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EXTERNAL DIFFUSION INFLUENCES ON CONTROLLING REGIMES IN REACTIONS IN POROUS CATALYSTS†

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EXTERNAL DIFFUSION INFLUENCES ON CONTROLLING REGIMES IN REACTIONS IN POROUS CATALYSTS†

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The influence of diffusional transport on the porous catalyst system behaviour is usually gauged through its effect on the effectiveness factor. In general, diffusional limitation will lower the effectiveness factor and has been studied extensively in the literature. Mehta and Aris (1971) have included the effect of external diffusional resistance on the system behaviour and obtained the generalized expression of effectiveness factor for various orders of reaction. The case of a simple slab geometry was considered in their analysis and the steady state equation was solved for a general *p*th order reaction. It is interesting to analyse the transient behaviour of such a system mainly for two reasons. First the analysis is more general since the chronological time appears in the equation and secondly many of the industrially operated systems require a finite time before the steady state distributions are attained.

In this analysis we consider a spherical catalyst pellet on which an isothermal, irreversible first-order reaction is occurring. As usual, the transient material balance equation in the dimensionless form

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r} - \phi^2 C \tag{1}$$

is solved subject to the boundary conditions

$$C(o, r) = 0$$

$$\frac{\partial C(t, 0)}{\partial r} = 0, \qquad \frac{\partial C(t, 1)}{\partial r} = \mathrm{Bi}(1 - C) \tag{2}$$

in the Laplace domain to obtain the concentration profile

$$\bar{C}(r, s) = \frac{\mathrm{Bi}\left(\dfrac{\sinh\sqrt{s+\phi^2}\,r}{\sinh\sqrt{s+\phi^2}}\right)}{rs\left[(\mathrm{Bi}-1) + \dfrac{\sqrt{s+\phi^2}}{\tanh\sqrt{s+\phi^2}}\right]} \tag{3}$$

One can then proceed to calculate the effectiveness factor at any instant, which can be easily reduced to the standard steady state form in the absence of external film diffusion resistance for a spherical pellet by putting $\mathrm{Bi} = \infty$ and $\tau = \infty$. For finite values of external diffusional resistance the steady state effectiveness factor is given by (see Aris, 1975).

$$\eta = \frac{3}{\phi^2}\,\frac{(\phi\cosh\phi - \sinh\phi)\,\mathrm{Bi}}{(\mathrm{Bi}-1)\sinh\phi + \phi\cosh\phi} \tag{4}$$

This expression for effectiveness factor is a function of the Biot number which characterizes the external diffusional transport, and ϕ, the Thiele modulus which is a measure of the internal diffusional limitations.

Figure 1 shows a plot of the effectiveness factor *vs.* Thiele modulus for varying Biot number. In general, as the mass transfer resistance around the film surrounding the catalyst pellet increases as given by decreasing Bi, the effectiveness factor decreases. In addition, it can be seen from Figure 1 that the shifting of the operating regime from kinetic control to diffusional control depends on the values of the parameters ϕ and Bi. At very high values of Biot number ($\mathrm{Bi} \to \infty$) the value of Thiele modulus giving kinetic control and internal diffusion control can be fixed according to Petersen's asymptotic approximation (1965). Following the same procedure for finite values of Biot number the corresponding limiting values of ϕ can be plotted to give broadly classified regimes of operation. This classification involves the limitations on both Bi and ϕ values. In fact any criterion formulated to characterize the regime of operation must include the limitations on both these parameter values. Thus fixing of two parameters becomes necessary.

SINGLE PARAMETER REPRESENTATION

An alternative procedure is employed here to reduce the number of parameters required for the characteriza-

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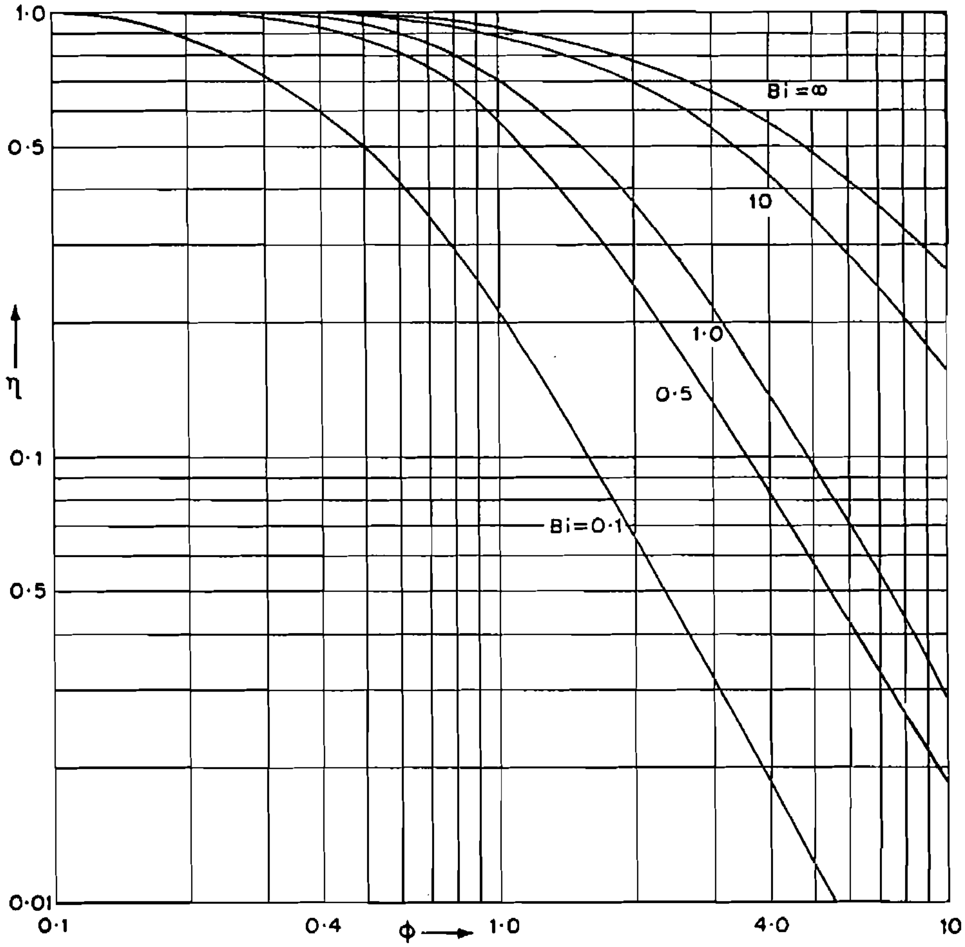

FIGURE 1 Effectiveness factor (η) as a function of Thiele modulus (φ) for various values of Biot number (Bi).

tion of the operating regime from two to one. In this method, a characteristic quantity is derived which depends on both Thiele modulus and Biot number. The development outlined here closely follows the method of calculation of the limiting Sherwood number for multiparticle systems. Such a calculation for systems with external diffusional resistance but no chemical reaction is given by Wakao *et al.* (1973) and Suzuki (1975). In their procedure, the flux at the surface of the particle is related to the increase of average concentration of the fluid (obtained by knowing the transient concentration profile) and the mass transfer coefficient is defined as

$$k_g = \tfrac{4}{3}\pi R^3 \frac{d\bar{C}}{dt} \Big/ 4\pi R^2 \bar{C} \tag{5}$$

By taking the limit as $t \to \infty$, we get the limiting value of the mass transfer coefficient which in turn gives the limiting Sherwood number. The rapidness of attainment of concentration equilibrium between fluid and particles can also be estimated.

Equation (5) is obtained in the real time plane. Instead of this consider a similar operation carried out in the Laplace domain to yield a dimensionless coefficient γ, defined as

$$\gamma(s) = -\left[\frac{d\bar{C}(s)}{ds}\right]_{s\to 0} \Big/ \bar{C}(s)_{s\to 0} \tag{6}$$

Taking the inverse transform will immediately reveal that the coefficient γ is nothing but the Fourier coefficient τ_s. Also, the limiting value as $s \to 0$ represents $t \to \infty$ and therefore equilibrium. Thus in the transformed plane we get the limiting value of γ as the characteristic time which is indicative of the time required for the system to come to a steady state value when the system undergoes a disturbance. Thus the

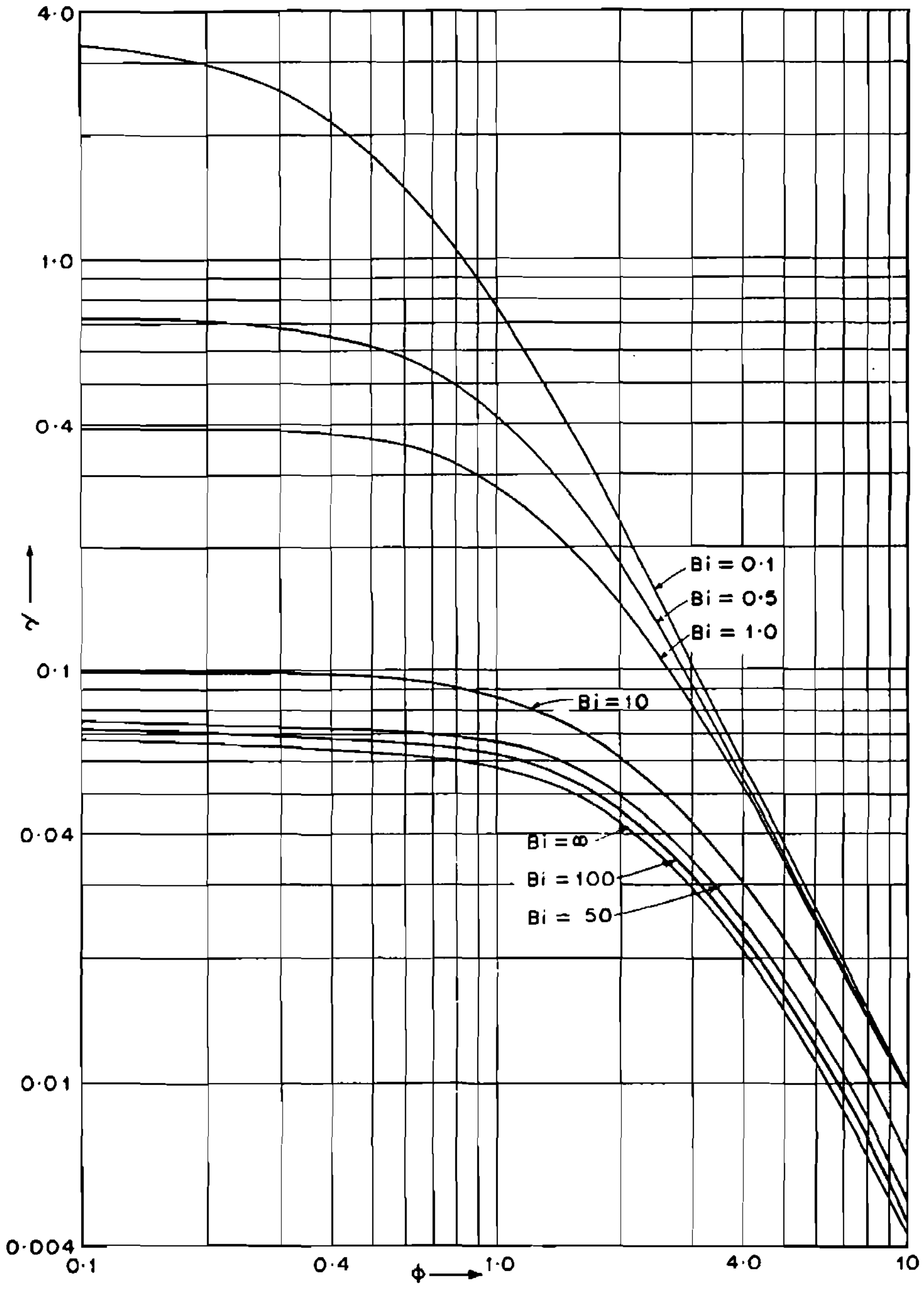

FIGURE 2 Characteristic time (γ) as a function of Thiele modulus (ϕ) for various values of Biot number (Bi).

magnitude of γ is a measure of the duration of the unsteady state period of the process. It may be noted that although the expressions for mass transfer coefficient k_g and the time coefficient γ are derived in a similar fashion, they do not in fact, have any relationship with each other.

Evaluation of the characteristic time γ of the process, however, requires the knowledge of the averaged concentration in the s plane. For this, Eq. (3) can be averaged by integrating this expression with respect to the radial parameter r between the limits zero and unity. The resulting equation for γ can then be written as

$$\gamma = -\frac{\sinh\phi}{2(\phi\cosh\phi - \sinh\phi)} + \frac{1}{\phi^2} + \frac{1}{2\phi}\,\frac{\mathrm{Bi}\cosh\phi + \phi\sinh\phi}{\{(\mathrm{Bi}-1)\sinh\phi + \phi\cosh\phi\}} \tag{7}$$

Thus we find that the characteristic time γ is also a function of the Biot number and the Thiele modulus. Equation (7) is plotted in Figure 2.

From Eqs. (4) and (7), it can be observed that both η and γ are functions of Biot number and Thile modulus. As already mentioned, these two parameters characterize the regime of operation. Thus superimposing the two equations offers us the possibility of expressing the effectiveness factor as a function of the characteristic time, wherein the Biot number and Thiele modulus are implicitly involved. A graphical procedure appears to be much simpler and thus in Figure 3, effectiveness factor is plotted against the characteristic time for constant values of Biot number and Thiele modulus.

Figure 3 shows the effect of external mass transfer on the effectiveness factor and the characteristic time required for the system to come to a steady state. As a general observation, it can be stated from Figure 3 that for a given value of ϕ the effectiveness factor tends to decrease and the characteristic time tends to increase as the external diffusion resistance increases. Thus taking the curve for constant $\phi = 5$, the effectiveness factor and characteristic time required under conditions of negligible external transport resistance ($\mathrm{Bi} \to \infty$) are 0.464 and 0.015 respectively. As the external diffusion resistance increases (say $\mathrm{Bi} = 1$) the effectiveness factor decreases to 0.1 and the characteristic time increases to 0.035. Thus the effectiveness factor is decreased 4.5 times whereas the time required to attain the steady state is more than doubled.

Now taking the case of low value of ϕ, say $\phi = 0.1$, the effectiveness factor and characteristic time required under conditions of no external resistance are 1.0 and 0.07 respectively. For the external diffusion resistance corresponding to $\mathrm{Bi} = 0.1$, the effectiveness factor is reduced to 0.96 whereas the characteristic time required increases to 3.26. Thus for low values of ϕ, the effectiveness factor has changed very little whereas the characteristic time has increased by a factor of as high a value as 50. Thus it can be concluded that as the internal diffusion resistance increases, the effect of external transport becomes more and more pronounced on the effectiveness factor and less and less on the characteristic time.

A careful observation of Figure 3 reveals some interesting observations. For low values of ϕ (<0.1) the system is unambiguously in the kinetic regime.

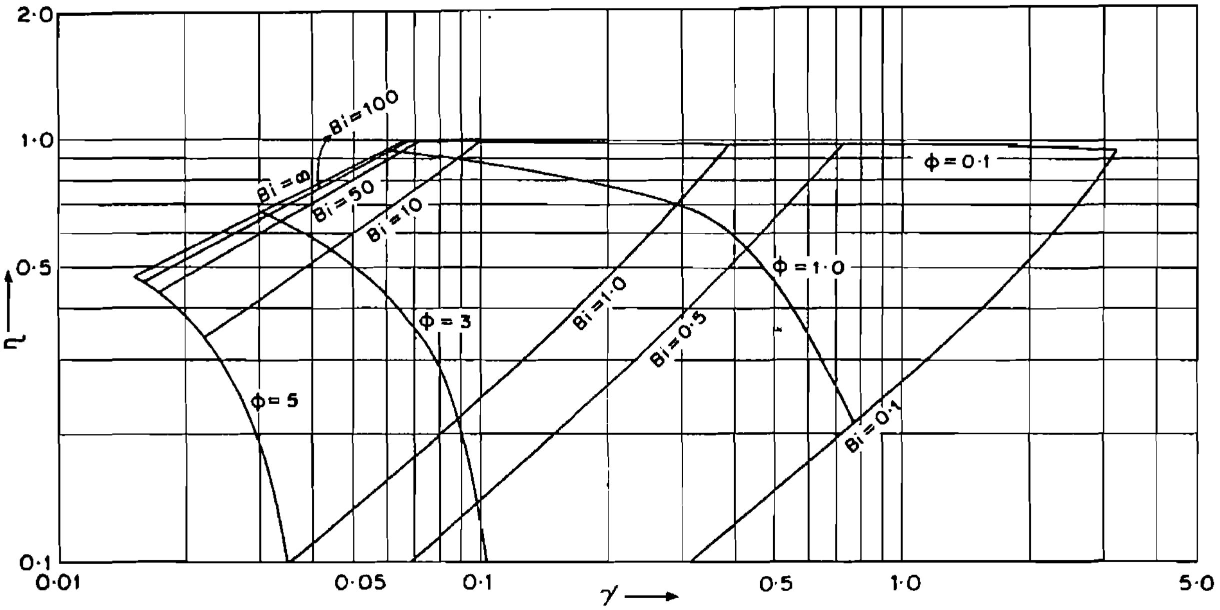

FIGURE 3 Effectiveness factor (η) as a function of characteristic time (γ) for various values of the parameter Bi and ϕ.

This is true even for very low values of Biot number (Bi = 0.1). However, the characteristic time is high when Biot numbers are small. As the value of Biot number increases the system remains in the kinetic regime but less time is required to attain the steady state.

For values of characteristic time less than 0.03 the system is in the internal diffusion controlled regime. This is so because for these values of γ for the system, a Biot number less than 10 and Thiele modulus less than 3 cannot exist. Under these conditions, trying to increase external mass transfer coefficient will yield no results but modification in the catalyst structure may be helpful. At values of $\gamma > 0.07$ the system can be in the kinetic regime when $\phi < 0.1$. For values of $\phi > 0.1$, the system experiences the diffusion resistance (both external and internal). Any increase in the value of γ beyond 0.1 will push the system in the direction of the external diffusion controlled zone since higher values of ϕ ($\phi > 3$) cannot be realized in this zone. Thus a characterization of the regime of operation is possible using a single parameter.

In the present work an attempt has been made to characterize the system behaviour in terms of a single parameter whereas conventionally two parameters Bi and ϕ have to be specified to characterize the system behaviour. Secondly the influence of external transport on the characteristic time of the process has been explicitly spelled out here for the first time.

NOMENCLATURE

Bi	Biot number, $k_g\delta/D$
c_s	concentration at the surface
C	dimensionless concentration, c/c_s
$\bar{C}$	concentration in Laplace domain
D	diffusivity
k	reaction rate constant
k_g	external mass transfer coefficient
r	dimensionless radial distance, x/R
R	radius of the particle
s	Laplace transform parameter
t	time
x	radial distance

Greek symbols

γ	characteristic time defined by Eq. (6)
δ	external film thickness
ϵ	porosity of particle
η	effectiveness factor
ϕ	Thiele modulus, $R\sqrt{k/D}$
τ	dimensionless time parameter, $Dt/\epsilon R^2$
τ_s	value of τ under steady state condition

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