Calculation of the Effectiveness Factor for a Porous Catalyst Particle-a Perturbation Approach

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***Abstract*—**An approximate analytical solution has been obtained for the calculation of the effectiveness factor of a porous catalyst particle under non-isothermal conditions. The solution has been obtained by choosing a trial function with unknown parameters to be determined such that the regular perturbation expansion of the trial function is equivalent to that of the original problem to a given order of the perturbation parameter. The results obtained are in good agreement with the numerical solution.

***Keywords*—** Catalyst particle, effectiveness factor, Frank Kamenetskii equation, perturbation.

I. Introduction

THE effectiveness factor is an important parameter in the design and simulation of fixed bed catalytic reactors. For its calculation a second order differential equation with two boundary conditions should be solved. This is a time consuming procedure especially if the differential equation is to be solved for every particle in the reactor bed. Finding an approximate solution for the effectiveness factor is thus of great importance.

Models of varying complexity have been proposed for the calculation of the effectiveness factor.

A one point collocation would be sufficient in many cases for low values of Thiele modulus. This would require the solution of one non-algebraic equation [1]. For large values of Thiele modulus, solution of a set of non-algebraic equations needs to be solved and this would be time consuming. Another approach is to develop empirical formulae for the calculation of the effectiveness factor [2,3].

In this paper we propose a non-iterative approximate analytical solution for the effectiveness factor of a catalyst particle under non-isothermal conditions with negligible external resistance to mass and heat transfer. The solution covers a large range of parameters including regions of multiple steady states and for different shapes of catalyst particles (slabs, cylinders and spheres). The validity of the solution is established by comparison with the numerical solutions.

The basic idea in developing the approximate solution is to find the regular perturbation expansion of the solution in terms of small perturbation parameter. Secondly we seek a trial function with unknown parameters to be determined such that its expansion in terms of the perturbation parameter is equivalent to that of the solution of the original problem to a given order of the perturbation parameter. The trial function was obtained from the analytical solution of the Frank Kamenetskii equation in a cylinder [4-6]. The solution is characterized by the existence of multiple steady states.

II. Mathematical Formulation

Consider a reaction with a dimensionless rate R(u) where u is the dimensionless concentration, v is the dimensionless temperature. The reaction is taking place non- isothermally inside a catalyst particle with no external resistance to mass transfer. We may write the describing equation as

$$\frac{1}{r^s}\frac{d}{dr}[r^s \frac{du}{dr}] = \phi^2 R(u) \tag{1}$$

with the boundary conditions

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

$$\frac{du}{dr}\Big|_{r=0} = 0 \tag{3}$$

$$R(u) = (\frac{1+K}{1+Ku})^m u^p \exp(\delta(1-u)/(1+\beta(1-u)) \tag{4}$$

$$\delta = \beta\gamma \tag{5}$$

$$v = 1+\beta(1-u) \tag{6}$$

Here r is the dimensionless space variable in the catalyst,

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http://dx.doi.org/10.15242/IICBE.C1213007

ϕ^2 is the Thiele modulus and *s* is the shape factor of the catalyst (*s* =0 for an infinite slab, *s* =1 for an infinite cylinder and *s* = 2 for a sphere). β is the dimensionless heat of reaction and γ is the dimensionless activation energy. The dimensionless reaction rate *R(u)* is normalized with respect to the reaction rate at the external surface of the catalyst and hence, at the external surface *r*=1, *u* = 1 and *R (1)* = 1. The effectiveness factor η is given by

$$\eta = \frac{(s+1)}{\phi^2}\frac{du}{dr}\bigg|_{r=1} = (s+1)\int_0^1 r^s R(u)dr = \frac{(s+1)}{\phi}\sqrt{2\int_0^1 r^{2s}R(u)\frac{du}{dr}dr} \tag{7}$$

Except for a few cases such as isothermal first-order and zero-order reactions, the analytical solution of the boundary value problem, Eqs. (7-9), or (12,13) is, in general, not feasible, and the problem can only be solved numerically.

III. Development of the Approximate Expressions

The first step in the analysis is to obtain the perturbation expansion of the concentration and the effectiveness factor η in terms of the perturbation parameter φ^2. This is done in Appendix I.

Also we express φ^2 and η in terms of the small parameter z_c *(z_c=1-u_c)* where u_c is the concentration at the centre of the particle.

We notice that if in the rate expression (4), *m*=*p*= β=0 (zero order reaction) but finite δ, equations (1-3) has an analytical solution for the case of a slab, and cylinder. This is known as Frank Kamenetskii equation[4-6]. The solution is characterized by the possibility of multiple solution for exothermic reaction (positive β). The analytical solution for the case of a cylinder gives explicit expression for the centre concentration with Thiele modulus. In this case we have;

$$\varphi^2 = \frac{8}{\delta}[\exp(\delta(1-u_c)/2)-1]/\exp(\delta(1-u_c)) \tag{8}$$

Which can be solved as quadratic equation in $\exp(\delta(1-u_c)/2)$ to give

$$u_c = 1-\frac{2}{\delta}\ln[\frac{4}{\delta\phi^2}(1\pm\sqrt{1-\delta\phi^2/2})] \tag{9}$$

Of course, u_c should lie between 0 and 1. Equation (9) could predict no solution, one solution and two solutions for. A further solution u_c =0 should be included through physical reasoning. This corresponds to the depletion of the reactant near the centre of the catalyst particle.

The second step is to obtain trial function for φ^2 and η in terms of the centre concentration, such that their expansion is the same as that of the original problem to a given order.

In view of equation (8), the trial function for the relation between φ and is chosen in the form,

$$\varphi^2 = \frac{(s+1)x(1+b_0x)}{(1+b_1x+b_2x^2)} \tag{10}$$

Where,

$$x = \frac{-2}{R'(1)}[\exp(-R'(1)(1-u_c)/2-1] \quad if \ \ \delta \neq p$$
$$x = z_c = 1-u_c \quad if \ \ \delta = p \tag{11}$$

The unknown parameters b_0, b_1, and b_2 are determined such that the expansion of φ^2 from equation (10) is the same to that of the original problem to a third order in z_c. In appendix II we obtain the following equations;

$$b_0 - b_1 = 2(s+1)c_1 + \frac{R'(1)}{4} \tag{12}$$

$$(\frac{-R'(1)}{4} - 2(s+1)c_1)b_1 - b_2 = 4(s+1)^2(2c_1^2 - c_2) + \frac{R'(1)}{2}(\frac{R'(1)}{4} + 2(s+1)c_1) \tag{13}$$

Where,

$$c_1 = \frac{R'(1)(s+5)}{4(s+1)(s+3)} \tag{14}$$

$$c_2 = \frac{[R'^2(1)(s^2+14s+61)+R''(1)(s^2+10s+33)]}{24(s+1)^2(s+3)(s+5)} \tag{15}$$

$$R'(1) = \frac{-mK}{1+K} + p - \delta \tag{16}$$

We still need a third equation which relates b_0, b_1, and b_2 . This is obtained by determining the smallest value of φ (φ_1) at which u_c=0. The value of x (x_1) corresponding to u_c=0 is given by

$$x_1 = \frac{-2}{R'(1)}[\exp(-R'(1)/2-1] \tag{17}$$

Thus

$$\varphi_1^2 = \frac{(s+1)x_1(1+b_0x_1)}{(1+b_1x_1+b_2x_1^2)} \tag{18}$$

Or

$$\frac{2(s+1)x_1^{\,2}}{\varphi_1^{\,2}}b_0 - x_1 b_1 - x_1^{\,2} b_2 = 1 - \frac{2(s+1)x_1}{\varphi_1^{\,2}} \tag{19}$$

This is the required third equation provided we know φ_1

For a pth order isothermal reaction occurring in a slab, it is known that;

$$\varphi_1^{\,2} = \frac{2(1+p)}{(1-p)^2} \quad \text{for} \quad -1 \le p < 1$$

And for $p \ge 1$ as $\varphi_1 \to \infty, u_c \to 0$

For a non-isothermal reaction or isothermal reaction occurring in any other shape, we can make use of the approximation suggested by Ramachandran et al. [7]. We assume that when u_c=0, the concentration profile can be approximated by

$$u = r^2 \tag{20}$$

This approximate solution satisfies equation (1) at appoint r=r_i which can be taken as the root of the Jacobi polynomial of order 1. Thus we obtain

$$\varphi_1^{\,2} = \frac{2(s+1)}{R(u_i)} \tag{21}$$

Where

$$u_i = r_i^{\,2} = (s+1)/(s+5) \tag{22}$$

$r_i^{\,2}$ can be also taken as a fitting parameter to improve on the results.

Now having obtained the center concentration we move on to calculate the effectiveness factor. It is well known for a slab

$$\eta = \frac{M(1,u_c)}{\varphi} \tag{23}$$

Where

$$M^2(1,u_c) = 2\int_{u_c}^{1} R(u)du \tag{24}$$

This integral can be evaluated by any suitable quadrature or analytically in some special cases.

For the cylinder and sphere the following formulae have been obtained through expansion equivalence and curve fitting

$$\eta_c = 2\frac{M(1,u_c)}{\phi\sqrt{[1+\frac{(\sqrt{8}(1+\frac{5}{48}y^2+0.015|R'(1)|y^4)z_c)^4}{(M(1,u_c)\phi(1+0.2z^4))^4}]}} \tag{25}$$

$$\eta_s = 3\frac{M(1,u_c)}{\phi\sqrt{[1+2\frac{(\sqrt{12}(1+\frac{1273}{4725}y^2+0.015|R'(1)|y^6)z_c)^6}{(M(1,u_c)\phi(1+0.2z_c^{\,6}))^6}]}} \tag{26}$$

Where

$$y = 1 - \exp\left(-|R'(1)|z_c/2\right) \tag{27}$$

We notice that as $\varphi \to \infty$

$$\eta_c = \frac{2M(1,0)}{\phi} \tag{28}$$

$$\eta_s = \frac{3M(1,0)}{\phi} \tag{29}$$

It can also be shown that the expansions of η_c and η_s are equivalent to second order in z_c the original problem.

IV. Numerical Results

We have compared the values of the centre concentration for an isothermal reaction in a slab from equation (10) with that of reference [5]. As shown in Fig. 1, the agreement is very good for p>-1. The effectiveness factor thus calculated is of reasonable accuracy.

The effectiveness factor for the case of non-isothermal first order reaction in a sphere is displayed in Fig. 2, for γ =20 and different values of β. The agreement for exothermic reactions with the numerical results of Weisz and Hicks[8] is not as good as that for for the slab with some deviations near the upper corner of the plot. For endothermic reactions (negative β) the agreement is very good. Similar results were obtained for the cases of γ=30, 40 reported by Weisz and Hicks [8].

V. Conclusion

Formulae have been obtained for the calculation of the effectiveness factor for a catalyst having the shape of an infinite slab, infinite cylinder, and sphere. These formulae are of good accuracy and cover a wide range parameters. They would make fixed bed reactors simulation very much faster.

Appendix I

Perturbation Series for the Concentration and Effectiveness Factor

Lee and Kim [9] obtained the perturbation series for equations (1-3) for small φ^2

At r=0

$$z_c = 1 - u_c = \frac{\phi^2}{2(s+1)}(1 - c_1\phi^2 + c_2\phi^4 + ...) \quad \text{(I-1)}$$

Where

$$c_1 = \frac{R'(1)(s+5)}{4(s+1)(s+3)} \quad \text{(I-2)}$$

$$c_2 = \frac{[R'^2(1)(s^2+14s+61) + R''(1)(s^2+10s+33)]}{24(s+1)^2(s+3)(s+5)} \quad \text{(I-3)}$$

Inverting the series, we obtain

$$\phi^2 = 2(s+1)z_c[1 + 2(s+1)c_1 z_c + 4(s+1)^2(2c_1^{\,2} - c_2)z_c^{\,2} + ...) \quad \text{(I-4)}$$

On the other hand evaluating the perturbation series at r=1, we obtain

$$\eta = \frac{(s+1)}{\varphi^2}\frac{du}{dr}\Big|_{r=1} = -\frac{(s+1)}{\varphi^2}\frac{dz}{dr}\Big|_{r=1}$$
$$= 1 - \frac{R'(1)}{(s+1)(s+3)}\varphi^2 + \frac{2R'^2(1) + R''(1)}{(s+1)^2(s+3)(s+5)}\varphi^4 + ... \quad \text{(I-5)}$$

Substituting equation (I-4) into equation (I-5) we obtain

$$\eta = 1 - \frac{2R'(1)}{(s+3)}z_c + [\frac{8R'^2(1) + 4R''(1)}{(s+3)(s+5)} - \frac{R'^2(1)(s+5)}{(s+3)^2}]z_c^{\,2} + ... \quad \text{(I-6)}$$

APPENDIX II

Perturbation Series for the Trial Function

The trial function is given by;

$$\varphi^2 = \frac{(s+1)x(1+b_0x)}{(1+b_1x+b_2x^2)} \quad \text{(II-1)}$$

Where

$$x = \frac{-2}{R'(1)}[\exp(-R'(1)(1-u_c)/2 - 1] \quad \text{(II-2)}$$

Expanding x in terms of z_c (z_c=1-u_c), we obtain

$$x = z_c - R'(1)\frac{z_c^{\,2}}{4} + \frac{R'(1)^2 z_c^{\,3}}{24} + ... \quad \text{(II-3)}$$

Expanding (II-1) using (II-3), we obtain

$$\varphi^2 = 2(s+1)z_c[1 + (b_0 - b_1 - \frac{R'(1)}{4})z_c + (\frac{-(b_0-b_1)R'(1)}{2} + \frac{R'(1)^2}{24} + b_1^{\,2} - b_2 - b_0b_1)z_c^{\,2} + ...)] \quad \text{(II-4)}$$

Comparing (II-4) and (I-4), we obtain equations (12-15)

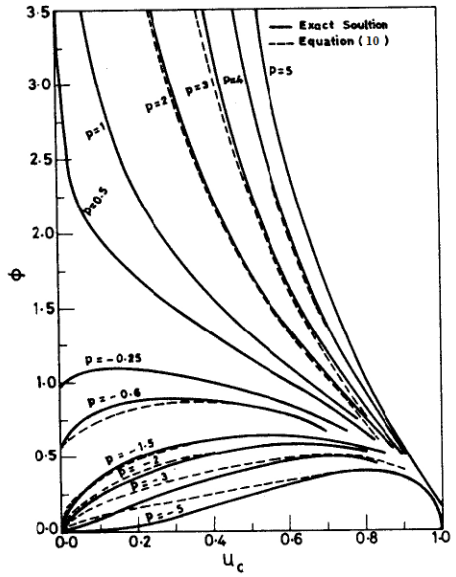

Fig.1 Centre concentration against Thiele modulus for an isothermal pth order reaction in a slab

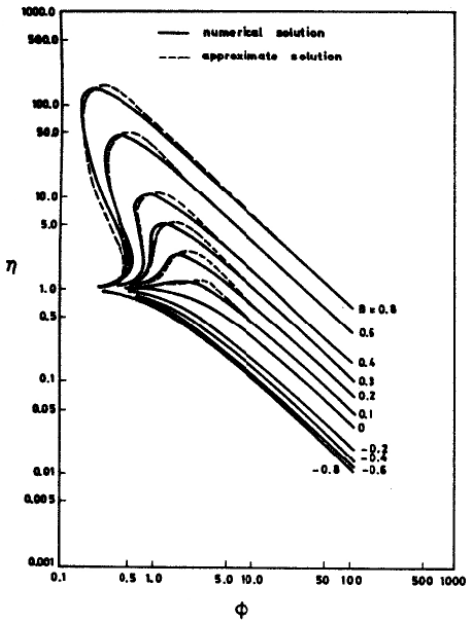

Fig.2 Effectiveness factor chart for first order reaction in spherical pellets for γ=20

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