Investigation of Heat Wave Propagation Model for an $A_0 \to A_1 \to A_2$ Catalytic Reaction

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Abstract

The problem of numerical study of a 1D heat wave propagation model is considered in the case of two consequent exothermic reactions in a catalytic fixed bed as an example. A modern efficient algorithm based on the orthogonal factorization method and Newton's method is presented, some recommendations on construction of initial approximation are developed, and influence of key physical and chemical parameters on the heat wave properties is studied.

Introduction

Investigation of the heat wave propagation phenomenon in heterogeneous media is a subject of big interest in the theory of unsteady-state catalytic processes in fixed bed reactors [1, 2]. The question how a heat wave type solution can be found, appears also while investigating some other chemical processes, such as gas-phase exothermic reactions in an inert porous medium, combustion of porous systems under condition of a heat transfer fluid filtration, combustion of condensed media, etc. An important characteristic of a heat wave is the velocity of its propagation.

The problem of finding a heat wave type solution often can be reduced to the boundary-value problem for a system of ordinary differential equations that involves the heat wave propagation velocity as an unknown parameter to be determined. Numerical and approximate analytic methods are basically used to study such a problem. In the paper a new approach to computational treatment of 1D models of heat wave propagation phenomenon is presented and applied to a catalytic process in fixed bed reactor.

Mathematical model

Quasihomogeneous model of the heat and mass transfer processes in a catalytic fixed bed while two consequent exothermic reactions following the scheme $A_0 \to A_1 \to A_2$ take place is considered like in [3, 4]. Inlet temperature is supposed to be absolute-zero. Let us notice that this suggestion allows us to avoid any additional restrictions on the reaction rate behaviour in a region of low temperature. We mean forced introduction of a "cutting temperature" below which the reaction rate is to be equal to zero [2]. The heat wave type solution is sought to be bounded and besides to satisfy the linear transport equation $\dfrac{\partial f}{\partial \tau} + \omega \dfrac{\partial f}{\partial \xi} = 0$, where ω is the velocity of wave propagation unknown a priori. If represented in the moving coordinate system associated with the wave front, the problem under consideration reduces to the boundary-value problem for the system of ordinary differential equations with independent variable $r = \xi - \omega\tau$ varying from $-\infty$ to $+\infty$:

$$u' = -a_1(u - z) - a_2(u - v), \tag{1}$$

$$z' = \frac{d_1}{1 - \sigma\omega} z \exp\left[\frac{-E_1}{RT_s(1-u)}\right], \tag{2}$$

$$v' = \frac{d_2}{1 - \sigma\omega} (v - \alpha z) \exp\left[\frac{-E_2}{RT_s(1-u)}\right], \tag{3}$$

with the boundary conditions:

$$r \to -\infty : \quad u, z, v \to 0, \qquad r \to +\infty : \quad u, z, v \to 1.$$

Here

$$a_1 = (1 - \sigma\omega)\frac{f_1 X_0}{T_s}, \qquad a_2 = (1 - \sigma\omega)\frac{f_2(1 - Y_0)}{T_s}, \qquad \alpha = \frac{X_0}{1 - Y_0},$$

u is normalized temperature, z and v are dimensionless concentrations of compounds A_0 and A_2. Physically T_s expresses the maximal temperature in the catalyst, it is unknown but connected with ω by a one-to-one function $T_s = T_s(\omega)$. Coefficients E_i, d_i, f_i $(i = 1, 2)$ and R, X_0, Y_0, σ in (1)-(3) are constant. The points $(0, 0, 0)$, $(1, 1, 1)$ are singular points for the system (1)-(3), they are the first order saddle and a degenerate point with two eigenvalues equal to zero, respectively.

In other words, we have to find a heteroclinic trajectory connecting two distinct fixed points of the system under consideration.

Numerical treatment of the problem

An efficient algorithm based on orthogonal factorization method and Newton's method [5] has been developed and used here for numerical treatment of the problem. It allows us to find out both the heat wave type solution and the unknown parameter.

The original problem posed in the whole space is approximated by the problem posed in a closed interval $[r_0,\ \bar{r}]$ provided by the boundary conditions as follows: at $r = r_0$ the trajectory belongs to the outgoing manifold associated with the singular point (0,0,0) (i.e., to the unstable manifold of this point) and at $r = \bar{r}$ it comes to a point $(u_0, 1, 1)$ in the incoming manifold associated with the point (1,1,1) (i.e., in the stable manifold of the point). The value of u_0 may stand for the "cutting temperature" and it is supposed to be close enough to 1.

If some approximation of the solution and of the parameter ω is known, we shall make linearization of the ODEs system (1)-(3) and use the iterative algorithm developed in [5]. In this paper the question how the variation of different parameters of the algorithm influences on the program robustness has been investigated with the model (1)-(3) of an exothermic catalytic process as a test example. It has been shown that even if one starts running the program from an initial approximation being rather far from the solution, eventually the convergence of iterations can be obtained. In this sense, the algorithm holds the stability property.

As far as the original problem is approximated by the other one posed in a bounded regoin, it is necessary to take rather lengthy interval for the sake of more precise approximations. Certainly, the length of the interval should be at least several times more then the wave front's width. We propose a procedure for sequential extension of the choosen bounded interval and construction of initial approximation. Therefore it is possible to solve the problem in long enough intervals.

The following values of parameters have been used in numerical examples: $E_1 = E_2 = 5800\ cal/mol$, $d_1 = 160.032$, $d_2 = 1600.32$, $f_1 = 57.23$, $f_2 = 171.69$, $X_0 = 1$, $Y_0 = 0$, $\sigma = 10^{-3}$, and $R = 1.987\ cal/(mol\ K)$ is the universal gas constant. Figure 1 shows the u, z and v profiles on the interval $[0, 10]$ and for the value of "cutting temperature" taken equal to 0.9. Maximal value of the temperature in this case appears to be $T_s = 652.00349K$.

Interval extension to the left

One of the main questions is the construction of initial approximation. In a rather short interval we can use a linear approximation of functions u, z and v, but for a long enough $[r_0,\ \bar{r}]$ that approach can not be effective.

For instance, let the solution be established at first in a not so long region with the use of linear initial data. If the solution in an interval $[-n\delta + r_0,\ \bar{r}]$ has already been established for some $n \geq 0$ and $\delta > 0$ then it can be extended to the left with a linear function that is equal to zero at the point $r = -(n+1)\delta + r_0$, and can be taken as a new approximation in the longer interval $[-(n+1)\delta + r_0,\ \bar{r}]$. This scheme takes into account the fact that $(u(\bar{r}), z(\bar{r}), v(\bar{r}))$ is a fixed point in phase space and hence the trajectory does not much vary near the right end of the interval $[-n\delta + r_0,\ \bar{r}]$ due to the Cauchy-Picards existence and uniqueness theorem and the continuous dependence of ODEs solution on the parameter T_s.

Computation results confirmed that the problem reduced to a bounded interval holds an one-parameter family of solutions which are generated by the parameter u_0. Elements of the family are the subsets of the entire trajectory in the phase space of the ODEs system (1)-(3). Indeed, Figure 2 shows the $u(r)$ profiles obtained for the different "cutting temperature" u_0 (here $r \in [0, 10]$ and $u_0 = u(10) = 0.81, 0.83, 0.85, 0.87, 0.89, 0.91, 0.93, 0.95, 0.97, 0.99$). If these profiles were shifted along the coordinate axis Or so that $u(5) = 0.5$ then all of them would coincide with the same smooth curve.

Interval extension to the right

It is obvious that the taken interval (see Fig.2) is not a very appropriate one because if $u_0 < 0.9$ then $u' \not\to 0$ at $r = \bar{r} = 10$ and if $u_0 > 0.96$ then the region of large gradients (i.e. front of the heat wave) strongly moves to the left and falls outside the interval. This negative effect almost disappears when the interval is much longer then the front's width. But in this case the use of a linear initial approximation demands the computing of very many iterations. To avoid this a special procedure is proposed for continuation of an obtained solution over the right end of interval.

Let the solution on $r \in [r_0, r_1]$ be obtained for some "cutting temperature" u_1. Let u_2 be another "cutting temperature", $u_2 > u_1$. In the neighborhood of the singular point (1,1,1) in the incoming manifold, the conditions $z', v' \approx 0$ and $z, v \approx 1$ hold. Hence, the equation (1) can be substituted by the approximate one: $u' = -(a_1 + a_2)u + (a_1 + a_2)$. So we obtain $u(r) \approx 1 - e^{-(a_1+a_2)r}$ for rather large r and

$$r_2 - r_1 \approx \frac{1}{(a_1 + a_2)} \ln \frac{1 - u_1}{1 - u_2}$$

if $u(r_1) = u_1,\ u(r_2) = u_2$. Then we can extend the interval to the right by lasting as long as $r_2 - r_1$. So, for the next iteration step we can combine the solution already obtained in interval $[r_0,\ r_1]$ and functions

$$u = u_1 + \frac{u_2 - u_1}{r_2 - r_1} r, \qquad z = v \equiv 1$$

for $r \in [r_1,\ r_2]$ as the initial approximation on the longer interval.

Due to sequential extension of the interval and construction of more precise initial data, this procedure reduces essentially the number of iterations being necessary.

As result of computational experiment the analysis of the influence of key physical and chemical parameters (i.e. activation energies of chemical reactions $E_1,\ E_2$ (see Fig.3, a and b), initial concentrations of reagents, linear velocity of reaction mixture blown through the catalyst bed) on the major characteristics of the heat wave, such as propagation velocity, maximal temperature T_s, and front's width d is presented.

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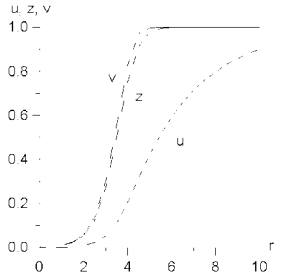

Figure 1.

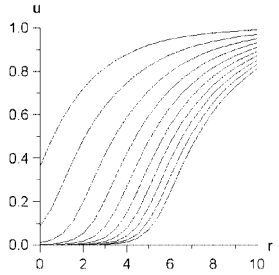

Figure 2.

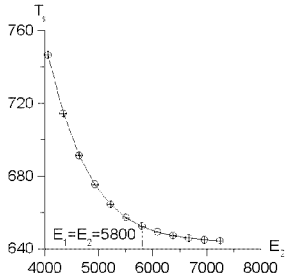

Figure 3a.

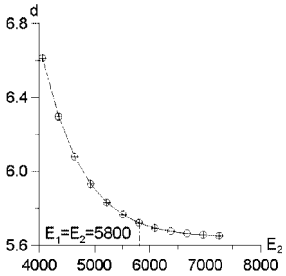

Figure 3b.