Comparison Between Dispersion and Plug-Flow Models for Fixed-Bed Enzyme Reactors

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Introduction

The axial dispersion model is widely used to represent the flow of fluid inside packed-bed reactors, despite the inaccuracy of some of its predictions (Sundaresan et al., 1980). One of these inaccuracies is the fact that dispersion model predicts backmixing whereas it has been experimentally shown by Hiby (1963) that there is virtually no fluid backmixing in a packed-bed. It also predicts, because of the parabolic nature of the equation, an infinite speed of signal propagation. Sundaresan et al. (1980) have compared the dispersion model to other simple models and concluded that, despite these drawbacks, it is the most adequate for design purposes for medium or low dispersion.

However, when other phenomena present in the reactor, that is, mass transfer and reaction, are taken into account, the resolution of the resulting equations may be a lengthy task. This is why a simplification like the plug-flow is popular, although its accuracy may be questioned. It is known that in the case of immobilized enzyme reactors, the presence of dispersion has no effect on the substrate conversion in the zero order region of the Michaelis-Menten kinetics (Kobayashi and Moo-Young, 1971) whereas in the first-order region the conversion is lower in the presence of dispersion (Fogler, 1980), but is has also been observed that a plug-flow model can be used to represent experimental data obtained with immobilized enzyme fixed-bed reactors (Marrazzo et al., 1975; Lortie and Thomas, 1986) or even fluidized-bed reactors (Vallat et al., 1986).

The objective of this article is first to assess the use of a plug-flow model to represent and analyze experimental data obtained with a fixed-bed reactor in which axial dispersion is present and secondly to evaluate the significance of the results, especially the identified parameters, obtained in such case. To do so, data were generated with the dispersion model, by solving the second-order differential equation coupled to an algebraic equation representing the external mass transfer and the reaction rate. These data were then used to identify the parameters of the plug-flow model with external mass-transfer resistance by a nonlinear regression method. The ability of the plug-flow model to represent the data was verified and the parameters used in the model were compared to those in the original dispersion model.

Theory

Considering the reactor at steady state, taking axial dispersion into account and representing the transfer between the liquid and the solid phase by the stagnant film model, the mass balance over the substrate in the liquid phase is given by:

$$0 = D\frac{d^2S}{dz^2} - v\frac{dS}{dz} - k_La(S - S_i) \tag{1}$$

with the usual Danckwerts (1953) boundary conditions

$$\text{at} \quad z = 0,\ S = S_0 + \frac{D}{v}\frac{dS}{dz} \tag{2}$$

$$\text{at} \quad z = L,\ \frac{dS}{dz} = 0 \tag{3}$$

It has been shown that, in the case of an immobilized enzyme obeying Michaelis-Menten kinetics, the global reaction rate may be represented by a simple rate equation using apparent parameters and interfacial concentration, even in the presence of internal diffusion (Lortie and André, 1990). The mass balance over the substrate at the interface is then given by

$$k_La(S - S_i) = \frac{V''_{\max}S_i}{K''_M + S_i} \tag{4}$$

These equations may be rewritten in dimensionless form by defining the following variables:

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$$x = z/L \quad \text{and} \quad c = S/K_M'' \tag{5}$$

$$0 = \frac{1}{Pe_r}\frac{d^2c}{dx^2} - \frac{dc}{dx} - St(c - c_i) \tag{6}$$

$$\frac{1}{Da}(c - c_i) = \frac{c_i}{1 + c_i} \tag{7}$$

with

$$\text{at} \quad x = 0, \; c = c_0 + \frac{1}{Pe_r}\frac{dc}{dx} \tag{8}$$

$$\text{and at} \quad x = 1, \; \frac{dc}{dx} = 0 \tag{9}$$

It should be noticed that for the sake of simplicity and to avoid the use of a void fraction coefficient, k_La and $V''_{\max}$ are reported per unit volume of solution.

By neglecting the dispersion term, the plug-flow model is obtained:

$$0 = \frac{dc}{dx} + St(c - c_i) \tag{10}$$

$$\frac{1}{Da}(c - c_i) = \frac{c_i}{1 + c_i} \tag{11}$$

with

$$\text{at} \quad x = 0, \; c = c_0 \tag{12}$$

The objective of this article is to assess the use of this latter model by generating data with the dispersion model and trying to represent them with the plug-flow model.

The dispersion model was solved by a Petrov-Galerkin finite element method using piecewise linear elements (Reddy, 1984). This approach ensures that, for high values of the Péclet number, no spurious oscillations are generated in the numerical solution (Teztuyar et al., 1987). The resulting system of algebraic equations was solved by Newton's method and Gaussian elimination.

Conversions were calculated for 11 input concentrations, ranging from $c_0 = 0.1$ to $c_0 = 5.0$ for each combination of Pe_r, St and Da. These data were then used to evaluate the two parameters of the plug-flow model, St and Da. To do so, Eq. 10 was solved by a fourth order Runge-Kutta method, the value of c_i being calculated from Eq. 11 every time it is needed, and the routine written to solve this set was used as a subroutine in a nonlinear least-square regression program using Marquardt's algorithm.

Results and Discussion

The fit between data generated by the dispersion model and the plug-flow model is excellent, even when the dispersion is high ($Pe_r = 5$), as can be seen from the three examples shown on Figure 1. All the other calculations showed the same quality of fit. As expected, when the degree of dispersion is very low ($Pe_r \geq 1{,}000$) the dimensionless parameters identified using the plug-flow model are identical to those used in the dispersion model. When the importance of dispersion increases, the dimensionless parameters identified with the plug-flow start to depart from the original ones, as seen on Figures 2 to 4.

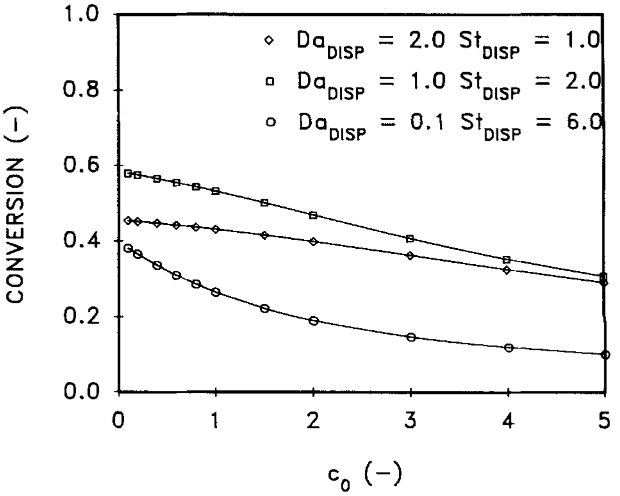

Figure 1. Comparison between conversions calculated with the dispersion model (points) and the plug-flow model (solid curves) for $Pe = 5$.

When the degree of dispersion is low, since $St_{\text{Disp}} \approx St_{\text{PFR}}$ and L and v are design parameters, one can say that the value of k_La identified using a plug-flow model is exact, and since $Da_{\text{Disp}} \approx Da_{\text{PFR}}$, the ratio $V''_{\max}/K''_M$ should also be correct. If experimental data are available in both zero and first-order regions, the individual values of the parameters can be identified.

To evaluate the exactness of the dimensional parameters for higher dispersion, we plotted the value of $Da_{\text{PFR}}/Da_{\text{Disp}}$ against $St_{\text{Disp}}/St_{\text{PFR}}$ for $Pe_r = 5$. As can be seen on Figure 5, $Da_{\text{PFR}}/Da_{\text{Disp}} \approx St_{\text{Disp}}/St_{\text{PFR}}$, except for $Da_{\text{Disp}} = 5.0$. This means that

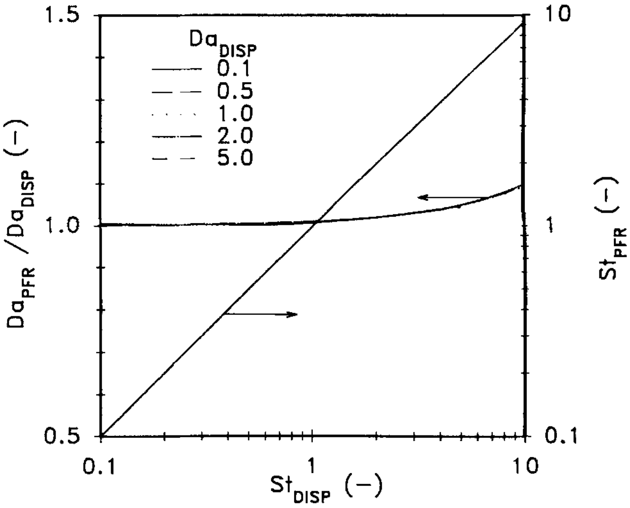

Figure 2. Variation of the dimensionless parameters estimated with the plug-flow model for $Pe = 100$.

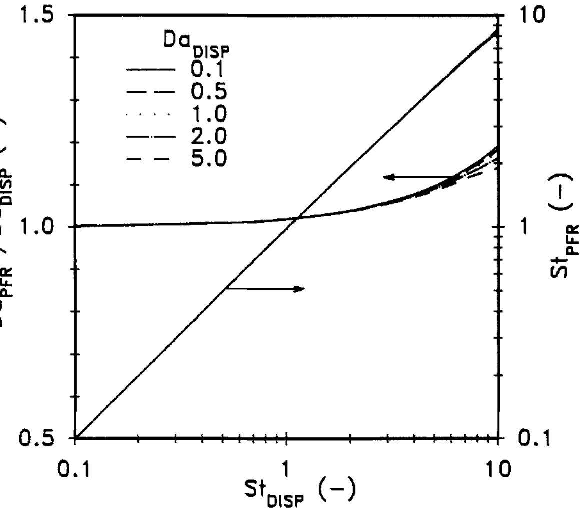

Figure 3. Variation of the dimensionless parameters estimated with the plug-flow model for *Pe* = 50.

$$\frac{k_L a_{\mathrm{Disp}} L}{v}\,\frac{v}{k_L a_{\mathrm{PFR}} L} = \frac{\dfrac{V''_{\max_{\mathrm{PFR}}}}{k_L a_{\mathrm{PFR}} K''_{M_{\mathrm{PFR}}}}}{\dfrac{V''_{\max_{\mathrm{Disp}}}}{k_L a_{\mathrm{Disp}} K''_{M_{\mathrm{Disp}}}}} \tag{13}$$

$$\frac{V''_{\max_{\mathrm{PFR}}}}{K''_{M_{\mathrm{PFR}}}} = \frac{V''_{\max_{\mathrm{Disp}}}}{K''_{M_{\mathrm{Disp}}}} \tag{14}$$

Once again, the ratio $V''_{\max}/K''_M$ identified with the plug-flow model is exact and the individual parameters may be identified correctly by making measurements in the two limit regions. However, when the dispersion is important, the value identified for $k_L a$ is different from the original one and they are linked by:

$$k_L a_{\mathrm{PFR}} = k_L a_{\mathrm{Disp}} \frac{St_{\mathrm{PFR}}}{St_{\mathrm{Disp}}} \tag{15}$$

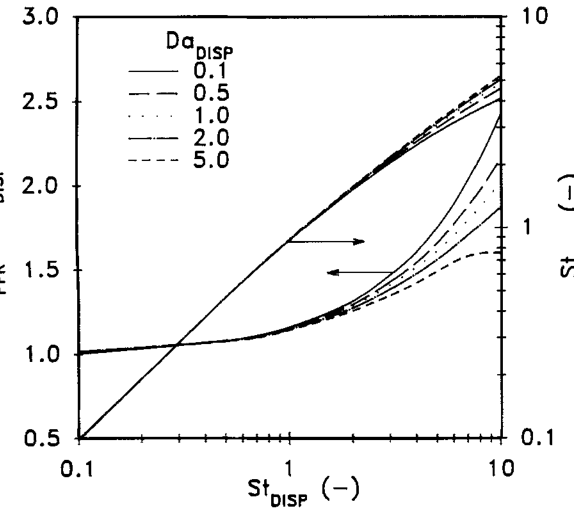

Figure 4. Variation of the dimensionless parameters estimated with the plug-flow model for *Pe* = 5.

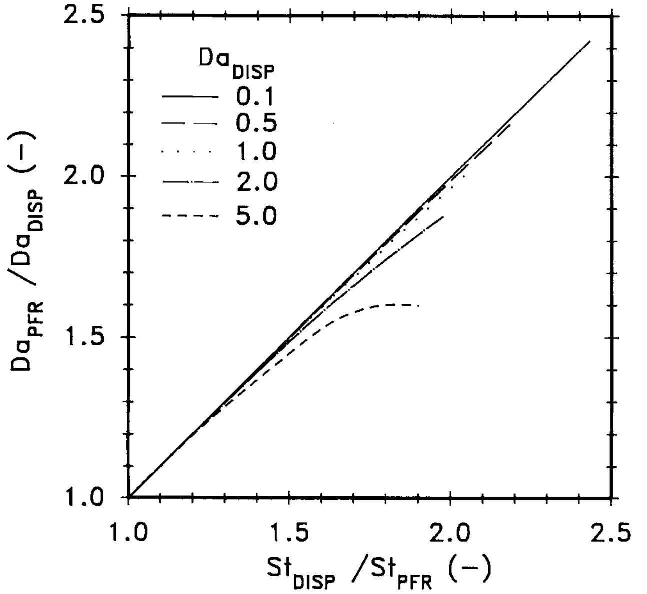

Figure 5. Comparison between the identified dimensionless parameters identified with the plug-flow model and used in the dispersion model.

As can be seen from Figures 2–4, the ratio $St_{\mathrm{PFR}}/St_{\mathrm{Disp}}$ decreases when the dispersion increases, for given values of Da_{Disp} and St_{Disp}, meaning that the value of $k_L a$ identified becomes much smaller than the true value when dispersion increases. The lower values of the mass-transfer coefficient serve to diminish the conversion calculated with the plug-flow model to fit with the lower conversion caused by the presence of dispersion. The lower mass-transfer coefficient has little effect on conversion in the zero-order region and diminishes the calculated conversion in the first-order region, just as the dispersion. This also explains the dependence of both St_{PFR} and Da_{PFR} on St_{Disp} and Da_{Disp}: when Da_{Disp} is low, the reaction is limited by the kinetics and the mass-transfer coefficient has little effect on the conversion, it is then necessary to vary $k_L a$ significantly to adjust the plug-flow model to the results and this will reflect on the values of St_{PFR} and Da_{PFR}. The same reasoning applies to the dependence on St_{Disp}: when the parameter is high, there is little influence of the mass-transfer on the conversion, high variations of $k_L a$ are then necessary to adjust the plug-flow model. Since the diminution of the mass-transfer coefficient serves to tune the plug-flow model when dispersion increases in the reactor to be represented, it is normal that the dependence of St_{PFR} and Da_{PFR} on St_{Disp} and Da_{Disp} increases when the dispersion becomes more important.

It should be noticed that for the high values of Da and St for which the error on the estimated value of $k_L a_{\mathrm{PFR}}$ is the highest, the substrate conversion is almost total (95–99.9%) and not very sensitive to the changes in the input concentration, so that these conditions should be avoided in the characterization of a reactor.

Conclusions

The results obtained in this study explain the findings of previous works (Marazzo et al., 1975; Lortie and Thomas, 1986) stating that it is not necessary to take the axial dispersion into account to describe an immobilized enzyme fixed-bed reactor at steady state.

If the dispersion can be evaluated, either by simple pulse response experiments or by use of correlations, and the reactor Péclet number is found to be greater than 100–200, the value of the mass-transfer coefficient has a physico-chemical meaning. However, if the dispersion is high, the mass-transfer coefficient acts as a tuning parameter to diminish the calculated conversion and has no direct meaning.

Since the plug-flow model can represent data as well as the dispersion model, the dispersion coefficient and the global mass-transfer coefficient are highly correlated. When using the dispersion model to analyze experimental data, the dispersion coefficient should be determined independently and one should be aware that any inaccuracy on its value will reflect on the mass-transfer coefficient.

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Notation

c = dimensionless concentration
D = axial dispersion coefficient (L^2t^{-1})
Da = Damköhler number, $V''_{\max}/(K''_M k_L a)$
$k_L a$ = global mass-transfer coefficient (t^{-1})
K''_M = apparent Michaelis constant of immobilized enzyme ($M \cdot L^{-3}$)
L = length of the reactor (L)
Pe_r = reactor Péclet number, $(\nu L)/D$
S = substrate concentration ($M \cdot L^{-3}$)
St = Stanton number, $(k_L a L)/\nu$
ν = interstitial velocity ($L \cdot t^{-1}$)
$V''_{\max}$ = apparent maximal reaction rate ($M \cdot L^{-3} \cdot t^{-1}$)
x = dimensionless axial coordinate
z = axial coordinate (L)

Subscripts

0 = inlet concentration
Disp = used in the dispersion model
i = interfacial concentration
PFR = used in the plug-flow model

Literature Cited

Danckwerts, P. V., "Continuous Flow Systems. Distribution of Residence Times," *Chem. Eng. Sci.*, **2**, 1 (1953).

Fogler, H. S., *Elements of Chemical Reaction Engineering*, Prentice-Hall, Englewood Cliffs, NJ (1980).

Hiby, J. W., "Longitudinal and Transverse Mixing During Single-Phase Flow Through Granular Beds," *Interactions Between Fluids and Particles*, p. 312, Institute Chemical Engineers, London, England (1963).

Kobayashi, T., and M. Moo-Young, "Backmixing and Mass-Transfer in the Design of Immobilized-Enzyme Reactors," *Biotechnol. Bioeng.*, **13**, 893 (1971).

Lortie, R., and G. André, "On the Use of Apparent Kinetic Parameters for Enzyme-Bearing Particles with Internal Mass-Transfer Limitations," *Chem. Eng. Sci.*, **45**, 1133 (1990).

Lortie, R., and D. Thomas, "Heterogeneous One-Dimensional Model for Fixed Bed Enzyme Reactors," *Biotechnol. Bioeng.*, **28**, 1256 (1986).

Marrazzo, W. N., R. L. Merson, and B. J. McCoy, "Enzyme Immobilized in a Packed-Bed Reactor: Kinetic Parameters and Mass Transfer Effects," *Biotechnol. Bioeng.*, **17**, 1515 (1975).

Reddy, J. N., *Introduction to the Finite Elements Method*, McGraw-Hill, New York, NY (1984).

Sundaresan, S., N. R. Amundson, and R. Aris, "Observations on Fixed-Bed Dispersion Models: The Role of the Interstitial Fluid," *AIChE J.*, **26**, 529 (1980).

Teztuyar, T. E., Y. J. Park, and H. A. Deaus, "Finite Element Procedures for Time-Dependent Convection-Diffusion-Reaction Systems," *Introduction to the Numerical Methods in Fluids*, **7**, 1013 (1987).

Vallat, I., P. Monsan, and J. P. Riba, "Maltodextrine Hydrolysis in a Fluidized-Bed Immobilized Enzyme Reactor," *Biotechnol. Bioeng.*, **28**, 151 (1986).

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