LETTERS TO THE EDITOR

To the Editor:

In the article titled "Dynamic Analysis of Viscous Flow and Diffusion in Porous Solids," Doğu et al. (1989) ignored previous work in the area of diffusion, intraparticle convection, and reaction. I would like to make some comments.

1. The "new" dimensionless group $D=\gamma L/2D_e$ is not new! It was introduced by Nir and Pismen (1977) in their paper on "Simultaneous Intraparticle Forced Convection, Diffusion and Reaction in a Porous Catalyst." They called it $\lambda = v_0 a/D_e$. Note that γ(Doğu) $= v_0$(Nir/Pismen) is the intraparticle convective velocity and a is the pellet characteristic dimension. Since it compares intraparticle convective flow and diffusive flow, I called it intraparticle Peclet number (Rodrigues et al., 1982). Equation 4 in that paper is also Eq. 4 in Doğu's paper.

2. D. Cresswell (1985) published a paper in which he measured intraparticle convection in a similar cell for various catalyst supports. This paper was also ignored.

3. From Doğu's paper, model equivalence between diffusion model and diffusion/convection model (by making the equality of Eqs. 12 and 15, when the flow rate in the bottom chamber F goes to infinite) leads to:

$$D_{e_0}/D_e = 1/f(\lambda)$$

a result already obtained by Rodrigues et al. (1982), when measuring effective diffusivity of a large pore catalyst. In this equation, D_{e0} is the "apparent" effective diffusivity we get from a model which considers diffusion as the only mechanism for mass transport inside pellets, D_e is the "true" effective diffusivity from a model which separates the contributions of diffusion and intraparticle convection and

$$f(\lambda)=\frac{3}{\lambda}\left[\frac{1}{\tanh\lambda}-\frac{1}{\lambda}\right]$$

I believe these references are related directly to the paper published by Doğu et al. and should not have been ignored. I also feel that the authors should have stressed the region of operation of such diffusion/convection cell. Moreover, the boundary condition used for the bottom of the pellet is valid only under certain conditions which should have been quantified.

Literature cited

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Reply:

We thank Prof. Rodrigues for pointing out the literature references on effects of intraparticle convection to the observed rates of reactions catalyzed by porous catalysts, which we missed. I agree that the dimensionless parameter D also appears in the work of Nir and Pismen (1977), who studied the effects of intraparticle-forced convection and diffusion on the rate of a heterogeneous reaction. Convective transport effects on the effectiveness factor were considered first by Weekman and Gorring (1965) considering a gas reaction with volume change. Aris and Kehoe (1973) also investigated a similar problem. Later, Nir and Pismen (1977) analyzed the effects of intraparticle-forced convection on the effectiveness factor, and Cresswell (1985) studied activity and selectivity variations caused by the convective term. In all these references, significant contributions were made to the area of convective transport effects on the observed rates in porous catalysts.

In our article, a dynamic single-pellet technique was introduced for the measurement of effective diffusivity and Darcy coefficient, and for the investigation of relative significance of diffusion and viscous flow terms in porous solids. Cresswell (1985) also reported some diffusion and convection results in a Wicke-Kallenbach (1941)-type diffusion cell. The major difference of our work from Cresswell's study is that ours is a dynamic technique while Cresswell carried out steady-state experiments.

Rodrigues et al. (1982) also considered intraparticle-forced convection in the development and reported some experimental results obtained in a packed-bed system. One of the pioneering dynamic studies on a packed bed was conducted by Schneider and Smith (1968). Although the intraparticle convection term is neglected by Schneider and Smith, their first-moment expression for an inert tracer is exactly the same as the first-moment expression reported by Rodrigues et al. In the theoretical expressions derived by Rodrigues et al., such system parameters as effective diffusion coefficient, intraparticle convection time, Peclet number, and Biot number appear in the variance (second central moment) expression. This indicates that the evaluation of these parameters from the response data will be very sensitive to experimental errors, especially in the tail region of the response peaks. On the other hand, our work showed that the viscous flow parameter and effective diffusivity appeared in the zeroth- and first-moment expressions for the single-pellet system. This is one of the major advantages of the single-pellet dynamic technique over the packed-bed studies. It is interesting to note that the ratio of diffusivities predicted by considering and neglecting forced-convection term (Eq. 20 of Rodrigues et al.) is also predicted from Eqs. 15 and 18 of the single-pellet theory (Doğu et al., 1989).

As Dr. Rodrigues pointed out in his letter, in the single-pellet system, the boundary condition at the bottom of the pellet is valid under certain conditions. These conditions were discussed in detail in the earlier work (Doğu, 1974; Doğu and Smith, 1975; Burghardt and Smith, 1979). The experimental system used in our work was designed considering these conditions.

Literature cited

Aris, R., and J. P. G. Kehoe, "Communications on the Theory of Diffusion and Reaction: IX. Internal Pressure and Forced Flow for Reactions with Volume Change," *Chem. Eng. Sci.*, **28**, 2094 (1973).

Burghardt, A., and J. M. Smith, "Dynamic Response of a Single Catalyst Pellet," *Chem. Eng. Sci.*, **34**, 267 (1979).

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To The Editor:

In the article titled "Robust Error-in-Variables Estimation Using Nonlinear Programming Techniques," Kim, Liebman, and Edgar (July 1990, Vol. 36, p. 985) describe various algorithms to carry out estimation problems when all the variables appearing in the model are subject to error.

While we share the authors' view that model linearization can lead to serious numerical difficulties, we believe the following remarks are to the point.

1. The authors state, "*all* previously proposed EVM algorithms use linear approximations of the model equations." This is not correct. In our article "Fitting of Experimental Data to Implicit Models Using a Constrained Variation Algorithm" (*Comp. & Chem. Eng.*, Vol. 13, 731, 1989), we describe an algorithm that uses a rigorous model to carry out the data reconciliation step.

2. The authors claim that their algorithms can handle "bounds or nonlinear (we presume inequality) constraints" as opposed to previous algorithms. This statement is not correct if bounds and other inequality constraints apply to parameters (again, our algorithm is capable of dealing, at least in theory, with all types of constraints, and the method described by Reilly-PatinoLeal can also be generalized in a straightforward way to include this class of constraints). On the other hand, if constraints apply to the unknown true values of data and there is a nonvanishing probability of these constraints being active, the correct probability distribution would be far from being normal. This discrepancy would introduce a severe bias in the estimated values computed using an objective function of the type:

$$(z-z')^T V^{-1}(z-z') = \min$$

3. The final algorithm results in a decoupled optimization with respect to parameters and data. According to our experience, this is where the most severe convergence difficulties turn up. A method for removing this drawback is reported in our article, where the unknown values of data are expressed implicitly as functions of the parameters.

To sum it up, we believe that the method proposed by Kim, Liebman, and Edgar is not new in addressing model nonlinearities directly and does not tackle the most important difficulty, that is, nested, but coupled, optimization with respect to data and parameters.

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Reply:

The article by Doví and Paladino appeared after our original literature search was completed, and we apologize for not referencing their contribution. The availability of this article in some respects strengthens our hypothesis that EVM with nonlinear programming is a powerful approach. We, however, should respond to the specific comments by Doví and Paladino.

1. While the probability distribution would no longer be normal, this does not guarantee the introduction of a "severe bias." The possible introduction of bias must be weighed against the cost of reconciling results, while ignoring constraints. We fully recognize that we are violating assumptions to solve a meaningful problem. While there are no guarantees, real-world problems can be addressed. We believe that our use of a modern nonlinear programming code is superior to the equation-solving ap-

proach (necessary conditions) proposed by Doví and Paladino.

2. We fully acknowledge the lack of any convergence guarantee. In our experience, however, very few convergence difficulties have arisen due to the decoupling of the parameter estimation and the data reconciliation portions of the algorithm. As discussed in our article, frequent difficulties arose due to the linearization step. Our algorithm avoids such difficulties. As an aside, Doví and Paladino utilize a different decoupling scheme in their article. They also implicitly recognize that the decoupling seems to work but provides no guarantee.

We feel that our article is a significant contribution to current EVM research efforts. In particular, it documents a weakness in many current EVM problems. All current techniques (ours and Doví and Paladino's included) have limitations and inherent assumptions that restrict their applicability. The comments by Doví and Paladino reflect their emphasis on a different set of assumptions and priorities.

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