An Integral Equation Formulation for Solving Reaction-Diffusion-Convection Boundary-Value Problems

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Abstract

Many interesting problems that include convective transport arise in chemical reactor engineering (for example, tubular reactors). To solve these boundary-value problems, finite-difference schemes with a type of discretization of the convection term have been traditionally used. Some controversy about the discretization form of the convection term has arisen because of the different possibilities, including backward, forward and central discretizations. To overcome this problem, the usage of Green’s function formulations for the numerical solution of typical chemical engineering problems with both linear and nonlinear kinetics, diffusion and convection phenomena, is presented. A distinctive feature of the proposed scheme is that boundary conditions are exactly incorporated. The results show that the integral formulation is, in general, superior in accuracy to the different finite-differences schemes. That is, more accurate calculations of the performance factor are obtained in terms of less mesh points and computer time.

KEYWORDS: reaction-diffusion-convection, Green’s function, integral formulation, performance factor, tubular reactor

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1. INTRODUCTION

Inaccuracies in the numerical solution of distributed parameter models in systems such as chemical tubular reactors are induced by poor approximations for spatial derivatives of any order. Differentiation schemes based on standard finite-differences schemes are commonly used to obtain numerical solutions within, e.g., optimization and parameter estimation schemes (Smith, 2004). Signal processing is commonly used in applied process control and has shown that differentiators are highly sensitive to round-off errors. Differentiation schemes are very likely to magnify the propagation of approximation errors and, hence, to reduce the accuracy of numerical solutions. Generally, this drawback is compensated by the use of more sophisticated meshing procedures. Since differential operators are analytically inverted within a Green’s function formulation for distributed parameter processes, the integral equation formulation (IEF) approach becomes an appealing alternative to avoid the usage of approximate differentiators. In this approach, the differential equation is converted into an integral, Fredholm-type, equation where boundary conditions are incorporated without any assumption. In fact, Axelsson and Gololobov (2003) recently proposed to combine (unstable) central-difference and (stable) local Green’s function method for linear singularly perturbed convection-diffusion problems obtaining almost second order convergence. Moreover, Sacco (1993) provided a proof of a convergence theorem for Petrov-Galerkin finite element schemes for one dimensional diffusion-convection equation. Using as test function the corresponding Green’s function, Sacco was able to show that the numerical scheme was second-order accurate. The stabilizing effect of the IEF in convection-diffusion problems has also been showed by Li and Evans (1991); these authors presented a combination of the Boundary-Element method with Green’s function formulations. In their work they studied problems with both linear and nonlinear boundary conditions. It is worth mentioning that many of the above contributions did not involve the inclusion of homogeneous sources in the differential equations.

In order to have a clear idea of the integral equation formulation, some comments on the mathematical basis of this approach are presented to later direct the attention to some of the literature about the applications of the IEF. To this end, consider the following steady-state unidirectional differential equation:

\[
L[y(x)] = F(x, y(x)), \ \forall x \in (0,1)
\]

(1)

with corresponding boundary conditions. Here, \(L[\cdot]\) represents a linear differential operator of a given order and \(F\) is, in general, a non-linear source term. Associated to the linear operator \(L\), it is convenient to introduce the inner product of \(L[y(x)]\) and an arbitrary function \(G(z, x)\), as
\[ \langle G, L[y(x)] \rangle = \int_{0}^{1} G(z, x) L[y(x)] \, dx \]  

(2)

where \( x \) is a dummy integration variable. Taking the inner product in both sides of Eq. (1) leads to

\[ \langle G, L[y(x)] \rangle = \langle G, F(x, y(x)) \rangle \]  

(3)

The result of integrating by parts the left hand side of the above equation is

\[ \langle G, L[y(x)] \rangle = \left[ y(x) L[G(z, x)] \right]_{0}^{1} + \int_{0}^{1} y(x) L'[G(z, x)] \, dx = \left[ y(x) L[G(z, x)] \right]_{0}^{1} + \langle y(x), L'[G] \rangle \]  

(4)

where \( \left[ \cdot \right]_{0}^{1} \) are terms evaluated at the boundaries, and \( L^* \) is the formal adjoint differential operator associated with \( L \). Computation of the IEF requires the computation of the adjoint operator \( L^* \). Eq. (4) is commonly known as the Green’s formula (Haberman, 2004). Substitution of Eq. (4) into Eq. (3) gives

\[ \left[ y(x) L[G(z, x)] \right]_{0}^{1} + \langle y(x), L'[G] \rangle = \langle G, F(x, y(x)) \rangle \]  

(5)

In order to obtain a solution of Eq. (1), it is necessary to define the following differential problem for \( G(z, x) \) (Greenberg, 1971)

\[ L'[G(z, x)] = \delta(z - x), \ \forall x \in (0,1) \]  

(6)

where \( \delta(z - x) \) is the Dirac delta function. In addition, it is known that

\[ \langle y(x), \delta(z - x) \rangle = y(z) \]  

(Greenberg, 1971). Therefore, Eq. (5) may be expressed (after formally substituting \( z \to x \)) as

\[ y(x) = -\left[ y(z) L[G(z, x)] \right]_{0}^{1} + \int_{0}^{1} G(z, x) F(z, y(z)) \, dz \]  

(7)

Notice that, in the above equation, it was imposed that \( G(z, x) \) is symmetric, i.e., \( G(z, x) = G(x, z) \). This equation corresponds to a Fredholm-type IEF for the differential equation (1). If, for example, \( L = \frac{d}{dx} \left( p(x) \frac{dy}{dx} \right) \), Eq. (7) yields to

\[ y(x) = \int_{0}^{1} G(z, x) F(z, y(z)) \, dz \]

\[ -\left[ p(z) \left( \frac{dy}{dz} G(z, x) - \frac{dG(z, x)}{dz} y(z) \right) \right]_{z=0}^{z=1} \]

(8)

Notice that if the source term is only a function of the position, i.e., \( F(x, y(x)) = F(x) \), Eq. (7) is the explicit analytic solution of the problem. However, if \( F(x, y(x)) \) is a nonlinear function of the unknown \( y(x) \), Eq. (7) becomes a nonlinear integral equation. The Green’s function \( G(z, x) \) is computed from the
linear differential equation [Eq. (6)]. Moreover, if $L$ is self-adjoint (i.e., $L = L^*$), the corresponding boundary conditions for $G(z, x)$ depend directly from the original system boundary conditions.

Before solving a particular problem, it is pertinent to review some contributions where the IEF has been used. As exemplified by Mishra et al. (1991), the applications of integral equation formulations based on Green’s functions may go from chemical kinetics to quantum dynamics. However, many applications of Green’s functions schemes in chemical reactor engineering have been constrained mainly to reaction-diffusion processes. The underlying idea behind this approach is to invert the diffusion operator, via Green’s functions, to subsequently obtain a set of non-linear (algebraic) equations from a suitable spatial discretization. This approach was explored by Amundson and Schilson (1961) who computed the Green’s function for isothermal linear reaction in a sphere, and solved the resulting linear Fredholm-type integral equation via successive approximation techniques. Later on, Denn and Aris (1965 a,b,c) solved optimization systems relying on integral equation formulations, showing that this methodology leads to iterative schemes that reduce the computational work. Kesten (1969) applied this approach to determine concentration profiles for ammonia decomposition in a spherical catalytic pellet. Moreover, Dixit and Tavlarides (1982) were the first to use Newton iteration schemes to solve nonlinear Fredholm-type equations arising from reaction in a sphere and an infinite cylinder. Subsequently, Mukkavilli et al. (1987a, b) solved numerically an IEF for nonisothermal reaction in a finite cylinder, considering diffusion in both axial and radial directions, with and without taking into account external transport resistances. They solved the underlying Green’s function differential equation by means of eigenfunction expansions and developed a modified Green’s function method to accelerate the convergence of the series by two orders of magnitude. In addition, since the resulting integral equation was implicit, they used a Newton-Kantorovich iteration scheme to obtain the concentration and temperature profiles. Additionally, Mishra et al. (1994), based on Green’s functions analysis, studied the problem of steady-state diffusiv-conveктив mass transport for the combustion of a laminar premixed $CO/H_2/O_2$ flame. Recently, Onyejekwe et al. (1995, 1996, 2002) used IEF to propose a Green’s function solution for nonlinear reaction-diffusion equations. Extensive numerical simulations have showed the stability and accuracy of the proposed method compared to standard finite-difference schemes, as shown by Valdes-Parada et al. (2007, 2008) for diffusion and reaction processes.

On the application of integral equation formulations to convection and diffusion problems, it is important to mention the work of Arce et al. (1988) on the analysis of tubular reactors under laminar flow regime involving n-th ($n > 0$) order reactions. This approach was applied to the case of mass transfer from the
interior of a capillary tube with semipermeable walls to an external fluid by Grau et al. (1988). The resulting solution was advantageous because of its independence of the Sherwood number. Later on, Arce et al. (1996) introduced an integral-spectral approach for flow in a tubular reactor involving both bulk and wall chemical reaction, i.e., with homogeneous and heterogeneous sources.

Results in this issue are of prime importance due to the many chemical engineering systems that incorporate convective transport. Contrary to the diffusion operator that is inherently stable, the convective operator is marginally stable, meaning that the numerical solution is sensitive to the discretization scheme used in finite-difference approaches (Smith, 2004). This work focuses in this issue by applying a Green’s function approach to solve chemical reaction systems with diffusion and convection transport considering both linear and nonlinear kinetics. In this approach, both the diffusion and the convection operators are taken as a single operator which, after the incorporation of an integration factor, yield to a self-adjoint differential operator that can be inverted to obtain an integral equation with a structure given by Eq. (7). Contrary to classic finite-differences schemes, within this formulation, the problem of choosing a suitable discretization scheme for the convection term is no longer present since both phenomena (diffusion and convection) are accounted by the Green’s function that propagates the information along the domain. Ultimately, the numerical scheme can be seen as a type of central finite-difference scheme with asymmetry where mesh points in the direction of the convective transport have a larger weighting than mesh points in the opposite direction to the convective transport as suggested by the recent work of Alvarez-Ramirez et al. (2007). Three numerical examples are used to highlight the main features of the proposed approach. To provide a frame of reference, the results are compared with those obtained using standard finite-difference schemes.

2. INTEGRAL EQUATION FORMULATION FOR THE REACTION-TRANSPORT PROBLEM

Consider the following dimensionless differential equation:

\[
\frac{d^2 y}{dx^2} - Pe \frac{dy}{dx} = R(y), \quad \forall x \in (0,1)
\]

with boundary conditions

\begin{align}
\text{At } x = 0, & \quad y = y_m \\
\text{At } x = 1, & \quad \frac{dy}{dx} = 0
\end{align}

where \( y \) may denote the reactant concentration or temperature, \( Pe \) is the so-called Péclet number and \( R(y) \) is the reaction term, which can be nonlinear. When \( Pe=0 \),
Eq. (9) is reduced to a reaction-diffusion whose solution via Green’s functions has been previously explored and compared with finite-difference schemes (Amundson and Schilson, 1961; Onyejekwe et al., 1995, 1996, 2002; Valdes-Parada et al., 2007, 2008, among many others). For simplicity, the boundary-value problem, given by Eqs. (9)-(11), represents an isothermal tubular reactor. The extension to more realistic situations is straightforward since, as show below, a Green’s function formulation focuses mainly in the inversion of linear differential operators (in our case, the diffusion-convection operator), and not in the reaction term. In this way, extension to systems including more variables, e.g., concentration and temperature, requires only the inversion of differential operators in each differential equation.

Since the diffusion-convection operator 
\[ L[y(x)] = \frac{d^2y}{dx^2} - Pe \frac{dy}{dx} \] is not self-adjoint, the methodology outlined in the Introduction may not be used. The following result from Greenberg (1971) shows how to modify \( L \) in order to obtain self-adjointness property.

“Consider the second-order operator \( L = a(x)\left(\frac{d^2}{dx^2}\right) + b(x)\left(\frac{d}{dx}\right) + c(x) \). Then, the modified operator \( \sigma L \) will be self-adjoint if one chooses the ‘integration factor’ \( \sigma = \exp \left[ \int \frac{b(x) - a'(x)}{a(x)} dx \right] \).”

In the problem under consideration, we have that \( a(x) = 1, \ b(x) = -Pe \) and \( c(x) = 0 \). Therefore, the integration factor is \( \sigma = \exp(-Pe x) \). In this form, the departing equation for the derivation of the Green’s function is

\[ \exp(-Pe x)\left(\frac{d^2y}{dx^2} - Pe \frac{dy}{dx}\right) = Q(x, y), \] which can be written as

\[ \frac{d}{dx} \left( \exp(-Pe x) \frac{dy}{dx} \right) = Q(x, y) \] (12)

where \( Q(x, y) = \exp(-Pe x)R(y) \). The IEF for Eq. (12) can be easily obtained from Eq. (8) by substituting \( p(z) = \exp(-Pe z) \),

\[ y(x) = \int_0^1 G(z, x)Q(z, y) \, dz \]

\[ - \left[ \exp(-Pe z) \left( \frac{dy}{dz} G(z, x) - \frac{dG(z, x)}{dz} \frac{dy}{dz} \right) \right]_{z=0}^{z=1} \] (13)

Since \( y(1) \) and \( \frac{dy(0)}{dz} \) are not available, it is convenient to impose the following boundary conditions for the Green’s function:
Using boundary conditions (10) and (11), allows reducing Eq. (13) to
\[ y(x) = \int_0^1 G(z, x) Q(z, y) \, dz - \frac{dG(z, x)}{dz} \bigg|_{z=0} y_{in} \tag{16} \]

Since the differential operator in Eq. (12) is self-adjoint, the differential equation that governs \( G(z, x) \), is given by
\[ \frac{d}{dz} \left( \exp(-Pe z) \frac{dG(z, x)}{dz} \right) = \delta(z-x) \tag{17} \]

The solution of the above equation, subject to boundary conditions (14) and (15), is given by:
\[ G(z, x) = \begin{cases} Pe^{-1} \left(1 - \exp(Pe z)\right), & \text{for } z < x \\ Pe^{-1} \left(1 - \exp(Pe x)\right), & \text{for } z > x \end{cases} \tag{18} \]

It is noticed that, in the limit as \( Pe \to 0 \) (no convection), the above equation becomes
\[ G(z, x) = \begin{cases} -z, & \text{for } z < x \\ -x, & \text{for } z > x \end{cases} \tag{19} \]

which is the Green’s function for diffusion processes. The derivative of \( G(z, x) \) is
\[ \frac{dG(z, x)}{dz} = \begin{cases} -\exp(Pe z), & \text{for } z < x \\ 0, & \text{for } z > x \end{cases} \tag{20} \]
so that \( \frac{dG(z, x)}{dz} \bigg|_{z=0} = -1 \), and Eq. (16) reduces to
\[ y(x) = \int_0^1 G(z, x) Q(z, y) \, dz + y_{in} \tag{21} \]

Eq. (21) together with the Green’s function (18) become the IEF for the reaction-transport problem (9) with boundary conditions (10) and (11). As remarked previously, Eq. (21) is an implicit solution whenever \( Q(z, y) \) depends of \( y \), thus a numeric procedure is required to determine the concentration profiles. In the next section we will briefly describe such procedure that will enable solving the examples presented in Section 4.
3. NUMERICAL SOLUTION OF THE INTEGRAL FORMULATION

It is expected that the chemical reaction term $R(y)$ to be nonlinear, so that an analytical solution for Eq. (21) is, in general, not possible. Eq. (21) can be expressed as

$$y(x) = N(y(z), x) + y_m$$  \hspace{1cm} (22)

where $N(\cdot)$ is the nonlinear integral operator $\int_0^1 G(z, x)Q(z, y) \, dz$. In order to solve Eq. (22), a finite-dimensional approximation could be considered, say $y^a \in \mathbb{R}^n$, for the infinite-dimensional function $y(x)$. For instance, a practical approach for estimating $y^a$ is taking a $n$-dimensional vector corresponding to a regular mesh in the normalized domain $[0,1]$. That is, $y^a = [y_1, y_2, \ldots, y_n]^T$, where $y_i = y(x_i)$ and $x_i = i\Delta x$, $i = 1, 2, \ldots, n$, and the mesh distance is $\Delta x = 1/(n+1)$. If Eq. (22) is forced to be satisfied at every mesh point $x = x_i$, it yields $y^a_i = y_m + N\left(y^a, x_i\right)$, $i = 1, 2, \ldots, n$, or in vectorial notation

$$y^a = \varphi_m + M(y^a)$$  \hspace{1cm} (23)

where $M(y^a) = \left[N\left(y^a, x_1\right), N\left(y^a, x_2\right), \ldots, N\left(y^a, x_n\right)\right]^T$, $\varphi_m = [y_m, \ldots, y_m]^T$. Eq. (23) becomes a $n$-dimensional nonlinear equation of the unknown $y^a \in \mathbb{R}^n$. Two alternatives to solve numerically Eq. (16) are the following:

a) **Newton-Raphson Iterations.** Defining $\Phi(y^a) = y^a - \varphi_m - M(y^a)$, a Newton-Raphson iteration scheme can be used to obtain the solution. The classical one is simply $y_k^a = y_{k-1}^a - J\Phi\left(y_{k-1}^a\right)^{-1}\Phi\left(y_{k-1}^a\right)$, $k = 1, 2, \ldots$, although more stable and sophisticated variants can be considered (see, for instance, Ortega and Rheinboldt, 1970). The main requirement for implementation of this iteration scheme is the computation of the Jacobian matrix and its inverse $J\Phi\left(y_{k-1}^a\right)^{-1}$. More economic schemes use partial update procedures for the Jacobian inverse, which results in a weaker convergence rate that is commonly compensated for less complex and expensive computational algorithms (Willy and Govaerts, 2000). It should be commented that the convergence process of this scheme runs into difficulties for functions of roots of higher order multiplicity, as can be the case of the non-isothermal catalyst pellet. To overcome this situation, continuation or homotopy methods (Keller, 1977; Govaerts, 2000) can be
used, which are able to provide the whole bifurcation diagram of the underlying non-linear system, although slowed convergence rates can be induced.

b) **Nonlinear Fixed-point (Picard) Iterations.** This scheme takes into account the natural fixed-point structure of the IEF. In fact, a straightforward iteration for Eq. (23) is

\[ y_k^a = y_m - M(y_{k-1}^a), \quad k = 1, 2, \ldots \]

The implementation of this scheme requires only numerical quadrature procedures, although stability is not always guaranteed. In fact, convergence to a fixed-point requires that the norm \( \| JM(y_m^a) \| < 1 \).

Modified iteration schemes have been proposed to stabilize and improve convergence. Optimization techniques were studied, in order to work out equations of particular interest (Guy et al., 1986).

**4. APPLICATION EXAMPLES**

In this section, the usefulness of the IEF to produce accurate solutions for reaction-transport equations is explored. To this end, let us consider three examples; namely, one with linear kinetics having an analytical solution, and another with nonlinear kinetics; in both cases the results are compared with those obtained with different finite-differences scheme. The third example consists of a two-phase tubular reactor involving axial dispersion with nonlinear reaction taking place in porous particles. Numerical solution of the resulting set of equations was solved with standard matrix inversion for the linear case, and with Newton-Raphson method for the nonlinear cases.

**4.1 Example 1.** Consider an isothermal first-order kinetics taking place in a homogeneous tubular reactor. The differential equation that governs this case is given by Eq. (9) with \( R(y) = \Phi^3 y \), subject to boundary conditions (10) and (11). This physical situation results in a linear boundary-value problem whose analytical solution can be easily found and it is well-known (Aris, 1975) namely,

\[
\frac{y(x)}{y_m} = \frac{m_2 \exp(m_2x + m_2) - m_1 \exp(m_1x + m_1)}{m_2 \exp(m_2) - m_1 \exp(m_1)}
\]  

where

\[
m_{1,2} = \frac{Pe \pm \sqrt{Pe^2 + 4\Phi^2}}{2}
\]

As a comparison criterion, a performance factor \( \sigma \) is considered, which is defined as the overall reaction rate relative to the reaction rate evaluated at the entrance of the system,
\[
\int_{0}^{1} R(y(x)) \, dx \\
\sigma = \frac{R(y(x))}{R(y(x))_{|y=0}}
\] (26)

For this case, the exact expression for the performance factor is given by

\[
\sigma = \frac{m_2^2 \exp(m_2) [\exp(m_1) - 1] - m_1^2 \exp(m_1) [\exp(m_2) - 1]}{m_1 m_2 (m_2 \exp(m_2) - m_1 \exp(m_1))}
\] (27)

Numerical solutions were obtained for both the differential and the integral equation formulations. This last is given by Eq. (21) with \(Q(x, y) = \exp(-Pe \, x) \Phi^{2} \, y\). Actually, the above is not the best choice of solution, since the self-adjoint operator can be defined as

\[
L = \frac{d}{dx} \left( \exp(-Pe \, x) \frac{d}{dx} \right) - \Phi^{2},
\]

leading to a solution equivalent to Eq. (24). Nevertheless, for comparison purposes, it is convenient to use Eq. (21) in order to study the convergence of the iterative procedure. Simpson quadratures were used to evaluate integral in Eq. (21) under a regular mesh discretization of the domain. For finite-differences approximation, central finite-differences were used for the diffusion operator. On the other hand, three different schemes (backward, forward and central finite-differences) were used for the convection operator. In all cases, the resulting finite-dimensional linear system was solved via standard matrix inversion methods, i.e., using Thomas algorithm. For \(Pe = 1\) and three different values of the Thiele modulus \(\Phi\), Figure 1 shows the performance factor \(\sigma\) as a function of the mesh size \(N\). The following can be observed:

- The IEF gives better results for small Thiele modulus values. This result is expected since, in this case, the mass transport mechanisms dominate over the consumption by chemical reaction. Given that the Green’s function is the inverse of the transport operator, numerical solutions from integral equation formulations recover more closely the behavior of the solution.
- For large Thiele modulus values, all solutions give similar results for a given mesh size, although the best solution is given by the forward finite-difference scheme. Here, the reaction mechanism dominates over the transport phenomena, such that the inverse of the transport operator (i.e., the Green’s function) is unable to reflect fully the overall reaction-diffusion-convection phenomena.
- In general, the IEF provides acceptable solutions over a wide range of Thiele modulus values (\(\leq 10\)). In fact, although forward discretization of the convective operator outperforms the IEF scheme, mesh sizes of the order of \(N = 50\) suffice to obtain small approximation errors of the order of 1%, which is accurate enough for many applications.
Figure 1. Computed performance factor as a function of the mesh size for linear kinetics with $Pe = 1$ and a) $\Phi = 1$, b) $\Phi = 5$ and c) $\Phi = 10$.

Figure 2 shows the results of the performance factor for $\Phi = 3$ and three different values of the Péclet number. In this case, the Green’s function formulation provides better results than the three different finite-differences schemes. This shows that the potential numerical instabilities induced by the convection operator can be reduced by posing it into an IEF, leading to better numerical solutions with reduced mesh sizes (Axelsson and Gololobov, 2003).

4.2 Example 2. Let us reconsider Example 1 but now involving the following Langmuir-Hinshelwood kinetics

$$R(y) = \frac{\Phi^2 (1+\gamma)^n y}{(1+\gamma y)^n}, \gamma > 0$$ (28)
In this case, an analytical solution is not available, in general. However, if the numerical scheme is available, the estimated performance factor should converge to a constant value as the number of mesh points is increased. For $\gamma = 5$, $n = 2$ and $Pe = 1$, Figure 3 shows the behavior of the estimated performance factor as a function of the mesh size $N$ for three different values of the Thiele modulus $\Phi$. It is observed that all numerical schemes (the IEF and the three different finite difference schemes) converge to a constant value as the number of nodes is increased. However, as expected from the previous example, the numerical scheme based on the Green’s function formulation converges faster for relatively small values of $\Phi$ where the transport mechanism dominates over the kinetics one.

![Graphs showing performance factor convergence](image)

Figure 2. Computed performance factor as a function of the mesh size for linear kinetics with $\Phi = 3$ and a) $Pe = 0.1$, b) $Pe = 1.0$ and c) $Pe = 10$.

For relatively large values of $\Phi$, the performance of this scheme is similar to the central finite-difference scheme. Interestingly, the finite-differences scheme with central discretization of the convection operator presents the best
performance in the finite-differences group, contrary to the linear case in Example 1 where the forward scheme was the best. This means that the best discretization scheme for the convection term depends on the nonlinearity $R(y)$.

![Graphs showing performance factor vs. number of nodes for Backwards, Central, Forward, and Green schemes.](image)

Figure 3. Computed performance factor as a function of the mesh size, for Langmuir-Hinshelwood kinetics, with $Pe = 1$, $\gamma = 5$ and a) $\Phi = 2$, b) $\Phi = 4$ and c) $\Phi = 10$.

One concludes that the method based on the Green’s function offers the better convergence properties over the wide range of parameters. That is, although a specific finite-differences scheme can provide better convergence properties for certain range of parameters, the Green’s function approach offers good performance over a wider range of system parameters. This property is also shown in Figure 4 where the convergence of the estimated performance factor is displayed for $\Phi = 5$ and three different values of the Péclet number. In fact, fast convergence of the Green’s function scheme is obtained for large values of $Pe$ where convective transport is important. This feature is accounted for the Green’s
function, which retains the propagation of information due to transport mechanisms along the system.

The examples analyzed so far have dealt with the influence of the ratios of convective/diffusive transport and reaction/transport within a homogeneous tubular reactor. However, for practical applications it is relevant to analyze two (or more)-phase systems, thus in the next example the influence of external mass transfer resistances is studied.

4.3 Example 3. Consider the following dimensionless differential equations that govern the transport in the fluid and disperse phases within a tubular reactor, respectively.
\[
\frac{d}{dZ} \left( e^{-\psi} \frac{dU_f}{dZ} \right) + e^{-\psi} \psi \frac{d}{dZ} \left( U_p \bigg|_{\xi=1} - U_f \right) = 0, \quad \forall Z \in (0,1) \quad (29)
\]
\[
\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial U_p}{\partial \xi} \right) - R \left( U_p \right) = 0, \quad \forall \xi \in (0,1) \quad (30)
\]
which are subject to the following boundary conditions

At \( Z = 0 \),
\[ 1-U_f = -\frac{1}{Pe} \frac{dU_f}{dZ} \quad (31) \]

At \( Z = 1 \),
\[ \frac{dU_f}{dZ} = 0 \quad (32) \]

At \( \xi = 0 \),
\[ \frac{\partial U_p}{\partial \xi} = 0 \quad (33) \]

At \( \xi = 1 \),
\[ -\frac{\partial U_p}{\partial \xi} = Bi \left( U_p \bigg|_{\xi=1} - U_f \right) \quad (34) \]

The nonlinear reaction-rate in Eq. (30) is the Langmuir-Hinshelwood kinetics given in Eq. (28). For convenience, both Eqs. (29) and (30) are expressed in a self-adjoint form. Following the developments in Section 2, the solution of these differential equations are

\[ U_f (Z) = 1 - B(Z) \quad (35) \]
\[ U_p (\xi, Z) = 1 + A(\xi, Z) - B(Z) \quad (36) \]

where, for simplicity we introduced

\[ A(\xi, Z) = \int_{0}^{\xi} x^2 R \left( U_p (x_0), Z \right) G_p (\xi, x_0) \] \[ dx_0 \quad (37) \]
\[ B(Z) = \psi Pe \int_{0}^{Z} A(1, Z_0) G_f (Z, Z_0) e^{-\psi Z} dZ_0 \quad (38) \]

With the Green’s functions for the fluid and disperse phases given by

\[ G_f (Z, Z_0) = Pe^{-Z} \begin{cases} 1 & Z < Z_0 \\ 1 & Z > Z_0 \end{cases} \quad (39) \]
\[ G_p (\xi, x_0) = \begin{cases} 1 & \xi < x_0 \\ 1 & \xi > x_0 \end{cases} \quad (40) \]

The computer routine developed to carry out the evaluation of the solution consists of the following steps:

1. Propose an assumed field \( \left( U^{*}_{p,i} \right) \) for \( U_p \).
2. Using \( U^{*}_{p,i} \) and \( G_p (\xi, x_0) \) compute \( A(\xi, Z) \) by means of Eq. (37).
3. Substitute \( A(1,Z_0) \) and \( G_f(Z,Z_0) \) into Eq. (38) to obtain \( B(Z) \) and \( U_f \) by means of Eq. (35). Let us denote this result by \( U_{f,i}^* \).

4. With the results of steps 2 and 3, compute \( U_p \) using Eq. (36).

5. From Eq. (30) one can obtain that \( \frac{1}{Bi} \frac{\partial U_p}{\partial \xi} \bigg|_{\xi=1} = A(1,Z) \), therefore, from boundary condition (34), it results that the fluid concentration can be also computed as \( U_f = U_p \bigg|_{\xi=1} - A(1,Z) \).

6. If the difference between \( U_{f,i}^* \) and \( U_f \) does not satisfy a given tolerance (in general \( 1 \times 10^{-4} \) yields acceptable results), propose a corrected assumed field and return to step 2.

In the above routine, we have taken the fluid phase concentration profile as the convergence variable. Although other options can be used (for example, the interfacial concentration or the average of the dispersed phase concentration), it is convenient to use \( U_f \) since it is the variable that can be more easily measured experimentally.

Moreover, from Eq. (37) it is noticed that the axial dependence of \( A(1,Z) \) relies on \( R(\xi,Z) \), if this is a weak dependence one may propose approximate approaches by using

\[
U_f(Z) = 1 - A^*(1)\varphi_p Pe \int_{\psi(Z)}^1 G_f(Z,Z_0) e^{-\rho\psi_0} dZ_0
\]

where \( A^*(1) \) may be set as \( A^*(1) = A(1,1/2) \) or \( A^*(1) = \int_0^1 A(1,Z) dZ = A(1,Z) \bigg|_{inv} \), although other possibilities may be proposed. The main advantage of this approach relies on a higher convergence rate. Interestingly, the numeric scheme using \( A(1,Z) \bigg|_{inv} \) converges more rapidly than using \( A(1,1/2) \).

In Figure 5 we show the fluid phase concentration profiles using the complete (Eq. (35)) and approximate (Eq. (41)) approaches as function of the Thiele modulus and the Biot number. Notice that as \( \Phi \) increases the differences between the complete and approximate approaches become more evident. This is due to the increment of the intraparticle reaction rate with respect to the intraparticle diffusive transport, as consequence the axial dependence of \( R(\xi,Z) \) increases and the approximate approach fails. This effect is also exhibited, when the external mass transfer resistances are increased (low \( Bi \) values) as shown in Figure 5b.
Figure 5. Axial response of the fluid concentration, for $Pe = 1$, $\gamma = 5$ and $\psi_p = 0.1$ as a function of a) $\Phi$ for $Bi = 20$ and b) $Bi$ for $\Phi = 5$. (——) Complete approach, (---) Approximate approach using $A(1,1/2)$, (●●●) Approximate approach using $A(1,Z)_{av}$.

In order to determine which approximate approach yields results closer to those obtained with the complete approach, in Table 1 we present the relative error percent on the computation of $U_{f,av} = \int_0^1 U_f(Z) dZ$ for the results in Figure 5a. From Table 1, it can be concluded that the approximate approach based on $A(1,Z)_{av}$ gives results closer to the complete approach. Moreover, the computational time involved when using the $A(1,Z)_{av}$ approximation was noticeably shorter than when using $A(1,1/2)$. Analogous conclusions were obtained when analyzing the results in Figure 5b.

Table 1. Error percent on the computation of $U_{f,av}$ using the approximate approaches for various values of $\Phi$ and fixing $Bi = 20$, $Pe = 1$ and $\psi_p = 0.1$.

<table>
<thead>
<tr>
<th>$\Phi$</th>
<th>Error % using $A(1,1/2)$</th>
<th>Error % using $A(1,Z)_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.01008</td>
<td>0.01008</td>
</tr>
<tr>
<td>5</td>
<td>0.00822</td>
<td>0.00925</td>
</tr>
<tr>
<td>10</td>
<td>0.04617</td>
<td>0.00944</td>
</tr>
<tr>
<td>50</td>
<td>0.07362</td>
<td>0.00541</td>
</tr>
</tbody>
</table>

The above results show that, although some preliminary analytical work must be made to compute Green’s functions, the IEF leads to more accurate
numerical solutions with smaller mesh sizes. From a computational viewpoint, this offers an advantage to reduce computation times within massive solution requirements.

5. CONCLUSIONS

This work explored the usage of Green’s function formulation to provide accurate numerical solutions for reaction-transport models that include convection mechanisms. The numerical simulations showed that, compared to finite-difference schemes, the numerical method based on Green’s functions offers better convergence properties over a wider range of system parameters. In fact, accurate estimates of performance factors are obtained with reduced-size discretization meshes. Moreover, using this approach we were able to solve the equations that describe mass transport with nonlinear reaction in a two-phase tubular reactor with axial dispersion. Based on the structure of the resulting equations, an approximate approach was proposed; which gives acceptable predictions whenever the axial dependence of the intraparticle reaction rate is weak. In this way, the IEF approach represents important application potential when massive solutions are required, as in on-line optimization and control of reaction-transport processes.

With the developments presented so far, the analysis can be extended to more complicated problems, such as transitory or multicomponent systems. To be more specific, note that by taking the Laplace transform of the transient version of Eq. (29), its structure does not change considerably, and thus, the solution procedure here outlined can be applied. On the other hand, for multicomponent systems, the problem can be presented as a vectorial boundary value problem whose solution can be obtained using the developments of Section 2. A more extended description of these applications, for diffusion and reaction, has been reported elsewhere (Valdés-Parada et al., 2007).

NOTATION

\[
\begin{align*}
Bi & \quad \text{Biot number} \\
F & \quad \text{source term} \\
G & \quad \text{Green’s function} \\
L & \quad \text{linear differential operator of a given order} \\
Pe & \quad \text{Péclet number} \\
R & \quad \text{dimensionless reaction rate term} \\
U_f & \quad \text{dimensionless fluid-phase concentration} \\
U_p & \quad \text{dimensionless dispersed-phase concentration} \\
x & \quad \text{dimensionless position}
\end{align*}
\]
\( x_0 \) dummy integration variable
\( y \) dimensionless dependent variable
\( z \) dummy integration variable
\( Z \) dimensionless axial position

Greek Letters
\( \delta \) Dirac delta function
\( \Phi \) Thiele modulus
\( \sigma \) performance factor
\( \xi \) dimensionless radial position

REFERENCES


