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Numerical length estimation for tubular flow reactors

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Abstract

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This work was motivated by the engineering problem of determining the optimal length for tubular flow reactors. We considered an isothermal nth-order chemical reaction occurring in a tubular flow reactor with axial mixing. The mathematical model describing the problem was a free boundary value one. The free boundary represented the reactor length. In this context we proved a theorem characterizing an upper bound for the free boundary. In order to solve the problem in point we introduced two different numerical methods. First a noniterative method was considered in order to obtain an upper bound of the free boundary. Then we used this upper bound in order to start an iterative method that allowed us to find an approximation of the free boundary. In closing we obtained numerical results either for an even or an odd order reaction.

Keywords: Tubular flow reactors; free boundary value problems; noniterative and iterative numerical methods.

1. Introduction

This paper is concerned with the engineering problem of estimating the optimal length for tubular flow chemical reactors. A preliminary version of this subject is considered in [4]. Moreover a recent paper [3] suggests a possible way to investigate numerically the existence and uniqueness question.

A chemical reactor is a vessel where materials through chemical transformations form products. Only two types of reactors are built: the tubular and the tank reactors [11]. If we

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consider a large amount of reactant, as for chemical plants, we have to use tubular reactors since the tank reactors are not suitable in this instance.

Our concern is about the following question: how long has to be taken the tubular reactor in order to get at the outlet side of it 90% of the product? Since the reactor length is unknown, we have to modify the boundary conditions usually imposed [17]. The mathematical model to be considered is that of a free boundary value problem of the type

$$\begin{aligned} &\frac{\mathrm{d}^2u}{\mathrm{d}x^2} = f\left(x, u, \frac{\mathrm{d}u}{\mathrm{d}x}\right), \quad x \in (0, s), \\ &g\left(u(0), \frac{\mathrm{d}u}{\mathrm{d}x}(0)\right) = 0, \quad u(s) = j(s), \quad \frac{\mathrm{d}u}{\mathrm{d}x}(s) = l(s), \end{aligned} \tag{1.1}$$

where $f(\cdot,\cdot,\cdot)$, $g(\cdot,\cdot)$, $j(\cdot)$ and $l(\cdot)$ are arbitrary functions of their arguments and s is the unknown free boundary. The conditions $u(s) = j(s)$ and $(\mathrm{d}u/\mathrm{d}x)(s) = l(s)$ define the value of s. We note that the estimation of process duration considered in [16] is a different problem. In fact, in that case we have only one condition at the free boundary s.

In order to solve the proposed problem we consider a noniterative transformation method and a simple shooting one. These methods are used successfully in [5] to solve a nonlinear free boundary test problem [10].

A way to define a shooting method is to set a shooting parameter and a shooting function. Dealing with a free boundary value problem we recognize that the free boundary has to be found in the resolution process. It appears to be simple to choose the free boundary value s as the shooting parameter and the boundary condition at zero as the shooting function. This shooting method can be seen as a trial method. A trial method for free boundary value problems is discussed in [2].

The noniterative transformation method is established in [8,9]. Some important applications to problems of current interest are considered in [4–9]. Here we applied the noniterative method in order to obtain an upper bound for the free boundary, see Theorem 1. Then, we used this upper bound in order to choose the starting values of the shooting parameter. Therefore, in this way we avoid the trial aspect of the shooting method.

In Section 2 we point our attention to isothermal tubular flow reactors with "axial missing" [13]. In Sections 3 and 4 we introduce the numerical methods. In closing, in Section 5, representative numerical results and some concluding remarks are given. There, we discuss an even and an odd order reaction.

2. Tubular chemical reactors

Let us consider an isothermal nth-order chemical reaction in a homogeneous tubular flow reactor with axial missing. We assume that in the chemical process only one species of reactant is involved and only one species of product is produced. At the inlet side we introduce only reactant of species A and at the outlet side we get the product B along with residual material A. A second-order reaction reads as $A + A \to B$, a third order as $A + A + A \to B$, and so on.

By using the material balance of the fluxes of species A it is possible to obtain for the concentration of the reactant A the following governing equation [14]:

$$\frac{d^2u}{dx^2} = N_{Pe}\left(\frac{du}{dx} + Ru^n\right). \tag{2.1}$$

In (2.1) x represents the dimensional length $0 \leqslant x \leqslant s$; $u(x) = C_A(x)/C_{A_0}$, $C_A(x)$ and C_{A_0} being the concentrations of reactant A, respectively, at the point x and at the inlet $x = 0$, so that $u \in [0, 1]$. N_{Pe} and R are respectively the dimensionless Peclet group and the reaction rate group, i.e., $N_{Pe} = v/E_a$ and $R = KC_{A_0}^{1-n}/v$, v is the axial velocity of species A, E_a is the diffusion coefficient and K is the rate of reaction. Here we remark that N_{Pe} and R are greater than zero.

The classical two-point boundary conditions associated to (2.1) are those considered in [17]. In the present context we consider (2.1) along with the free boundary conditions

$$u(0) - \frac{1}{N_{Pe}}\frac{du}{dx}(0) = 1, \quad u(s) = \tau, \quad \frac{du}{dx}(s) = 0. \tag{2.2}$$

The condition

$$u(0) - \frac{1}{N_{Pe}}\frac{du}{dx}(0) = 1$$

is because of the axial missing hypothesis [13]. Here zero has to be intended as 0^+. In fact we have a discontinuity in the value of u at zero where $u(0^-) = 1$ whereas $u(0^+) < 1$. $u(0^+) < 1$ since $N_{Pe} > 0$ and we expect, because of the reaction process, that $(du/dx)(0^+) < 0$. τ represents the residual material of species A at the free boundary, so that $0 < \tau < u(0^+)$. $(du/dx)(s) = 0$ physically means that no reaction is taking place at the free boundary.

In the mathematical model (2.1), (2.2) we can look at the free boundary as a function of the physical parameters N_{Pe}, R, n and τ. In order that the model be consistent with the physical context we have to verify that

$$\frac{\partial s}{\partial N_{Pe}} < 0, \quad \frac{\partial s}{\partial R} < 0, \quad \frac{\partial s}{\partial n} > 0 \quad \text{and} \quad \frac{\partial s}{\partial \tau} < 0. \tag{2.3}$$

Moreover, for physical reasons, $u(x)$ should be monotone decreasing in $[0, s)$.

Let us neglect, in order to consider a supplementary problem, the axial missing effect at the boundary $x = 0$. We will denote with $(u_w(x), s_w)$ the solution of the free boundary value problem where $u_w(0) = 1$. Moreover, for the same physical reasons $u_w(x)$ should be monotone decreasing in $[0, s_w)$. Next we prove the following theorem.

Theorem 1. *If the pairs $(u(x), s)$ and $(u_w(x), s_w)$ are respectively the solution for the problem with and without axial missing (defined as before), then an upper bound for the free boundary s is given by the value of s_w, i.e., $s < s_w$.*

Proof. First we prove that $(du/dx)(x) < 0$ for $x \in [0, s)$. Being $\tau > 0$ and $(d^2u/dx^2)(s) > 0$ it follows that u has a positive local minimum in s. Therefore $u(x) > \tau$ and $(du/dx)(x) < 0$ in

some left neighbourhood of s. If the mentioned neighbourhood is $[0, s)$, fine. Otherwise, it should be $du/dx > 0$ somewhere in $[0, s)$ and u should have a positive local maximum, say $x = m$, on the left of s. But this cannot be true since, from the differential equation, it follows that $d^2u/dx^2 > 0$ at m. With similar arguments it is possible to prove that $(du_w/dx)(x) < 0$ for $x \in [0, s_w)$.

Next we introduce the new independent variables

$$\begin{aligned} &\xi = s - x, \qquad \xi \in [0, s], \\ &\xi_w = s_w - x, \quad \xi_w \in [0, s_w], \end{aligned} \tag{2.4}$$

and we obtain for $u(\xi)$ and $u_w(\xi_w)$ the same governing differential equation and boundary conditions at zero but a different boundary condition at the free boundaries. For instance, the problem (2.1), (2.2) becomes

$$\frac{d^2u}{d\xi^2} = N_{Pe}\left(-\frac{du}{d\xi} + Ru^n\right), \tag{2.5a}$$

$$u(0) = \tau, \qquad \frac{du}{d\xi}(0) = 0, \qquad u(s) + \frac{1}{N_{Pe}}\frac{du}{d\xi}(s) = 1. \tag{2.5b}$$

Now, $u(\xi)$ and $u_w(\xi_w)$ are respectively monotone increasing in $(0, s]$ and in $(0, s_w]$. Since $u_w(s_w) = 1$ and taking into account that $N_{Pe} > 0$ and $(du/d\xi)(\xi) > 0$ in $(0, s]$ from the boundary condition at $\xi = s$, we can easily infer the thesis. □

3. A simple shooting method

In order to gain the advantage of integrating in a fixed interval we can introduce the so-called Landau transformation [1]

$$y = x/s. \tag{3.1}$$

The free boundary value problem (1.1) becomes

$$\begin{aligned} &\frac{d^2u}{dy^2} = s^2 f\left(sy, u, \frac{1}{s}\frac{du}{dy}\right), \\ &g\left(u(0), \frac{1}{s}\frac{du}{dy}(0)\right) = 0, \quad u(1) = j(1), \quad \frac{du}{dy}(1) = sl(1). \end{aligned} \tag{3.2}$$

Choosing a value of s we have the conditions we need at $y = 1$ in order to integrate the differential equation inwards in $[0, 1]$. Therefore, we can evaluate the shooting function

$$F(s) = g\left(u(0; s), \frac{1}{s}\frac{du}{dy}(0; s)\right); \tag{3.3}$$

here the notation $(\cdot; s)$ indicates that the latter argument is a parameter. We have now to find a zero of $F(s)$. In this instance, starting with two values s_0 and s_1, we can use the bisection (then we must require $F(s_0)F(s_1) < 0$) or the secant method [15]. This is the step that make:

the method an iterative one. If $F(s_k) \to 0$ as $k \to \infty$, then $s_k \to s$. The criteria for the convergence could be

$$|s_k - s_{k-1}| < \text{Tol} \quad \text{and} \quad |F(s_k)| < \text{Tol}, \tag{3.4}$$

where Tol is a prefixed tolerance.

We have to remark that every simple shooting method may have two weak points. First if the differential problem is stiff (we mean that it is unstable from an analytical point of view), then the shooting method will result in an ill-conditioned algorithm. In such a case the sequence of the shooting parameter fails to converge. Then it is necessary either to integrate numerically in the nonstiff direction or to resort to variants of the shooting method [12]. A further drawback is that the sequence of the shooting parameter does not converge when inaccurate initial values of it are chosen. It is possible to use a trial-and-error search method in order to find appropriate initial values of the shooting parameter. This strategy usually requires more numerical integrations than the iterative method. For the problem posed in Section 2, Theorem 1 given there allows us to find an upper bound for our shooting parameter. This upper bound can be found noniteratively by the method discussed in the next section.

4. A noniterative transformation method

Here we consider the class of free boundary value problems given by

$$\begin{aligned} &\frac{d^2u}{dx^2} = \Sigma\left(u, \frac{du}{dx}\right), \\ &u(0) = \alpha, \qquad u(s) = \beta, \qquad \frac{du}{dx}(s) = \gamma, \end{aligned} \tag{4.1}$$

where $\Sigma(\cdot,\cdot)$ is an arbitrary function of its arguments, α, β and γ are constants.

It is possible to solve numerically this type of problems by using a noniterative numerical method established in [8,9]. Let us summarize that method here. By assuming $\alpha \neq \beta$, we introduce the new variables

$$t = \frac{u - \alpha}{\beta - \alpha} \exp(x), \qquad z = \exp(x), \tag{4.2}$$

and we suppose $z = z(t)$, so that

$$\frac{du}{dx} = (\beta - \alpha)\frac{z - t\dfrac{dz}{dt}}{z\dfrac{dz}{dt}}, \tag{4.3}$$

$$\frac{d^2u}{dx^2} = -(\beta - \alpha)\frac{z^3\left(\dfrac{dz}{dt}\right)^2 - tz^2\left(\dfrac{dz}{dt}\right)^3 + z^4\dfrac{d^2z}{dt^2}}{z^3\left(\dfrac{dz}{dt}\right)^3}. \tag{4.4}$$

Owing to (4.2)–(4.4) the free boundary value problem (4.1) transforms to

$$\frac{d^2z}{dt^2} = \frac{t}{z^2}\left(\frac{dz}{dt}\right)^3 - \frac{1}{z}\left(\frac{dz}{dt}\right)^2 - \frac{1}{(\beta-\alpha)z}\left(\frac{dz}{dt}\right)^3 \Sigma\left[(\beta-\alpha)\frac{t}{z}+\alpha, (\beta-\alpha)\frac{z-t\dfrac{dz}{dt}}{z\dfrac{dz}{dt}}\right], \tag{4.5}$$

$$z(0)=1, \qquad z(S)=S, \qquad \frac{dz}{dt}(S) = \frac{\beta-\alpha}{\gamma+\beta-\alpha},$$

where $S = \exp(s)$.

We note that (4.5) is partially invariant with respect to the stretching group

$$t^* = \lambda t, \qquad S^* = \lambda S, \qquad z^* = \lambda z, \tag{4.6}$$

where λ is the exponential of the group parameter. Partial invariance means that the differential equation (4.5) along with the boundary conditions at $t = S$ are invariant under (4.6), whereas the boundary condition $z(0) = 1$ does not.

In order to obtain the noniterative numerical solution of (4.1) we guess a value of $S^* > 0$ and we integrate numerically the transformed equation in (4.5), with initial conditions $z^*(S^*) = S^*$ and $(dz^*/dt^*)(S^*) = (\beta-\alpha)/(\gamma+\beta-\alpha)$, backwards in $[0, S^*]$. In this way we get a value of $z^*(0)$. If $z^*(0) = 1$, we have the numerical solution. Otherwise, from (4.6) we can find

$$S = \frac{S^*}{z^*(0)}, \qquad \frac{dz}{dt}(0) = \frac{dz^*}{dt^*}(0), \tag{4.7}$$

and then

$$s = \ln(S), \qquad \frac{du}{dx}(0) = (\beta-\alpha)\left[\frac{dz^*}{dt^*}(0)\right]^{-1}. \tag{4.8}$$

In the above discussion the value S^* is completely arbitrary. Therefore we may use different values of S^* and compare the numerical results.

5. Numerical results and discussion

In this section we discuss some numerical results for the posed problem.

First we consider the upper bound for the value of the free boundary s. By applying the transformation of Section 4 we find the transformed problem

$$\frac{d^2z}{dt^2} = (1+N_{Pe})\left[\frac{t}{z^2}\left(\frac{dz}{dt}\right)^3 - \frac{1}{z}\left(\frac{dz}{dt}\right)^2\right] - \frac{N_{Pe}R}{(1-\tau)z}\left(\frac{dz}{dt}\right)^3\left[(1-\tau)\frac{t}{z}+1\right]^n, \tag{5.1}$$

$$z(0)=1, \qquad z(S)=S, \qquad \frac{dz}{dt}(S)=1.$$

Table 1
An even ($n = 2$) order reaction with axial missing

k	s_k	$F(s_k)$	$u(0)$	$\frac{du}{dx}(0)$ [a]
0	4.0	−0.634956		
1	5.0	−0.144354		
6	5.119831	−0.15D−05	0.831273	−1.012352
7	5.119832	−0.29D−09	0.831274	−1.012354
8	5.119832	−0.51D−15	0.831274	−1.012354

[a] Here and in Table 2 the values of $(du/dx)(0)$ have been obtained through the formula $du/dx = (1/s)\,du/dy$.

Then in order to apply the shooting method we have to consider the problem

$$\frac{d^2u}{dy^2} = sN_{Pe}\left(\frac{du}{dy} + sRu^n\right),$$
$$u(0) - \frac{1}{sN_{Pe}}\frac{du}{dy}(0) = 1, \qquad u(1) = \tau, \qquad \frac{du}{dy}(1) = 0. \tag{5.2}$$

As a first case we assume the following numerical values:

$$N_{Pe} = 6, \qquad R = 2, \qquad \tau = 0.1, \qquad n = 2. \tag{5.3}$$

A proof of the existence and uniqueness of the solution of (2.1), (2.2) in the case characterized by (5.3) is given in [3]. By solving (5.1) with the method of Section 4, setting indifferently $S^* = 0.5$ or $S^* = 1.0$, we obtained $s_w = 5.260967$ and $(du_w/dx)(0) = -1.409545$. As remarked in Section 3 the value of s_w found by the noniterative transformation method was used as a hint for the shooting method. In the numerical solution of (5.2) we used the secant method with the convergence criteria as in (3.4) and Tol = 1D−06; here and in the following the symbol D indicates a double-precision arithmetic. The numerical iterations are listed in Table 1.

In order to validate directly the numerical results we used the computed value of s. The differential equation (2.1) was integrated backwards in $[0, s]$ with initial data at $x = s$ as in (2.2). So doing we found $u(0) = 0.831274$ and $(du/dx)(0) = -1.012353$. We have agreement with the values of Table 1 up to the sixth digit.

The present approach can be used for considering a generic nth-order chemical reaction and for different values of the other parameters involved. Let us discuss here a second case $n = 3$ and N_{Pe}, R and τ as in (5.3). For the problem without axial missing we found $s_w = 25.878363$ and $(du_w/dx)(0) = -1.296238$. Then 25.878363 has to be an upper bound of the free boundary for the axial missing case. Table 2 lists the numerical results obtained by means of the shooting method. The secant method was used again with Tol = 1D−06. A direct validation of these results, as discussed before, led to $u(0) = 0.854897$ and $(du/dx)(0) = -0.870613$. The agreement reaches the sixth digit.

In the numerical integrations we used the DIVPAG integrator with step-size and local error control, in the IMSL MATH/LIBRARY [18]. The tolerance we used for the error control, within the DIVPAG integrator, was of 1D−12.

Table 2
An odd ($n = 3$) order reaction with axial missing

k	s_k	$F(s_k)$	$u(0)$	$\frac{du}{dx}(0)$
0	25.0	−0.437512		
1	25.5	−0.218592		
7	25.738232	−0.34D−05	0.854895	−0.870609
8	25.738234	0.16D−08	0.854898	−0.870615
9	25.738234	−0.26D−13	0.854898	−0.870615

So far we have described a possible way to solve the proposed problem. The shooting method was specially intended for free boundary value problems. We selected the unknown free boundary as the shooting parameter. The choice of a different shooting parameter will result, since the value of s is unknown, in a more complicated algorithm. Only if we get an ill-conditioned algorithm, it seems worth considering to resort to a more complicate one. In order to be efficient any shooting method needs to start with appropriate values of the shooting parameter. Theorem 1 of Section 2 and the application of the noniterative method allowed us to use effectively the shooting method.

For illustrative purpose we considered an even and an odd order reaction. In both cases we choose to validate directly the numerical results. More computational experiments, although not reported here, suggest that, as expected, the conditions (2.3) are verified.

The formulation (2.5) may suggest to integrate (2.5a) forwards with initial conditions as in (2.5b) checking at every step if the boundary condition at $\xi = s$ is verified. This strategy could be inappropriate and cost-effective, for large values of s at least, having to use a small step size in order to achieve the required accuracy.

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