used to interpret experimental measurements, in the design of chemical reactors, and in large-scale reactive flow simulations. The exothermic nature of such reactions leads to complex nonlinear transient interaction of convection, heat conduction, mass diffusion, and chemical reactions, resulting in steep concentration and temperature gradients. In such circumstances, a better understanding of the system behaviour can only be accomplished by conducting very fine grid numerical simulations to capture the frontal behaviour of the process. However, fine grid numerical simulations of industrial scale gas-solid reactions are computationally expensive. On the other hand, coarse grid block numerical simulations of these processes using low-resolution numerical schemes would yield excessive front dissipation/smearing that would impair interpretation of the experimental data and negatively affect the design of industrial processes. It is for this reason that high-resolution numerical schemes are designed to improve the accuracy of the numerical solutions in convection dominated flows.

The noted phenomenon of a numerical solution of convection dominated partial differential equations being prone to numerical diffusion has given rise to numerous studies reported in the literature which propose numerical schemes for mitigating this issue (Sweby, 1984). A comparative study of numerical methods with respect to convection dominated problems presented by Wang and Hutter (2001) shows that the
modified TVD (total variation diminishing) Lax-Friedrichs method is the most capable/comprehensive method for handling convection dominated problems with a steep spatial gradient of the variables. Alhumaizi et al. (2003) performed a numerical analysis of a homogeneous tubular reactor in which a cubic autocatalytic reaction is coupled to mass diffusion and convective transport. Their calculations show that special high resolution schemes such as ENO (essentially non-oscillatory) are necessary to track efficiently steep moving fronts exhibited by strongly convective problems. Alhumaizi (2004, 2007) studied the accuracy of several finite difference schemes to solve a one-dimensional convection-diffusion-reaction problem of an autocatalytic mutating reaction model and found that the Superbee and MUSCL (Monotone Upstream-centered Schemes for Conservation Laws) flux limiters are the most appropriate for simulating sharp fronts for convection-diffusion-reaction and convection-diffusion systems, respectively. Ataie-Ashtiani and Hosseini (2005) and Ataie-Ashtiani et al. (1996) developed a correction for the truncation error associated with a finite difference solution of convection and diffusion with a first order reaction. They compared numerical results with analytical solutions and suggested that truncation errors are not negligible. It was also shown that the Crank–Nicholson method is the most accurate scheme based on truncation error analysis.

The attention that has been given in the literature to devising suitable numerical schemes for improving the accuracy of convection-dominated problems has not been the case for problems involving convection-diffusion with Arrhenius type kinetics reaction; such investigations are rare. There are in fact only limited studies suggesting suitable high resolution numerical schemes for specific applications of convection-diffusion-reaction systems. Furthermore, there is no numerical scheme yet identified that performs in a superior manner for all problems; therefore, a choice is usually made based on experience. As far as is known to the authors, comparative studies of higher-order and flux-limiting methods for coupled heat and mass transfer in gas-solid systems with Arrhenius type reactions have never been reported in the literature. The objective of this study is therefore to perform a comparative study of flux-limiting methods for numerical simulation of gas-solid reactions with Arrhenius type reaction kinetics, where the exothermic nature of the reactions coupled with heat and mass transfer leads to steep
temperature and concentration gradients. Previous comparative studies of flux limiters
did not consider Arrhenius type reactions. Results of this study will find application in
numerical modeling of gas-solid reactions with Arrhenius type reaction kinetics involved
in various industrial operations.

This paper is organized as follows. First, numerical errors in convection-diffusion-
reaction systems are described. Next, the governing partial differential equations for gas-
solid reactions are presented. The finite difference discretization of the governing
equations and different numerical schemes for approximating convective flux are then
presented. Comparisons of different methods are described in the Results section,
followed by Summary and Conclusions.

2. Numerical errors in convection-diffusion-reaction systems

2.1 First order convection-diffusion-reaction system

The governing differential equation for a linear convection-diffusion-reaction
system is given by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - kC$$

where \(C\) is concentration of reactant, \(D\) is molecular diffusion coefficient, \(t\) is time, \(x\) is
the linear spatial coordinate, \(u\) is velocity, and \(k\) is the reaction rate constant. The forward
time and single-point upstream finite difference method of discretization lead to the
following approximation for the governing partial differential equation:

$$\frac{C_i^{n+1} - C_i^n}{\Delta t} = D \frac{C_i^{n}_{i+1} - 2C_i^n + C_i^{n}_{i-1}}{(\Delta x)^2} - u \frac{C_i^n - C_{i-1}^n}{\Delta x} - kC_i^n$$

where \(\Delta\) stands for increments in time or space, and \(i\) and \(n\) denote grid index and time
step index, respectively. Neglecting third and higher order terms, the reactant
concentration at different times and locations can be approximated by the following
expressions (Lantz, 1971; Chaudhari, 1971; Moldrup et al., 1992; Ataie-Ashtiani et al.,
1996):

$$C_i^{n+1} = C_i^n + \Delta t \frac{\partial C}{\partial t} + \frac{\Delta t^2}{2} \frac{\partial^2 C}{\partial t^2} + ....$$

(3)
The second time derivative of the reactant concentration in Eq. (3) can be obtained by taking the time derivative of the governing equation as given by the following expressions:

\[
\frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} \left( \frac{\partial C}{\partial t} \right) - u \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial t} \right) - k \frac{\partial C}{\partial t}
\]

(6)

Substituting for \( \partial C / \partial t \) from Eq.(1) results in:

\[
\frac{\partial^2 C}{\partial t^2} = D^2 \frac{\partial^2 C}{\partial x^4} - Du \frac{\partial^2 C}{\partial x^3} + u^2 \frac{\partial^2 C}{\partial x^2} + 2uk \frac{\partial C}{\partial x} - 2kD \frac{\partial^2 C}{\partial x^2} + k^2 C
\]

(7)

Neglecting the higher order derivatives \( \partial^3 C / \partial x^3 \) and \( \partial^4 C / \partial x^4 \) gives:

\[
\frac{\partial^2 C}{\partial t^2} = u^2 \frac{\partial^2 C}{\partial x^2} - 2kD \frac{\partial^2 C}{\partial x^2} + 2uk \frac{\partial C}{\partial x} + k^2 C
\]

(8)

Using Eqs. (3) to (5) and (8) and substituting in Eq.(2) we obtain:

\[
\frac{\partial C}{\partial t} = D(1 + u\Delta x / 2D - \Delta t u^2 / 2D + k\Delta t) \frac{\partial^2 C}{\partial x^2} - u(1 + k\Delta t) \frac{\partial C}{\partial x} - k(1 + k\Delta t / 2)C
\]

(9)

Comparing Eqs. (9) and (1) reveals that the numerical discretization modifies the diffusion coefficient, velocity, and reaction constant. The modified diffusion coefficient, velocity, and reaction constant are thus given by

\[ D_{\text{mod}} = D(1 + u\Delta x / 2D - \Delta t u^2 / 2D + k\Delta t), \quad u_{\text{mod}} = u(1 + k\Delta t), \quad \text{and} \quad k_{\text{mod}} = k(1 + k\Delta t / 2), \]

respectively. The components of the diffusion coefficient, velocity, and reaction constant attributable to numerical discretization are then \( D_{\text{num}} = D( u\Delta x / 2D - \Delta t u^2 / 2D + k\Delta t) \), \( u_{\text{num}} = uk\Delta t \), and \( k_{\text{num}} = k^2 \Delta t / 2 \), respectively, where the subscript “num” refers to the additional terms that are created because of the numerical discretization errors.

We scale distance \( x \) by \( L \), length of the reaction domain, and time by diffusion time scale, \( L^2 / D \). The modified form of Eq. (9) can therefore be represented by:

\[
\frac{\partial C}{\partial \tau} = (1 + Pe(1 - Co) / 2 + \phi^2 \Delta \tau) \frac{\partial^2 C}{\partial \chi^2} - Pe_s \left(1 + \phi^2 \Delta \tau\right) \frac{\partial C}{\partial \chi} - \phi^2 \left(1 + \phi^2 / 2 \Delta \tau\right) C
\]

(10)

where \( \tau \) is the dimensionless time, \( \chi \) is the dimensionless distance, \( Pe_s = uL / D \) is the system Peclet number, \( Co = u\Delta t / \Delta x \) and \( Pe = u\Delta x / D \) are grid block Courant and Peclet
numbers, respectively, and \( \phi^2 = kL^2 / D \) is the Thiele modulus (Fogler, 1998). The numerical diffusion, velocity, and reaction constant can then be respectively represented by:

\[
\frac{D_{num}}{D} = Pe(1 - Co)/2 + \phi^2 \Delta \tau
\]  

(11)

\[
\frac{u_{num}}{u} = \phi^2 \Delta \tau
\]  

(12)

\[
\frac{k_{num}}{k} = \frac{\phi^2}{2} \Delta \tau
\]  

(13)

The scaling analysis shows that, for a linear convection-diffusion-reaction system, numerical results are sensitive to both temporal and spatial discretization. Therefore, the accuracy of numerical solutions is affected by grid size.

3. Governing equations for gas-solid reactions

The mathematical model used in this study to perform numerical experimentations is based on a formulation presented by Rajaiah et al. (1988). Based on this model, the exothermic non-catalytic gas-solid reaction is assumed to take place in a one-dimensional flow system. The reaction that takes place is between a gaseous oxidizer (oxygen or nitrogen) and a solid phase that generates a gas or a solid. This model assumes that Fourier’s law of heat conduction in a solid is valid. Sintering effects are ignored and the system porosity remains constant during the process. The physical properties of the materials are assumed constant. Radiation effects are incorporated into an effective thermal conductivity and the reaction is considered to be first order with respect to gas and solid reactants. A pseudo-homogenous, one phase model is used. The governing differential equations for such a system are given by:

Energy balance:

\[
(\rho c_p) \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} - u \rho c_p \frac{\partial T}{\partial x} + k_c (\Delta H) C_s C_G \exp \left( -\frac{E}{RT} \right)
\]  

(14)

Gas mass balance:

\[
\varepsilon \frac{\partial C_G}{\partial t} = D_e \frac{\partial^3 C_G}{\partial x^3} - u \frac{\partial C_G}{\partial x} - k_o C_G C_s \exp \left( -\frac{E}{RT} \right)
\]  

(15)
Solid mass balance: \( (1 - \varepsilon) \frac{\partial C_S}{\partial t} = -k_0 C_e C_S \exp \left( -\frac{E}{RT} \right) \) (16)

where \( \rho c_p = \rho c_p + \rho_s c_p (1 - \varepsilon) \) is the effective heat capacity, \( T \) is temperature, \( C \) is concentration of reactant, \( \rho \) is density, \( c_p \) is heat capacity, \( \lambda \) is the average thermal conductivity, \( k_0 \) is the pre-exponential factor, \( E \) is activation energy, \( \Delta H \) is heat of reaction, \( R \) is the universal gas constant, \( D \) is molecular diffusion coefficient, \( u \) is velocity, \( \varepsilon \) is solid material porosity, \( t \) is time, and \( x \) is the spatial coordinate. The subscripts \( S \) and \( G \) denote solid and gas, respectively. The initial and boundary conditions as suggested by Rajaiah et al. (1988) are given by:

\[
T = T_0 \quad 0 \leq x \leq \infty, \quad t = 0 \quad (17.1)
\]

\[
C_G = C_{G_0} \quad 0 \leq x \leq \infty, \quad t = 0 \quad (17.2)
\]

\[
C_S = C_{S_0} \quad 0 \leq x \leq \infty, \quad t = 0 \quad (17.3)
\]

\[
-\lambda \frac{\partial T}{\partial x} = (\rho c_p) u(T_{inlet} - T) \quad \text{at} \quad x = 0 \quad (17.4)
\]

\[
\frac{\partial T}{\partial x} = 0 \quad \text{at} \quad x \to \infty \quad (17.5)
\]

\[
-\varepsilon D \frac{\partial C_G}{\partial x} = u(C_{G_{inlet}} - C_G) \quad \text{at} \quad x = 0 \quad (17.6)
\]

\[
\frac{\partial C_G}{\partial x} = 0 \quad \text{at} \quad x \to \infty \quad (17.7)
\]

The following dimensionless scaling groups are used to render the equations into dimensionless form:

\[
\theta = \frac{E(T - T^*)}{RT^*^2} \quad (18.1)
\]

\[
C_{DG} = \frac{C_G}{C_{G_{inlet}}} \quad (18.2)
\]

\[
C_{DS} = \frac{C_S}{C_{S_{inlet}}} \quad (18.3)
\]

\[
x_D = \sqrt[3]{\frac{\rho c_p}{\lambda}} \quad (18.4)
\]

\[
t_D = \frac{Ek_0(\Delta H)C_{G_{inlet}}}{\rho c_p RT^*^2} \exp \left( -\frac{E}{RT^*} \right) t \quad (18.5)
\]
Using the above scaling groups, the dimensionless form of the differential equations is given by:

\[
\frac{\partial \theta}{\partial t_D} = \frac{\partial^2 \theta}{\partial x_D^2} - Pe_H \frac{\partial \theta}{\partial x_D} + C_{GD} C_{SD} \exp\left(\frac{\theta}{\beta \theta + 1}\right) \tag{19}
\]

\[
\frac{\partial C_{GD}}{\partial t_D} = \frac{1}{Le} \left( \frac{\partial^2 C_{GD}}{\partial x_D^2} - Pe_M \frac{\partial C_{GD}}{\partial x_D} \right) - \gamma_G C_{GD} C_{SD} \exp\left(\frac{\theta}{\beta \theta + 1}\right) \tag{20}
\]

\[
\frac{\partial C_{SD}}{\partial t_D} = -\gamma_S C_{GD} C_{SD} \exp\left(\frac{\theta}{\beta \theta + 1}\right) \tag{21}
\]

The above in fact employs a standard scaling protocol available in the combustion literature to render the equations dimensionless (Merzhanov et al., 1973; Merzhanov & Borovinskaya, 1975; Puszynski et al. 1987; Merzhanov & Khaikin 1988; Rajaiah et al., 1988; Dandekar et al., 1990a; Dandekar et al., 1990b). The scaling variable \( x^* \)
corresponds to an approximate measure of the heating zone length and $x^* / t^*$ is a measure of the reaction front velocity (Dandekar et al., 1990b).

4. Discretization of the governing equations

The governing differential equations are discretized using an explicit-in-time finite difference approximation. A block-centered scheme is used, where the diffusive flux is calculated based on grid block center values, while the convective flux values are evaluated based on the grid block interface values. An explicit discrete finite difference formulation of the governing equations for temperature, gas concentration, and solid concentration is given by:

$$
\theta_{i}^{n+1} = \theta_{i}^{n} + \frac{\Delta t_{D}}{\Delta x_{D}^2} (\theta_{i+1}^{n} - 2\theta_{i}^{n} + \theta_{i-1}^{n}) - Pe_{D} \frac{\Delta t_{D}}{\Delta x_{D}} (\theta_{i+1/2}^{n} - \theta_{i-1/2}^{n}) + C_{GD}^{n} C_{SD}^{n} \Delta t_{D} \exp\left(\frac{\theta_{i}^{n}}{\beta \theta_{i}^{n} + 1}\right)
$$

(25)

$$
C_{GDi}^{n+1} = C_{GDi}^{n} \frac{\Delta t_{D}}{L_{e} \Delta x_{D}^2} \left(C_{GDi+1}^{n} - 2C_{GDi}^{n} + C_{GDi-1}^{n}\right) - Pe_{D} \frac{\Delta t_{D}}{L_{e} \Delta x_{D}} \left(C_{GDi+1/2}^{n} - C_{GDi-1/2}^{n}\right)
\gamma_{G} C_{GDi}^{n} C_{SD}^{n} \Delta t_{D} \exp\left(\frac{\theta_{i}^{n}}{\beta \theta_{i}^{n} + 1}\right)
$$

(22)

$$
C_{SDi}^{n+1} = C_{SDi}^{n} - \gamma_{S} C_{GDi}^{n} C_{SD}^{n} \Delta t_{D} \exp\left(\frac{\theta_{i}^{n}}{\beta \theta_{i}^{n} + 1}\right)
$$

(23)

where $\Delta t_{D}$ and $\Delta x_{D}$ are temporal and spatial increments, respectively. In the following section, different numerical schemes appropriate for approximating convective flux are presented.

4.1 Numerical approximation of convective flux

There are several options for discretizing advection terms in the flow and transport equations. The most commonly used method for approximating block interface properties is single-point upstream weighting. The single-point upstream weighting scheme approximates the value of a function at a grid block face with the value in the grid block on the upstream side. The drawback of such a scheme is that artificial diffusion is
introduced and might be considerable, thereby producing erroneous results unless a large number of grid blocks (i.e., a high degree of grid block refinement) is employed. An alternative method of reducing numerical diffusion is to employ a higher order method, such as two-point upstream weighting (Todd et al., 1972). Third-order methods (Leonard, 1979) as well as Total Variation Diminishing (TVD) schemes (Harten, 1983) have also been used to control numerical diffusion. In the following, a brief review of these numerical methods is presented.

4.1.1 Single-point upstream

This scheme is widely used in evaluating interface block properties, but as noted is prone to numerical diffusion. In this method, net convective flux into a cell can be approximated as:

\[
\frac{\partial}{\partial x} (uC) = \frac{1}{\Delta x} \left[ (1-\omega)C_i + \omega C_{i+1} \right] - u_{i+1/2} \left[ (1-\omega)C_{i+1} + \omega C_i \right]
\]

where \( \Delta x \) is the grid block size and \( \omega \) is the weighting factor and is equal to zero or one depending on the flow direction. It is noted that for the problem under investigation the fluid velocity \( u \) is constant and therefore the choice of interface values for velocity given by Eq.(24) is irrelevant.

4.1.2 Two-point upstream

This approximation was proposed by Todd et al. (1972). In this second-order method, the mesh interface values are obtained by using the values at two adjacent blocks that are dependent on the flow direction. Because the approximation is an extrapolation process, it is important to limit the computed values to physically acceptable values. However, in such cases, the method reverts to single-point upstream weighting which guarantees physically acceptable results. The block interface properties for an arbitrary grid block can be approximated as follows:

\[
f_{i+1/2} = f_{i-1} + \frac{\Delta x_{i-1}}{\Delta x_{i-1} + \Delta x_{i-2}} (f_{i-1} - f_{i-2})
\]

\[
f_{i+1/2} = f_i + \frac{\Delta x_i}{\Delta x_i + \Delta x_{i+1}} (f_i - f_{i-1})
\]
where $f = uC$ is the convective flux function. The block interface fluxes are calculated based on the single-point upstream value when the following conditions are not satisfied:

$$f_{i+1/2} \leq \text{the greater of } f_i \text{ or } f_{i+1} \quad \text{and} \quad f_{i-1/2} \leq \text{the greater of } f_i \text{ or } f_{i-1}$$

### 4.1.3 Third order methods

For third order methods, introduced by Leonard (1979), the grid block interface value is approximated by using three points adjacent to an arbitrary grid block. In this method the boundary grid blocks are approximated by the single-point upstream weighting. Saad et al. (1990) modified Leonard’s method to account for variable grid block size. For that third order method, the block interface properties are calculated based on the following approximations:

$$f_{i+1/2} = f_{i+1} + \Pi_{i+1/2} (f_{i+1} - f_{i+2}) + 2\Lambda_{i+1} (f_i - f_{i+1}), \quad (27)$$
$$f_{i-1/2} = f_i + \Pi_i (f_i - f_{i-1}) + 2\Lambda_i (f_{i+1} - f_i), \quad (28)$$

where

$$\Pi_i = \frac{1}{3} \frac{\Delta x_i}{\Delta x_i + \Delta x_{i-1}} \quad \text{and} \quad \Lambda_i = \frac{1}{3} \frac{\Delta x_i}{\Delta x_i + \Delta x_{i+1}} \quad (29)$$

The boundary points can be approximated by single-point upstream weighting because at least two upstream points and one down-stream point in each coordinate direction are needed for the higher order method. Similar to the previous case, the above formulation involves an extrapolation process, and it is necessary to constrain the computed values to physically admissible values. The other condition that must be fulfilled is the monotonicity constraint, which requires that the interface values of the calculated parameter be less than or equal to the larger concentration on either side of the grid block (Saad et al., 1990).

### 4.1.4 Total Variation Diminishing methods (TVD)

The TVD method was first introduced by Harten (1983) and later by Sweby (1984). The TVD property guarantees that the total variation of the solution of a function will not increase as the solution progresses in time. A numerical method is said to be TVD if:

$$TV(Q_{n+1}) \leq TV(Q^n) \quad (30)$$
where $TV$ is the total variation given by:

$$TV = \sum_j |Q^*_j - Q^*_{j+1}|$$  \hspace{1cm} (31)

The scheme limits the flux between grid blocks and then limits spurious growth in the grid block averages so that the above inequality is satisfied. A general approach is to multiply the jump in grid block averages by a limiting function. For our problem, the interface flux can be expressed by:

$$f_{i-1/2} = f_{i-1} + \frac{\Phi(r_1)}{2} [f_i - f_{i-1}]$$  \hspace{1cm} (32)

$$f_{i+1/2} = f_i + \frac{\Phi(r_2)}{2} [f_{i+1} - f_i]$$  \hspace{1cm} (33)

where

$$r_1 = \frac{f_{i-1} - f_{i-2}}{f_i - f_{i-1}}$$  \hspace{1cm} (34)

and

$$r_2 = \frac{f_i - f_{i+1}}{f_{i+1} - f_i}$$  \hspace{1cm} (35)

where $\Phi$ flux limiter function and $r$ is the ratio of successive gradients and is a measure of the smoothness of the solution. Making $\Phi = 0$ returns to the commonly used single-point upstream method as described previously. These types of flux limiters are called non-linear flux limiters. There are many TVD schemes found in the literature for solving convection dominated problems; Table 1 gives some of the flux limiters reported in the literature. Fig. 1 shows the acceptable flux limiter region for second-order TVD schemes as suggested by Sweby (1984).
Table 1

<table>
<thead>
<tr>
<th>Flux limiter</th>
<th>Flux limiter function $\Phi(r)$</th>
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<tbody>
<tr>
<td>van Leer (van Leer, 1974)</td>
<td>$(r+</td>
</tr>
<tr>
<td>MC (van Leer, 1977)</td>
<td>$\max[0, \min(2r, 0.5(r+1), 2)]$</td>
</tr>
<tr>
<td>van Albada -1 (van Albada et al., 1982)</td>
<td>$r(r+1)/\sqrt{r^2+1}$</td>
</tr>
<tr>
<td>Superbee (Roe, 1985, 1986)</td>
<td>$\max[0, \min(2r, 1), \min(r, 2)]$</td>
</tr>
<tr>
<td>Minmod (Roe, 1986)</td>
<td>$\max[0, \min(r, 1)]$</td>
</tr>
<tr>
<td>SMART (Gaskell &amp; Lau, 1988)</td>
<td>$\max[0, \min(2r, 0.75r + 0.25, 4)]$</td>
</tr>
<tr>
<td>H-QUICK (Leonard, 1987)</td>
<td>$2(r+</td>
</tr>
<tr>
<td>Koren (1993)</td>
<td>$\max[0, \min(2r, (2r+1)/3, 2)]$</td>
</tr>
<tr>
<td>OSPRE (Waterson &amp; Deconinck, 1995)</td>
<td>$1.5(r+1)/(r^2+r+1)$</td>
</tr>
<tr>
<td>CHARM (Zhou, 1995)</td>
<td>$r(1+3r)/(r+1)^2$</td>
</tr>
<tr>
<td>HCUS (Waterson &amp; Deconinck, 1995)</td>
<td>$1.5(r+</td>
</tr>
<tr>
<td>van Albada -2 (Kermani et al., 2003)</td>
<td>$2r/(r^2+1)$</td>
</tr>
</tbody>
</table>

![Fig. 1. (a) TVD region and (b) second order TVD region (Sweby 1984); $\Phi = 1$ and $\Phi = r$ correspond to central (Lax-Wendroff) and Beam-Warming scheme, respectively.](image-url)
5. Results

The governing partial differential equations of gas-solid reactions are solved using different numerical schemes. Two test problems of solid combustion that give different frontal characteristics are presented and results of different numerical schemes are compared. To estimate the accuracy of the various numerical solutions, we define numerical error using the following expression as a measure of numerical solution accuracy:

\[
\Xi = \left\{ \left[ \frac{\int (\psi - \psi_{\text{ref}})^2 \, dx_D}{\int \psi^2 \, dx_D} \right] \right\}^{1/2}
\]

where \(\psi\) can be either temperature or concentration and the subscript \(\text{ref}\) denotes reference solution. The convergence of the numerical solutions was verified by conducting tests for \(5 \times 10^3\), \(10 \times 10^3\), and \(15 \times 10^3\) grid blocks using the single-point upstream method. The data used in the numerical simulations are given in Table 2. Fig. 2 shows the reference numerical solutions for the two test cases. These reference solutions are used in the analysis that follows. Results demonstrate that large numbers of grid blocks (in excess of a thousand) are needed to find an accurate numerical solution using the single-point upstream method. In the following, we compare various flux-limiting schemes for the purpose of seeking an appropriate flux limiter. Such an appropriate flux limiter will facilitate an accurate numerical solution with fewer grid blocks as compared to the traditional single-point upstream method.

Numerical experiments were performed using all flux limiters given in Table 1 and using 50, 100, 500, and 1000 grid blocks. Fig. 3 shows temperature and concentration profiles obtained from different flux-limiting schemes and with 50 grid blocks. The corresponding numerical errors for \(N=50\) are summarized in Table 3. Results reveal that, for \(N=50\) and for both test cases, MC (van Leer, 1977), Superbee (Roe, 1985,1986), and van Albada-2 (Kermani et al., 2003) flux limiters are superior as compared to the other schemes. Results show that the single-point upstream method fails to model the reaction front accurately, while the flux limiting methods tend to correctly capture the sharp reaction front. Fig. 4 compares numerical solutions obtained by using different flux limiters and choosing total number of grid blocks equal to 100. While most of the flux
limiters could accurately capture almost all of the reaction front characteristics, the calculated numerical errors in Table 4 reveal that MC (van Leer, 1977), Superbee (Roe, 1985, 1986), and van Albada-2 (Kermani et al., 2003) are more accurate than the other flux limiters. Similar to the previous case (N=50), the single-point upstream method fails to resolve the reaction front. Figs. 5 and 6 show the calculated profiles with 500 and 1000 total numbers of grid blocks, respectively. Results shown in Figs. 5 and 6 and Tables 5 and 6 reveal that the flux limiters accurately capture the reaction front. Again, the single-point upstream results are still not accurate at N=1000. Results therefore suggest that using a flux-limiting approach allows conducting numerical simulations with significantly fewer numbers of grid blocks yet with the same accuracy of very fine grid simulation by the single-point upstream scheme.

Table 2
Data used in numerical simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\gamma_S$</th>
<th>$\gamma_G$</th>
<th>$\beta$</th>
<th>$\theta_0$</th>
<th>$\theta_{inlet}$</th>
<th>$Pe_H$</th>
<th>$Pe_M$</th>
<th>$Le$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test case 1</td>
<td>0.2138</td>
<td>0.100</td>
<td>0.0793</td>
<td>-4.677</td>
<td>0</td>
<td>50</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Test case 2</td>
<td>2</td>
<td>0.76</td>
<td>0.15</td>
<td>-0.5</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>1</td>
</tr>
</tbody>
</table>
Fig. 2. Dimensionless temperature (a), gas concentration (b), and solid concentration (c) for a gas-solid reaction of test case 1 at $t_D = 2.5$, and dimensionless temperature (d), gas concentration (e), and solid concentration (f) for a gas-solid reaction of test case 2 at $t_D = 0.6$ obtained by conducting tests with $5 \times 10^3$, $10 \times 10^3$ and $15 \times 10^3$ grid blocks using single-point upstream method.
Fig. 3. Dimensionless temperature (a), gas concentration (b), and solid concentration (c) for a gas-solid reaction of test case 1 at $t_D = 2.5$, and dimensionless temperature (d), gas concentration (e), and solid concentration (f) for a gas-solid reaction of test case 2 at $t_D = 0.6$ obtained by conducting tests with various flux limiters given in Table 1 and 50 grid blocks.

Table 3
Comparison of numerical error for total number of grid blocks N=50

<table>
<thead>
<tr>
<th>Flux limiter</th>
<th>Error (fraction)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test case 1</td>
<td>Test case 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\theta$</td>
<td>$C_{GD}$</td>
<td>$C_{SD}$</td>
</tr>
<tr>
<td>Single-point upstream</td>
<td>0.673</td>
<td>0.337</td>
<td>0.238</td>
</tr>
<tr>
<td>van Leer (van Leer, 1974)</td>
<td>0.259</td>
<td>0.185</td>
<td>0.149</td>
</tr>
<tr>
<td>MC (van Leer, 1977)</td>
<td>0.213</td>
<td>0.155</td>
<td>0.144</td>
</tr>
<tr>
<td>van Albada -1 (van Albada et al., 1982)</td>
<td>0.299</td>
<td>0.205</td>
<td>0.145</td>
</tr>
<tr>
<td>Superbee (Roe, 1985, 1986)</td>
<td>0.213</td>
<td>0.100</td>
<td>0.155</td>
</tr>
<tr>
<td>Minmod (Roe, 1986)</td>
<td>0.376</td>
<td>0.238</td>
<td>0.123</td>
</tr>
<tr>
<td>SMART (Gaskell &amp; Lau, 1988)</td>
<td>0.278</td>
<td>0.195</td>
<td>0.139</td>
</tr>
<tr>
<td>H-QUICK (Leonard, 1987)</td>
<td>0.305</td>
<td>0.210</td>
<td>0.140</td>
</tr>
<tr>
<td>Koren (1993)</td>
<td>0.256</td>
<td>0.183</td>
<td>0.142</td>
</tr>
<tr>
<td>OSPRE (Waterson &amp; Deconinck, 1995)</td>
<td>0.273</td>
<td>0.192</td>
<td>0.149</td>
</tr>
<tr>
<td>CHARM (Zhou, 1995)</td>
<td>0.296</td>
<td>0.204</td>
<td>0.143</td>
</tr>
<tr>
<td>HCUS (Waterson &amp; Deconinck, 1995)</td>
<td>0.291</td>
<td>0.202</td>
<td>0.144</td>
</tr>
<tr>
<td>van Albada -2 (Kermani et al., 2003)</td>
<td>0.315</td>
<td>0.188</td>
<td>0.130</td>
</tr>
</tbody>
</table>
Fig. 4. Dimensionless temperature (a), gas concentration (b), and solid concentration (c) for a gas-solid reaction of test case 1 at $t_D = 2.5$, and dimensionless temperature (d), gas concentration (e), and solid concentration (f) for a gas-solid reaction of test case 2 at $t_D = 0.6$ obtained by conducting tests with various flux limiters given in Table 1 and 100 grid blocks.

Table 4
Comparison of numerical error for total number of grid blocks N=100.

<table>
<thead>
<tr>
<th>Flux limiter</th>
<th>Test case 1</th>
<th>Test case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta$</td>
<td>$C_{GD}$</td>
</tr>
<tr>
<td>Single-point upstream</td>
<td>0.585</td>
<td>0.292</td>
</tr>
<tr>
<td>van Leer (van Leer, 1974)</td>
<td>0.115</td>
<td>0.093</td>
</tr>
<tr>
<td>MC (van Leer, 1977)</td>
<td>0.114</td>
<td>0.078</td>
</tr>
<tr>
<td>van Albada -1 (van Albada et al., 1982)</td>
<td>0.127</td>
<td>0.105</td>
</tr>
<tr>
<td>Superbee (Roe, 1985, 1986)</td>
<td>0.187</td>
<td>0.072</td>
</tr>
<tr>
<td>Minmod (Roc, 1986)</td>
<td>0.190</td>
<td>0.133</td>
</tr>
<tr>
<td>SMART (Gaskell &amp; Lau, 1988)</td>
<td>0.134</td>
<td>0.102</td>
</tr>
<tr>
<td>H-QUICK (Leonard, 1987)</td>
<td>0.137</td>
<td>0.109</td>
</tr>
<tr>
<td>Koren (1993)</td>
<td>0.122</td>
<td>0.093</td>
</tr>
<tr>
<td>OSPRE (Watson &amp; Deconinck, 1995)</td>
<td>0.118</td>
<td>0.097</td>
</tr>
<tr>
<td>CHARM (Zhou, 1995)</td>
<td>0.138</td>
<td>0.114</td>
</tr>
<tr>
<td>HCUS (Watson &amp; Deconinck, 1995)</td>
<td>0.130</td>
<td>0.104</td>
</tr>
<tr>
<td>van Albada -2 (Kermani et al., 2003)</td>
<td>0.162</td>
<td>0.097</td>
</tr>
</tbody>
</table>
Fig. 5. Dimensionless temperature (a), gas concentration (b), and solid concentration (c) for a gas-solid reaction of test case 1 at $t_D = 2.5$, and dimensionless temperature (d), gas concentration (e), and solid concentration (f) for a gas-solid reaction of test case 2 at $t_D = 0.6$ obtained by conducting tests with various flux limiters given in Table 1 and 500 grid blocks.

Table 5
Comparison of numerical error for total number of grid blocks N=500

<table>
<thead>
<tr>
<th>Flux limiter</th>
<th>Error (fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test case 1</td>
</tr>
<tr>
<td></td>
<td>$\theta$ $C_{GD}$ $C_{SD}$</td>
</tr>
<tr>
<td>Single-point upstream</td>
<td>0.275 0.136 0.049</td>
</tr>
<tr>
<td>van Leer (van Leer,1974)</td>
<td>0.048 0.035 0.011</td>
</tr>
<tr>
<td>MC (van Leer,1977)</td>
<td>0.064 0.033 0.012</td>
</tr>
<tr>
<td>van Albada -1 (van Albada et al., 1982)</td>
<td>0.039 0.037 0.011</td>
</tr>
<tr>
<td>Superbee (Roe, 1985,1986)</td>
<td>0.089 0.036 0.014</td>
</tr>
<tr>
<td>Minmod (Roe, 1986)</td>
<td>0.021 0.039 0.011</td>
</tr>
<tr>
<td>SMART (Gaskell &amp; Lau, 1988)</td>
<td>0.061 0.039 0.012</td>
</tr>
<tr>
<td>H-QUICK (Leonard, 1987)</td>
<td>0.053 0.040 0.012</td>
</tr>
<tr>
<td>Koren (1993)</td>
<td>0.062 0.037 0.012</td>
</tr>
<tr>
<td>OSPRE (Waterson &amp; Deconinck, 1995)</td>
<td>0.045 0.035 0.011</td>
</tr>
<tr>
<td>CHARM (Zhou, 1995)</td>
<td>0.049 0.044 0.012</td>
</tr>
<tr>
<td>HCUS (Waterson &amp; Deconinck, 1995)</td>
<td>0.051 0.038 0.012</td>
</tr>
<tr>
<td>van Albada -2 (Kermant et al., 2003)</td>
<td>0.034 0.034 0.006</td>
</tr>
</tbody>
</table>
Fig. 6. Dimensionless temperature (a), gas concentration (b), and solid concentration (c) for a gas-solid reaction of test case 1 at $t_D = 2.5$, and dimensionless temperature (d), gas concentration (e), and solid concentration (f) for a gas-solid reaction of test case 2 at $t_D = 0.6$ obtained by conducting tests with various flux limiters given in Table 1 and 1000 grid blocks.

Table 6
Comparison of numerical error for total number of grid blocks N=1000

<table>
<thead>
<tr>
<th>Flux limiter</th>
<th>Error (fraction)</th>
<th>Test case 1</th>
<th>Test case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta$</td>
<td>$C_{GD}$</td>
<td>$C_{SD}$</td>
</tr>
<tr>
<td>Single-point upstream</td>
<td>0.181</td>
<td>0.090</td>
<td>0.031</td>
</tr>
<tr>
<td>van Leer (van Leer,1974)</td>
<td>0.043</td>
<td>0.023</td>
<td>0.006</td>
</tr>
<tr>
<td>MC (van Leer,1977)</td>
<td>0.051</td>
<td>0.024</td>
<td>0.008</td>
</tr>
<tr>
<td>van Albada -1 (van Albada et al., 1982)</td>
<td>0.038</td>
<td>0.022</td>
<td>0.006</td>
</tr>
<tr>
<td>Superbee (Roe, 1985,1986)</td>
<td>0.074</td>
<td>0.035</td>
<td>0.011</td>
</tr>
<tr>
<td>Minmod (Roe, 1986)</td>
<td>0.017</td>
<td>0.020</td>
<td>0.004</td>
</tr>
<tr>
<td>SMART (Gaskell &amp; Lau, 1988)</td>
<td>0.047</td>
<td>0.026</td>
<td>0.006</td>
</tr>
<tr>
<td>H-QUICK (Leonard, 1987)</td>
<td>0.043</td>
<td>0.026</td>
<td>0.006</td>
</tr>
<tr>
<td>Koren (1993)</td>
<td>0.048</td>
<td>0.025</td>
<td>0.007</td>
</tr>
<tr>
<td>OSPRE (Waterson &amp; Deconinck, 1995)</td>
<td>0.041</td>
<td>0.023</td>
<td>0.006</td>
</tr>
<tr>
<td>CHARM (Zhou, 1995)</td>
<td>0.041</td>
<td>0.028</td>
<td>0.006</td>
</tr>
<tr>
<td>HCUS (Waterson &amp; Deconinck, 1995)</td>
<td>0.042</td>
<td>0.025</td>
<td>0.006</td>
</tr>
<tr>
<td>van Albada -2 (Kermani et al., 2003)</td>
<td>0.023</td>
<td>0.020</td>
<td>0.006</td>
</tr>
</tbody>
</table>
6. Summary and conclusions

Physical processes involved in gas-solid reactive systems include diffusive (heat and mass) as well as reactive processes that have different intrinsic scaling characteristics. In most cases, the non-linearity of the processes does not allow analytical solution. Therefore, accurate numerical modeling is necessary in order to properly interpret experimental measurements, leading to developing a better understanding and design of industrial scale processes. Accurate fine grid numerical simulation of sharp reaction front propagation in gas-solid reactions is a challenging task. Indeed, in most practical cases, such as in situ combustion in heavy oil reservoirs, the use of small grid blocks is not feasible. The conventional single-point upstream scheme is also known to smear the fronts. Therefore, one needs to account for the small scale gradients that cannot be captured by coarse grid blocks when using the single-point upstream method. One possible option for reducing the smearing effect resulting from this method is to use flux limiters. In this paper, we conducted a comparative study of various flux limiters to find appropriate flux limiters for one-dimensional gas-solid reactive flow simulations with Arrhenius type reaction. Relatively fine grid numerical simulations of the gas-solid reactions show that most of the methods with the exception of single-point upstream perform well. More specifically, for small number of grid points which is of practical importance Superbee, MC, and van Albada-2 flux limiters are superior as compared to other schemes. These results will aid in choosing proper flux limiters in numerical modeling of gas-solid reactions with Arrhenius type reaction kinetics.

Acknowledgments
The financial support of the Alberta Ingenuity Centre for In Situ Energy (AICISE) is acknowledged.

Nomenclature

\[
\begin{align*}
    c_p & : \text{heat capacity, J kg}^{-1} \text{K}^{-1} \\
    C & : \text{concentration, kg/m}^3 \\
    Co & : \text{Courant number} \\
    D & : \text{molecular diffusion coefficient, m}^2/\text{s} \\
    E & : \text{activation energy, J kmol}^{-1} \\
    f & : \text{convective flux function} \\
    \Delta H & : \text{heat of reaction, J/kg}
\end{align*}
\]
\begin{itemize}
  \item $k$: pre-exponential rate constant, unit depends on reaction type
  \item $L$: length of reacting system, m
  \item $Le$: Lewis number, dimensionless
  \item $N$: total number of grid blocks
  \item $Pe$: Peclet number
  \item $Q$: numerical solution in TVD methods
  \item $r$: ratio of successive gradients
  \item $R$: universal gas constant, 8314.472 J kmol$^{-1}$ K$^{-1}$
  \item $t$: time, s
  \item $T$: temperature, K
  \item $u$: velocity, ms$^{-1}$
  \item $TVD$: total variation diminishing
  \item $x$: spatial coordinate, m

  \textbf{Greek letters}
  \item $\beta$: inverse of dimensionless activation energy
  \item $\gamma$: inverse of dimensionless heat of reaction
  \item $\Delta$: difference or increment
  \item $\varepsilon$: porosity
  \item $\theta$: dimensionless temperature
  \item $\Lambda$: weighting factor in third order method
  \item $\lambda$: effective thermal conductivity, J m$^{-1}$s$^{-1}$K$^{-1}$
  \item $\Xi$: numerical error
  \item $\Pi$: weighting factor in third order method
  \item $\rho$: density, kg m$^{-3}$
  \item $\tau$: dimensionless time used in section 2.1
  \item $\Phi$: flux limiter function
  \item $\phi$: square root of Thiele modulus
  \item $\chi$: dimensionless distance used in section 2.1
  \item $\psi$: variable in numerical error function; can be temperature or concentration
  \item $\omega$: weighting factor in single-point upstream method

  \textbf{Subscripts}
  \item $D$: dimensionless
  \item $G$: gas
  \item $H$: heat
  \item $f$: front
  \item $i$: grid block index
  \item $inlet$: inlet condition
  \item $L$: left
  \item $M$: mass
  \item $mod$: modified
  \item $num$: numerical
  \item $ref$: reference
  \item $s$: system
  \item $S$: solid
  \item $0$: initial value
\end{itemize}
* scale value

**Superscripts**

\( n \) time index
average
References


