Available online at www.sciencedirect.com
ScienceDirect
Computers and Chemical Engineering 32 (2008) 503–511
Computers & Chemical Engineering
www.elsevier.com/locate/compchemeng

On Green's function methods to solve nonlinear reaction–diffusion systems

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Received 15 September 2006; received in revised form 27 February 2007; accepted 18 March 2007
Available online 25 March 2007

Abstract

Recent studies have shown that the usage of classical discretization techniques (e.g., orthogonal collocation, finite-differences, etc.) for reaction–diffusion models cannot be stable in a wide range of parameter values as required, for instance, in model parameter estimation. Oriented to reduce the adverse effects of numerical differentiation, integral equation formulations based on Green's function methods have been considered, in the chemical engineering fields. In this paper, a further exploration of this approach for nonlinear reaction–diffusion transport is carried out. To this end, the Green's function problem is presented and solved for three geometries (i.e., rectangular, cylindrical and spherical), and three representative examples are worked out to illustrate the ability of the method to describe accurately the phenomena with respect to analytical and numerical solutions via finite-differences. Our results show that: (i) by avoiding numerical differentiation, the round-off error propagation is significantly reduced, (ii) boundary conditions are exactly incorporated without approximation order reduction and (iii) more accurate calculations are performed making use of less mesh points and computer time.

Keywords: Reaction–diffusion; Green's function; Iterative solution; Finite-differences; Effectiveness factor

1. Introduction

Modern computer-based process design, optimization and control methodologies can require massive on-line solution of detailed, commonly distributed-parameter models. For instance, optimization of chemical reactors with selectivity criteria requires the solution of the reaction-transport (diffusion and convection) model for catalytic pellet and/or reactor scales. At each step of the optimization cycle the underlying reaction-transport model must be solved numerically by means of stable and robust schemes. Finite-differences and finite-elements schemes are widely used given the existence of both theoretical results on stability and computational techniques for implementation. In this way, it is apparent that the development of stable procedures for massive solution of distributed-parameter models seems to be a solved issue. Recent studies have shown that the usage of classical discretization techniques (e.g., orthogonal collocation, finite-differences, etc.) for reaction–diffusion models cannot be stable in a wide range of parameter values as required, for instance, in model parameter estimation (Agrawal, Rangaiah, Ray, & Gupta, 2006; Asteasuain, Tonelli, Brandolin, & Bandoni, 2001). The main source of instability is the lower order approximations for boundary conditions compared to the higher-order used in the domain. Hence, the development of stable and robust numerical procedures for distributed parameter processes is still of prime importance within advanced process design and optimization methodologies.

Inaccuracies in the numerical solution of distributed parameter models are induced by inaccurate approximations for spatial derivatives of any order. From signal processing practice it is known that differentiators are, in fact, 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 usage of refined meshes. Since differential operators are analytically inverted within a Green's function formulation for distributed parameter processes, integral equation formulations for distributed parameter processes become a

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doi:10.1016/j.compchemeng.2007.03.013

serious 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 exactly. As is known in signal processing and process control theories, integrators are welcome because of their ability to wash-out and smooth round-off errors. In this way, integral equation formulations offer the advantage that approximations for differentiators have no longer to be considered, and potential numerical schemes could depend on numerical quadratures, that are unconditionally stable.

The application of Green's functions for solving reaction–diffusion processes in chemical engineering can be traced back to Amundson and Schilson (1961), who obtained the Green's function for isothermal linear reaction in a sphere, and solved the resulting linear Fredholm integral equation via a successive approximation technique. Kesten (1969) applied Green's function analysis to obtain concentration profiles for ammonia decomposition in a spherical catalytic pellet. Dixit and Tavlarides (1982) were the first to use Newton iteration schemes to solve nonlinear Fredholm equations arising from reaction in a sphere, and applied their results to the Fischer-Tropsch synthesis. Subsequently, Mukkavilli, Tavlarides, & Wittmann (1987a, 1987b) presented and solved numerically an integral equation formulation for reaction in a finite cylinder with Dirichlet and Robin-type boundary conditions. They solved the underlying Green's function differential equation by means of eigenfunction expansions. Recently, Onyejekwe (1995, 1996, 2002) used integral equation formulation to propose a Green element solution for nonlinear reaction–diffusion equations. In that work, the main idea was to invert the diffusion operator, via Green's functions, to subsequently obtain a set of nonlinear (algebraic) equations from a suitable spatial discretization. Extensive numerical simulations showed the stability and accuracy of the proposed method compared to standard finite-difference schemes.

Maybe due to the boom of finite-differences and finite-element methods, the application of Green's function theory for solving nonlinear reaction-transport process has been rarely explored. However, as mentioned earlier, integral equation formulations offer interesting implementation advantages, including exact incorporation of boundary conditions and enhanced stability in the face of round-off errors. In this paper, a further exploration of integral equation formulation for nonlinear reaction–diffusion transport is carried out. To this end, the Green's function problem is posed and solved for three geometries (i.e., rectangular, cylindrical and spherical), and three representative examples are worked out to illustrate the ability of the method to describe accurately the phenomenae with respect to analytical and numerical solutions via finite-differences.

2. Reaction–diffusion model

Following the classical formulation described by Aris (1975), which assumes a homogeneous porous pellet and using effective transport coefficients, the steady state concentration and temperature profiles for a single chemical reaction are given by

$$\nabla_m^2 y = \phi^2 R(y, \theta) \tag{1}$$

and

$$\nabla_m^2 \theta = -\beta\phi^2 R(y, \theta) \tag{2}$$

where the one-dimensional operator ∇_m^2 is given by

$$\nabla_m^2 = \frac{1}{x^m}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^m \frac{\mathrm{d}}{\mathrm{d}x}\right) \tag{3}$$

$x = x'/l_m$ is the dimensionless spatial coordinate, y and θ are dimensionless concentration and temperature, respectively. In addition, ϕ is the Thiele modulus, and β is the Prater number. The corresponding boundary conditions are

$$y(1) = 1 \quad \text{and} \quad \frac{\mathrm{d}y(0)}{\mathrm{d}x} = 0 \tag{4}$$

for concentration, and for temperature

$$\theta(1) = 1 \quad \text{and} \quad \frac{\mathrm{d}\theta(0)}{\mathrm{d}x} = 0 \tag{5}$$

Notice that the external surface is located at $x = 1$. Following Prater (1958), the dimensionality of this system can be reduced as follows. Let $a = \beta y + \theta$. From Eqs. (1) and (2), it is possible to obtain the differential equation $\nabla_m^2 a = 0$, whose solution under the corresponding boundary conditions is $a(x) = \beta + 1$, for all $x \in [0, 1]$. This implies that the dimensionless concentration and temperature are related by

$$\theta(x) = 1 + \beta(1 - y(x)) \tag{6}$$

This relationship can be used in Eq. (1) to obtain a differential equation depending only on concentration:

$$\nabla_m^2 y = Q(y) \tag{7}$$

where the term in the r.h.s. of the above equation is given by

$$Q(y) = \phi^2 R(y, 1 + \beta(1 - y)) \tag{8}$$

In this form, the reduced boundary-value problem is given by the differential Eq. (7) together with the boundary conditions (4). Once the concentration field $y(x)$ has been computed, the temperature field $\theta(x)$ is computed from Eq. (6). Which states that the solutions of the reaction-diffusion system lies on the solutions manifold $\Sigma = \{(y(x), \theta(x)) : \theta(x) = 1 + \beta(1 - y(x)),\ \text{for all}\ x \in [0, 1]\}$. The reduced model given by Eqs. (4) and (7) describes the reaction and diffusion phenomena in a catalytic pellet. If the reaction rate $R'(C, T)$ is linear, the corresponding model is also linear and an analytical solution can be found by means of well-established methods. However, if the reaction rate $R'(C, T)$ is nonlinear, the model (7) is nonlinear and its solution would, in most cases, require some kind of approximation.

3. Integral equation formulation

The reaction–diffusion model described in the above section is represented as a differential equation. In this section, following