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Studies on the Method of Orthogonal Collocation: V. Multiple Steady States in Catalyst Particles

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Abstract. Efficient numerical schemes are developed in this paper to solve the boundary value problems of diffusion with chemical reaction in catalyst particles. These schemes are based on the fact the concentration profiles can be divided into reaction and dead zones. The reaction zone can be further divided into two zones at a defined critical point. New transformations are used to minimize the number of collocation points needed to obtain accurate solutions. With the help of the continuation package AUTO, the modified collocation schemes are used to obtain the multiple steady states and the locations of the concentration profiles zones for different values of Thiele modulus.

Nomenclature

a	Shape factor in Eq. (1)
r	Dimensionless particle radius
s	Coordinate transformation used in Eq. (18)
u	Dimensionless reactant concentration
x	Symmetric coordinate transformation
y	Coordinate transformation in the outer zone
z	Coordinate transformation in the dead zone
$\beta\beta$	Dimensionless heat generation
η	Effectiveness factor
$\gamma\beta$	Dimensionless activation energy
ϕ	Thiele modulus
λ_1	Dimensionless location of the critical point
λ, λ_2	Dimensionless location of the dead zone for the slab and sphere shapes respectively.

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Introduction

For catalyst particles in the form of a slab, a cylinder, a sphere, multiple steady state concentration profiles are possible for exothermic reactions. In a slab or a cylinder three solutions are possible whereas in spheres a large number of solutions may exist. This subject is studied in detail in the papers by Hlavacek and Marek [1], Copelowitz and Aris [2], and Michelsen and Villadsen [3] and the books of Aris [4] and Villadsen and Michelsen [5]. Diffusion and reaction in catalyst particles can be described by a set of differential equations for mass and heat balances of the boundary value type. Although the method of global orthogonal collocation is well suited to directly solving this type of boundary value problems, an extremely large number of collocation points may be needed in the extreme cases of highly exothermic reaction with extremely large activation energy in spherical particles. This makes the method impractical in this case. For this reason, Michelsen and Villadsen [3] developed a stepwise spline collocation method which is applied to an initial value version of this problem. Finlayson[6] and Carey and Finlayson [7], on the other hand used a similar spline collocation method and called it orthogonal collocation on finite elements.

In this paper we extend the spline collocation method developed by Soliman [8] to this problem. In particular we notice that because of the rapid change in the profiles, we need to divide the concentration profiles into three zones in the case of sphere. In addition, we use the software AUTO [9] to explore the regions of steady-state multiplicity.

The Problem

We treat in the paper the problem of diffusion with non-isothermal first order chemical reaction in a catalyst particle given by:

$$\frac{d^2u}{dr^2}+\frac{a}{r}\frac{du}{dr}=\phi^2 u \exp\left(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}\right) \tag{1}$$

with the boundary conditions

$$u(1)=1 \tag{2}$$

$$u'(0)=0 \tag{3}$$

The effectiveness factor η is given by

$$\eta = (a+1)\int_0^1 r^a u \exp\left(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}\right)du \qquad (4)$$

Here u is the dimensionless concentration and a equals 0,1,2 for a slab, a cylinder and a sphere respectively.

Using the transformation

$$x = r^2 \qquad (5)$$

equations (1-4) become

$$4x\frac{d^2u}{dx^2} + 2(a+1)\frac{du}{dx} = \phi^2 u \exp\left(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}\right) \qquad (6)$$

$$u(1) = 1 \qquad (7)$$

$$\eta = \frac{(a+1)}{2}\int_0^1 x^{\frac{(a-1)}{2}} u \exp\left(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}\right) dx \qquad (8)$$

Transformation (5) implies that the solution u is symmetric and thus condition (3) is automatically satisfied.

Development of the Numerical Procedure

For the case of a slab (a=0), we notice from Eq. (1) that the second derivative of u will be always positive. As ϕ increases, the profile of u becomes steeper until we reach a situation where the center concentration becomes very close to zero. In this case we can divide the profile into two zones; a reaction zone and a dead zone where the concentration is zero. The point ($r = \lambda$) dividing the two zones is determined by the solution of the Eq. [10]

$$u(\lambda)\frac{d^2u}{dr^2}\Big|_{r=\lambda} = 0 \qquad (9)$$

For the case of a sphere, profiles presented in references[2-5], show that for some values of ϕ, the second derivative $\frac{d^2u}{dr^2}$ could become negative near r = 1. At the center it should be positive because $\frac{a}{r}\frac{du}{dr} \rightarrow a\frac{d^2u}{dr^2}$ as $r \rightarrow 0$. Thus the critical point ($r = \lambda_1$) is a point in which we can divide the profile into two zones[8]. At this point we have the following condition:

$$\frac{a}{r}\frac{du}{dr}\Big|_{r=\lambda_1} = \phi^2 u \exp\left(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}\right)\Big|_{r=\lambda_1} \tag{10}$$

together with the continuity conditions

$$u\Big|_{r=\lambda_1^+} = u\Big|_{r=\lambda_1^-} \tag{11}$$

and

$$\frac{du}{dr}\Big|_{r=\lambda_1^+} = \frac{du}{dr}\Big|_{r=\lambda_1^-} \tag{12}$$

The simultaneous solution of Eqs. (10-12) together with the collocation equations in the two zones determine λ_1 and concentration profiles in the two zones.

For some values of ϕ, we will have a third zone at the center (dead zone) in which there is no reaction. Condition (9) is applied at λ_2 giving the point at which the third zone starts.

For the domain of the solution to be in [0,1], we use the transformation

$$y = \frac{r-\lambda_1}{1-\lambda_1} \tag{13}$$

$$z = \frac{r-\lambda_2}{\lambda_1-\lambda_2} \tag{14}$$

Thus Eq. (1) becomes in the first zone,

$$\frac{1}{(1-\lambda_1)^2}\frac{d^2u}{dy^2} + \frac{a}{((1-\lambda_1)y+\lambda_1)(1-\lambda_1)}\frac{du}{dy} = \phi^2 u \exp\left(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}\right) \tag{15}$$

and in the second zone

$$\frac{1}{(\lambda_1 - \lambda_2)^2}\frac{d^2u}{dz^2}+\frac{a}{((\lambda_1-\lambda_2)z+\lambda_2)(\lambda_1-\lambda_2)}\frac{du}{dz} = \phi^2 u \exp(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}) \quad (16)$$

Since in the second zone we have a boundary condition of the type $\frac{du}{dz}\Big|_{z=0} = 0$

we can use the transformation $x=z^2$ in this zone although the solution u in this case is not symmetric in z for $\lambda_2 \neq 0$. Equation (15) is solved using the orthogonal collocation method at the zeros of Legendre polynomials which is a Jacobi polynomial of the form $P^{(0,0)}(y)$, [5]. Equation (16) is solved using the zeros of Jacobi polynomial suitable for the particular shape which is $P^{(1,(a-1)/2)}(z^2)$, [5]. We can further reduce the number of collocation points for the solution of equation(16) if we can transform it to a slab type equation for which the collocation method does not require too many points. The following co-ordinate transformation can do this job for a sphere (a=2)

$$s=\frac{(r-\lambda_1)}{(1-\lambda_1)r}=\frac{y}{(1-\lambda_1)y+\lambda_1} \quad (17)$$

by which Eq. (15) becomes

$$\frac{d^2u}{ds^2}=\frac{\lambda_1^2(1-\lambda_1)^2\phi^2}{(1-(1-\lambda_1)s)^4}\, u \exp(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}) \quad (18)$$

We solve this equation using collocation at the zeros of legendre polynomial. For the case of a cylinder (a=1), one uses the transformation

$$s=\frac{\ln(\lambda_1)-\ln(r)}{\ln(\lambda_1)} \quad (19)$$

to obtain

$$\frac{d^2u}{ds^2}=\lambda_1^{2(1-s)}\,(\ln(\lambda_1))^2\,\phi^2 u \exp(\frac{\beta\gamma(1-u)}{1+\beta(1-u)}) \quad (20)$$

Numerical Results

First we study different numerical procedures on Eqs. (1-4) for a sphere and for the case of $\gamma=28$, $\beta^{\cdot}=1$, $\phi=0.18$ where the system has three solutions. The results for the intermediate solution are reported. In Table 1 we show the results of applying the standard collocation method on Eqs. (6,8) using the zeros of $P^{(1,0.5)}(x)$ as collocation points with different number of collocation points (N). The results are presented in the first three columns in terms of the center concentration u_0 and the effectiveness factor η. This is followed by three columns representing the results of the collocation method with the zeros of Legendre polynomials as collocation points. Finally in the next four columns the results of applying the spline collocation method (Eqs. (15), (16)) developed in this paper are presented. N_1 indicates the numbers of collocation points in the first zone ($r \in [\lambda_1, 1]$) and N_2 is the number of collocation points in the second zone ($r \in [\lambda_2, \lambda_1]$). The first row in the spline collocation table represents the numerical exact solution and is obtained by choosing N_1=28, N_2=6. Increasing the number of collocation points further does not improve the results. Now using up to 16 points with the standard collocation method and the zeros of $P^{(1, 0.5)}(x)$ the solution is very far from the exact solution. Although using up to 20 points with the zeros of $P^{(0,0)}(r)$ gives better results, we are not still close to the exact solution. With the present method and with 18 points we are very close to the exact solution.

Table 1. Comparison between standard collocation method and developed spline collocation method for the case of sphere

Standard collocation method with the zero of $P^{(1, 0.5)}(x)$			Standard collocation method with the zero of $P^{(0,0)}(r)$			Spline collocation Eq. (15,16)			
N	u_0	η	N	u_0	η	N_1	N_2	u_0	η
6	0.7654	10.4244	10	0.4675	6.462	28	6	0.2082	4.5909
8	0.6505	9.4239	12	0.3812	5.570	18	6	0.2075	4.596
10	0.6257	8.7874	14	0.2953	4.850	18	4	0.2074	4.5887
12	0.6066	8.3279	16	0.2204	4.3576	18	2	0.2128	4.6442
14	0.5872	7.9685	18	0.1588	4.137	16	6	0.2038	4.5690
16	0.5690	7.6715	20	0.1656	4.417	16	4	0.2037	4.568
						15	4	0.2004	4.544
						14	6	01974	4.514
						14	4	0.1972	4.513
						13	6	0.1969	4.485
						12	6	0.2019	4.476

Using Eq. (18) in the outer zone and Eq. (16) in the inner zone, we obtain the results shown in Table 2. It is noticed that the number of collocation points (N_1) in the outer zone using the new transformation Eq. (17) is about four points less than the corresponding (N_1) for the solution of Eq. (16) for the same accuracy in η.

Table 2. Results of the spline collocation method with the s transformation (Eqs.18, 16)

Spline collocation Eqs. (18, 16)			
N_1	N_2	u_0	η
6	4	0.2283	4.2127
8	4	0.2219	4.4729
10	2	0.244	4.6633
10	4	0.2147	4.5566
12	4	0.2109	4.5819
14	4	0.2092	4.5886
16	4	0.285	4.5900

The methods presented in this paper allows us to represent the problem with low number of nonlinear algebraic equations which can be solved easily with any nonlinear solver. AUTO continuation software [9] is used to solve the resulting nonlinear algebraic system for all values of ϕ. The change of the effectiveness factor, the inner-outer zone location (λ_1,λ_2) with the Thiele modulus are shown in Fig. 1-a,b,c. The number of collocation points used in these results are 13 for the outer zone and 4 for the inner zone. With this quite low number of collocation points, the effectiveness factor curve (Fig. 1-a) shows similar behavior to the results obtained by Michelsen and Villadsen [3]. The $\eta(\phi)$ curve shows that one, three and five steady states can be found for the studied case. The top and bottom steady state branches in Figure 1-a are found to be stable while the intermediate branch is not stable. The concentration profiles for selected points are plotted in Fig. 2. In Fig. 1,b,c it can be seen that the concentration profiles in the ignited steady state region (top branch) consist of three zones. The concentration profiles for points A,B, and C locating in this branch are depicted in Fig. 2. In the quenched steady state (bottom branch), the concentration profiles consists of two zones (point H) or one flat zone. The intermediate unstable branch can be divided into two parts; the concentration profile can be represented either by two zones for ($0.109 \leq \phi \leq 0.359$) or three zones for ($0.018 \leq \phi \leq 0.109$). The concentration profiles in this zone (D,E,G,F) show that as ϕ increases, the location of the critical point λ_1 decreases until it reaches the small multiplicity region, then it increases until it reaches unity in the bottom branch of the $\eta(\phi)$ curve.

The suggested transformations are applied to the slab case. The variation of the effectiveness factor with the Thiele modulus is shown in Fig. 3 with two (dot line) and four (solid line) collocation points. The profiles shape for this problem can be divided into two zones. The dead zone can be only found for large values of ϕ.

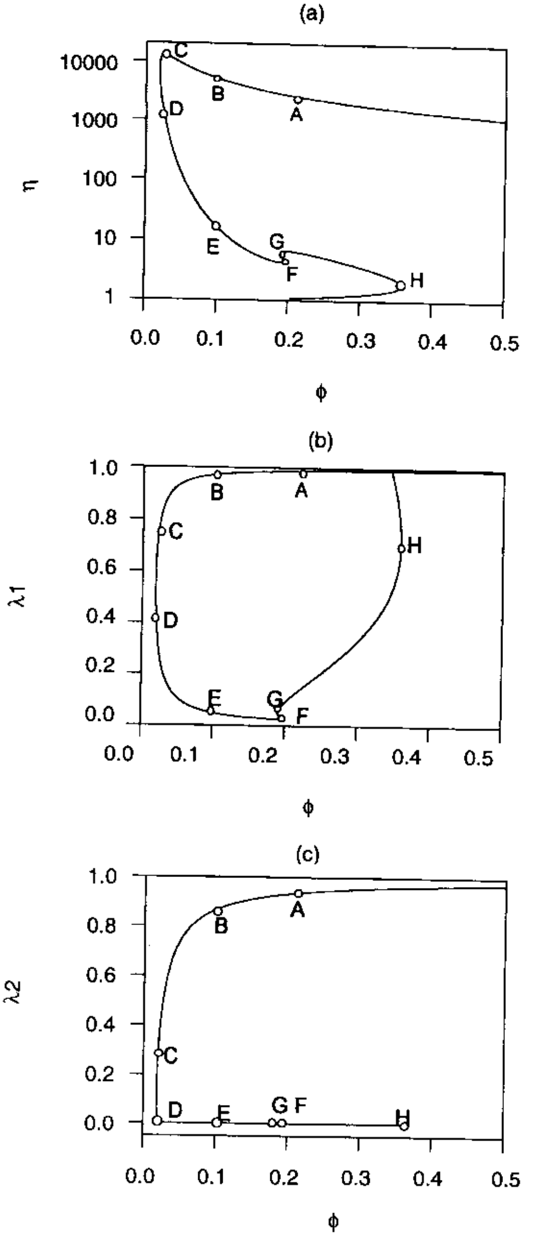

Fig. 1. Variation of (a) effectiveness factor, (b) critical point, (c) dead zone with Thiele modulus for spherical particles and $(\gamma,\beta) = (28,1)$.

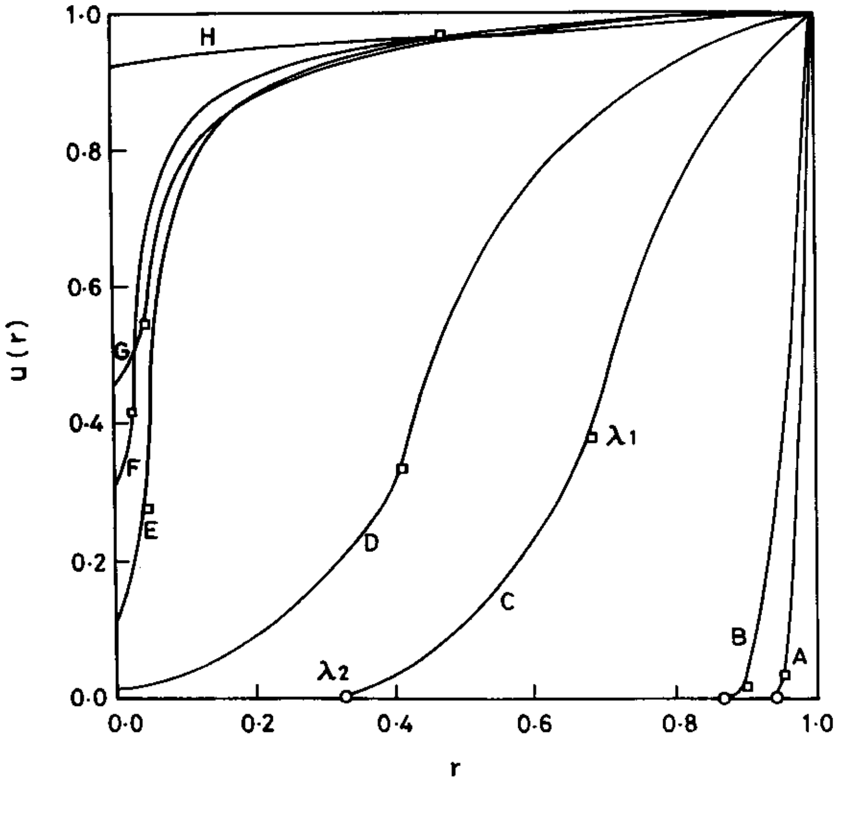

Fig. 2. Concentration profiles corresponding to points in Fig. 1. (square: critical points, circle: dead zone point).

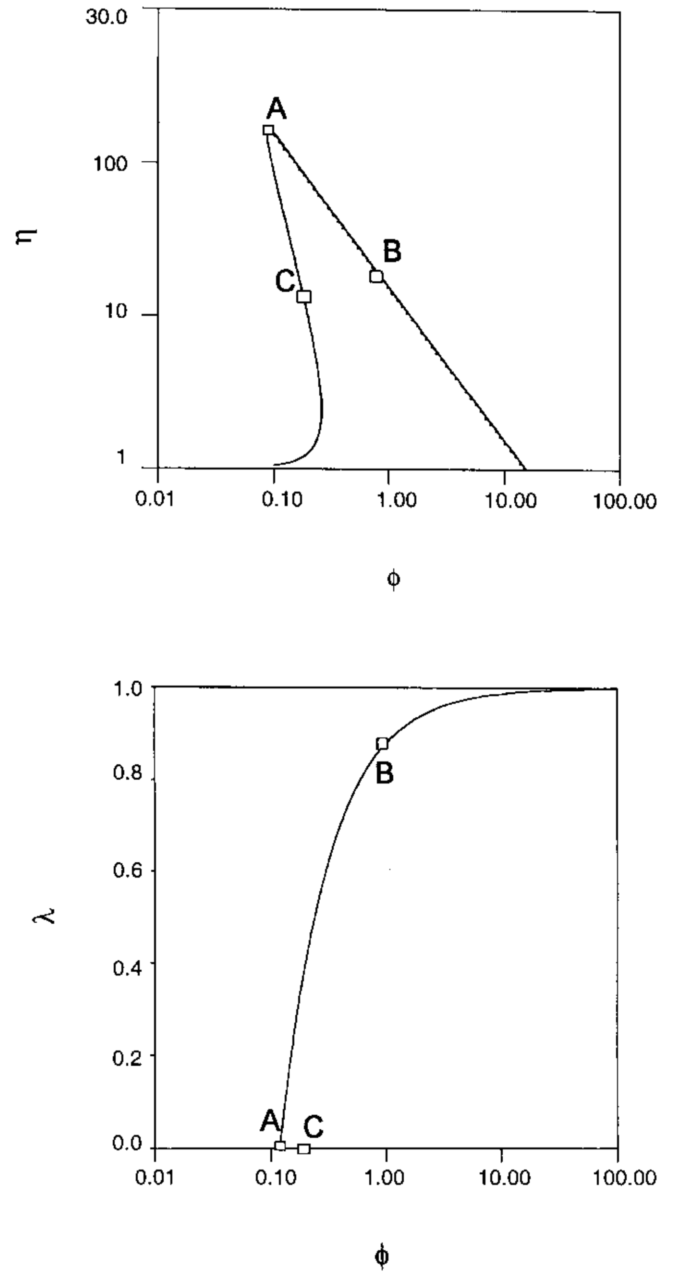

Fig. 3. Variation of the effectiveness factor and the dead zone boundary location with Thiele modulus for the slab case.

Conclusions

The spline collocation method presented in this paper can reduce significantly the number of collocation points required to solve the boundary value problem of diffusion with chemical reaction in catalyst particles. All possible multiple steady states for this problem are obtained by solving the resulted system using continuation subroutines such as AUTO. This method can be used with problems having many steep sections by repeatedly using equations of the type (10-12).

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دراسات على طريقة التنظيم المتعامد – ٥. تعددية الحلول في الجسيمات الحفازة

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ملخص البحث. احتوت هذه الورقة على طرق حسابية عالية الكفاءة تم تطويرها لحل المعادلات التفاضلية الحدية المستنتجة من حالة الانتشار بوجود تفاعل كيميائي في جسيمات محفزة. اعتمدت هذه الطرق على إمكانية تقسيم نطاق تغير التركيز داخل هذه الجسيمات إلى نطاقين: **الأول** نطاق متغير بسبب حدوث التفاعل **والثاني** نطاق ساكن. قسم نطاق التفاعل أيضا إلى جزئين آخرين عرفت حدودهما عند نقطة حرجة. استخدمت معادلات تحويلية جديدة لتقليل عدد نقاط التنظيم المتعامد المطلوبة للحصول على حل دقيق. كما استخدمت طرق التنظيم المطوّرة مع برنامج حل معادلات جبرية بشكل مستمر (أوتو) لتحديد الحلول العديدة للنظام المدروس وكذلك تحديد المواقع المميزة لمناطق تغير التركيز لقيم متعددة من معامل ثيل.