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LETTERS TO THE EDITORS

Comments on "Reactor Dynamics in the Evaluation of Photocatalytic Oxidation Kinetics"

Davis and Hao (*1*) presented a reactor analysis of a situation common in photocatalysis: a plug flow photoreactor in a recirculation loop with a well-stirred, nonreacting mixing tank often used to provide aeration and/or monitoring probes such as pH, halide ion, dissolved oxygen, or CO_2 electrodes (*3–5*). The authors note that for a differential conversion recirculating reactor "the apparent reaction rate . . . is a composite expression consisting of elements originating in chemical kinetics and reactor dynamics." We agree with this observation. We maintain, however, that our interpretation of the experimental rate data is correct and that the author's analysis is based on an incorrect assumption relating to the reactor model. In this letter, we briefly summarize the authors' argument, point out its flaw, and then present what we hold to be the correct model derivation. For the sake of clarity, we use the nomenclature of Davis and Hao.

Davis and Hao model the reactor system, a recirculating differential conversion reactor, as a plug flow reactor (PFR) in series with a continuous stirred tank reactor (CSTR). Figure 1 shows a schematic diagram of their model system. The photocatalytic reaction is occurring in the PFR, the kinetics of which obey the Langmuir–Hinshelwood (LH) rate expression

$$\text{rate} = -\frac{dc}{dt} = \frac{K_1 c}{1 + K_2 c}, \tag{1}$$

while the CSTR is simply a mixing tank. The authors derive expressions for the change in reactant concentration with respect to space time for both the CSTR and the PFR and then derive relationships between the measured and actual kinetic rate constants in the limits of low and high solute concentration. The purpose of restricting the analysis to these limits is due to the awkward algebraic form of the LH rate expression.

For a single-volume system that follows the kinetics of Eq. (1), it is intuitive that the rate should approach K_1c at low concentrations of c ($1 \gg K_2c$) and K_1/K_2 at high values of c ($1 \ll K_2c$). It follows, therefore, that in the limit, as the mixing tank volume (V_1) goes to zero, the rate expressions derived by Davis and Hao should also approach these values. They present the following equations for the limiting values:

$$\text{rate} = K_{\text{app}}^{\text{low}} c; \quad K_{\text{app}}^{\text{low}} = \frac{\theta_2}{\theta_1} K_1 = \frac{V_2}{V_1} K_1 \tag{2}$$

$$\text{rate} = K_{\text{app}}^{\text{high}}; \quad K_{\text{app}}^{\text{high}} = \frac{\theta_2 K_1}{\theta_1 K_2} = \frac{V_2 K_1}{V_1 K_2}. \tag{3}$$

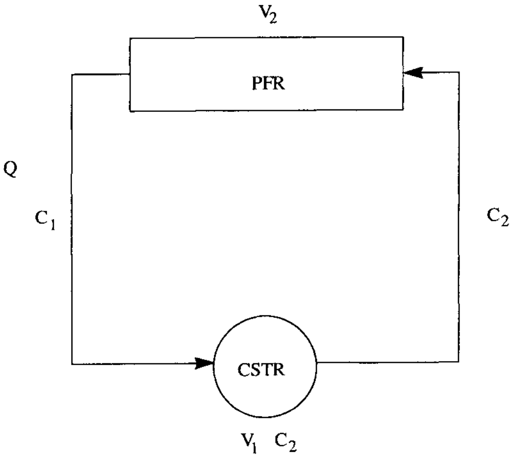

FIG. 1. Schematic diagram of the differential conversion recirculating system of Davis and Hao (*1*).

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TABLE 1

Equations Relating the Inlet and Outlet Concentrations of a PFR when Both Are Changing with Time

Equation	$t < \theta_2$	$t \geq \theta_2$
Exact	$\ln(C_o/c_1(t)) + K_2(C_o - c_1(t)) = K_1 t$	$\ln(c_2(t - \theta_2)/c_1(t)) + K_2(c_2(t - \theta_2) - c_1(t)) = K_1\theta_2$
First order	$c_1(t) = C_o \exp(-K_1 t)$	$c_1(t) = c_2(t - \theta_2) \exp(-K_1\theta_2)$
Zeroth order	$c_1(t) = C_o - (K_1/K_2)t$	$c_1(t) = c_2(t - \theta_2) - (K_1/K_2)\theta_2$

These are Eqs. (8) and (9c) in their note (Θ_n is the space time in vessel n, V_n/Q). In the above equations, as $V_1 \rightarrow 0$, both of these apparent rate constants approach infinity, indicating some inconsistency in the analysis.

A close examination of the integrated PFR design equation [Eq. (6) of Davis and Hao] shows that it is very subtly flawed. This equation is exact only if $c_1(t)$ and $c_2(t)$ are constant (i.e., if the system is at steady state). Since this is a dynamic system (both c_1 and c_2 are changing with time), this temporal dependence must be addressed. The fundamental equations describing this system are

$$\frac{\partial c_{pfr}(t,\theta_{pfr})}{\partial t} = -\frac{\partial c_{pfr}(t,\theta_{pfr})}{\partial \theta_{pfr}} - r \tag{4}$$

$$\frac{dc_2(t)}{dt} = \frac{1}{\Theta_1}(c_1(t) - c_2(t)). \tag{5}$$

Equation (4) has the boundary conditions $c_{pfr}(t,0) = c_2(t)$ and $c_{pfr}(0,\theta_{pfr}) = C_o$. Equation (5) has the initial condition $c_2(0) = C_o$ and is essentially Eq. (2) in Davis and Hao's note. However, where only the inlet and outlet conditions of the PFR are of interest, we can simplify the analysis as depicted in Table 1.

After one residence time (i.e., for $t \geq \theta_2$), the outlet concentration of the PFR $c_1(t)$ is related to the inlet concentration one residence time ago $c_2(t - \theta_2)$. Only for a PFR operating at steady state is the inlet concentration constant, $c_2(t - \theta_2) = c_2(t)$, and thus Eq. (6) of Davis and Hao correct. Note that for all three rate expressions (LH, first-order or second-order kinetics), the equations in Table 1 are exact. Thus, Eq. (5), from a mass balance around the mixing tank, along with the appropriate equations from Table 1, completely describes the reactor system for all $t > 0$, regardless of the extent of conversion in the PFR.

To demonstrate how the subtlety regarding the residence time in the PFR affects the subsequent analysis, we write the design equation for the low concentration range (i.e., for first-order kinetics in the reactor) for $t \geq \theta_2$:

$$c_1(t) = c_2(t - \theta_2) \exp(-K_1\theta_2). \tag{6}$$

Substitution of Eq. (6) into Eq. (5) yields an expression involving $c_2(t)$ and $c_2(t - \theta_2)$. Since by definition $c_2(t) \neq c_2(t - \theta_2)$, we must use some approximation to relate these two quantities. An elementary relation, valid for small values of θ_2, is the first-order backward difference equation

$$c_2(t - \theta_2) \approx c_2(t) - \theta_2 \frac{dc_2(t)}{dt}. \tag{7}$$

Upon substitution of Eq. (7) into Eq. (6), substitution of the result into Eq. (5), and rearrangement, we find

$$\frac{dc_2(t)}{dt} \times (\theta_1 + \theta_2 + K_1\theta_2^2) = -\theta_2 K_1 c_2(t). \tag{8}$$

For small values of θ_2, the third term in parentheses can be neglected, and we obtain the correct relationship:

$$\frac{dc_2(t)}{dt} = -\frac{\theta_2}{\theta_1 + \theta_2} K_1 c_2(t)$$

$$= -\frac{V_2}{V_1 + V_2} K_1 c_2(t). \tag{9}$$

A similar treatment for zeroth-order kinetics in the PFR yields the same ratio between the observed and the actual kinetics. Thus, the correct method for normalizing kinetic data obtained in differential conversion recirculating reactors is not multiplication by the ratio of the active volume to the inactive volume V_2/V_1 as suggested by Davis and Hao, but by the ratio of the active volume to the total volume $V_2/(V_1 + V_2)$.

The derivation of Eq. (9) presented in this communication was based on a differential conversion system (small θ_2) which allows us to neglect the $K_1\theta_2^2$ term in Eq. (8). Thus, Eq. (9) is an approximation although the equations in Table 1 are exact. As pointed out by Davis and Hao, if substantial conversion per pass is obtained, one must certainly account for the mixing in the dark tank. Under these conditions one cannot simply ratio the observed kinetics by $V_2/(V_1 + V_2)$ to arrive at the "true" kinetics. The appropriate equations from Table 1 along with Eq. (5) must be solved simultaneously to obtain expressions for $c_1(t)$ and $c_2(t)$, which can then be used to determine the appropriate rate constants. This methodology can be used to solve numerically for the concentration profile in any recirculating batch process and has yielded excellent fits to the data from a pilot-scale solar photocatalytic water detoxification system (*2*).

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