ACKNOWLEDGMENT

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NOTATION

A = constant, Eq. 3
B = constant, Eq. 4
J = constant, Eq. 2
M_W = molecular weight
P_C = critical pressure, atm
T = temperature, K
T_0 = constant, Eq. 3
T_f = freezing point temperature, K
T_c = critical temperature, K
T_r = reduced temperature, K
V_0 = intrinsic molal volume, cm^3·mol^{-1}
V_c = critical volume, cm^3·mol^{-1}
V_r = function defined by Eq. 10
V_{SC} = scaling parameter, Eq. 8

Greek Letters

Γ = function defined by Eq. 11
η_L = liquid viscosity, cP
η_L^+ = pseudocritical viscosity
θ = group contribution parameter, Eq. 1
ρ_L = liquid density
ω = acentric factor

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The Adsorption of Dyestuffs from Aqueous Solutions Using Activated Carbon: An External Mass Transfer and Homogeneous Surface Diffusion Model

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Adsorption has been used extensively in industrial processes for the purposes of separation and purification. The removal of colored and colorless organics from water is an important application of adsorption. A study of agitated batch adsorbers yields important kinetic and design data useful in the prediction of batch adsorber performance. In the present work the adsorption of two dyestuffs, deorlene yellow (basic) and telon blue (acidic), in aqueous solution onto activated carbon has been studied using an agitated batch adsorber. The equilibrium isotherm for each single component system has been determined and a mass transfer model has been proposed to enable calculation of the time-dependent concentration decay curves.

In this paper the mass transport model is based on external mass transfer and homogeneous solid phase diffusion. In a previous model, based on film and solid phase diffusion, Matthews and Weber (1976) developed a mathematical technique for predicting concentration versus time decay curves. This initial procedure enabled the diffusion transport equation for batch adsorption to be evaluated using a numerical solution for both dimensionless time and dimensionless distance using the Crank-Nicholson method. The procedure developed in the present paper incorporates a time-dependent analytical solution for dimensionless distance and a numerical component for dimensionless time.

EXPERIMENT

The adsorption of two dyestuffs, telon blue (Acid Dye 25) and deorlene yellow (Basic Yellow 11), onto activated carbon (Filtrasorb 400 supplied by Chemviron, Ltd.) has been studied. The carbon was sieved before use and the particle size range used in all experiments was 500 to 710 μm. Kinetic studies have been performed in a baffled, well-agitated batch adsorber. The apparatus, experimental procedues, and the results of isotherm and batch contact time studies have been reported in detail by McKay (1982).

Mathematical Development

External Mass Transfer and Intraparticle Diffusion Model for Batch Adsorption. Adsorption rate data from batch reactors has been analyzed using a model that includes the effects of external mass transfer, unsteady state intraparticle diffusion in the particle, and nonlinear adsorption isotherm.

Fundamental Equations. The mechanistic processes that are considered in presenting single component adsorption are (a) film diffusion from the fluid phase to the surface of the particle; (b) adsorption on the surface; and (c) diffusion in the particle. In addition, a material balance equation for the batch system is necessary to describe the adsorption process.

The rate of change of concentrations of the solid phase is equated to the rate of mass transfer of the solute from the fluid phase through the film to obtain

$$\frac{d\overline{Y}_t}{dt} = \frac{K_f S_p}{V_{pe}(1 - \epsilon_p)}[C_t - C_s] = \frac{3K_f}{R_e(1 - \epsilon_p)}(C - C_s) \qquad (1)$$

since $S_p = 4\pi R^2$ and $V_p = 4/3\pi R^3$.

The theoretical model is basically that of Matthews and Weber (1976) and involves the simultaneous solution of Eqs. 2 to 13. The previous model incorporated a scheme whereby Eq 9 was solved numericaly using the Crank-Nicholson method. Using the same technique in several experimental situations reported in this paper, the program ran into stability problems when evaluating Eq. 9. A more stable procedure has been evolved using a semianalytical solution of Eq. 9 represented by Eq. 14, thus avoiding direct numerical solution of Eq. 9.

The average concentration of the particle is obtained by averaging the point concentration over the volume of the particle:

$$\overline{Y}_t = \frac{3}{R^3}\int_0^R Y_r r^2 dr \qquad (2)$$

The isotherm expression can be written in the general form of the three-parameter Redlich-Peterson isotherm (Jossens et al., 1978):

$$Y_s = \frac{K_m C_s}{1 + b_m (C_s)^{\beta_m}} \qquad (3)$$

where $\beta_m < 1.0$.

For a spherical particle, the variation of the solid-phase concentration in the radial direction is given by

$$\frac{\partial Y_r}{\partial t} = D_p\left[\frac{\partial^2 Y_r}{\partial r^2} + \frac{2}{r}\frac{\partial \overline{Y}_r}{\partial \overline{r}}\right] \qquad (4)$$

$$V\frac{dC_t}{dt} = -W\frac{d\overline{Y}_t}{dt} \qquad (5)$$

Initial conditions, at $t = 0$:

$$Y_r(r,t) = 0 \text{ and } C_t = C_0, \qquad (6)$$

and boundary conditions

$$Y_r(R,t) = Y_s(R,t) = Y_s(t) \qquad (7)$$

and

$$\frac{\partial Y_r(0,t)}{\partial r} = 0 \qquad (8)$$

The independent variables in Eq. 4 can be transformed into dimensionless variables:

$$\tau = D_p t/R^2 \quad \text{and} \quad z = r/R$$

Subsequent change of variable with $u = z \cdot Y_r$ and rearrangement give the following set of equations for adsorption in a batch reactor:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial z^2} \qquad (9)$$

$$\frac{\partial u(0,\tau)}{\partial z} = 0 = u(z,0) \qquad (10)$$

$$u(1,\tau) = u_s(\tau) \qquad (11)$$

$$\int_0^1 \frac{\partial u}{\partial \tau} z dz = \frac{3K_f R(C_t - C_s)}{D_p \rho(1 - \epsilon_p)} \qquad (12)$$

$$Y_t = 3\int_0^1 uzdz \qquad (13)$$

The system of Eqs. 3, 5, and 9 to 13 cannot be solved analytically, and finite-difference techniques must be employed.

Modified External Mass Transfer and Intraparticle Diffusion Model for Batch Adsorption

$$\frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial z^2} \qquad (9)$$

$U(Z,\tau)$ is a general solution to Eq. 9, as indicated in Carslaw and Jaeger (1959).

$$U(Z,\tau) = \int_0^\tau d\tau' f(\tau')\frac{1}{(\tau - \tau')^{0.5}} \times \left\{\exp\left[\frac{-(Z - 1)^2}{4(\tau - \tau')}\right] - \exp\left[\frac{-(Z + 1)^2}{4(\tau - \tau')}\right] - \exp\left[\frac{-(Z + 1)^2}{4(\tau - \tau')}\right]\right\} \qquad (14)$$

Equation 14 can be approximated (Abramowitz and Stegun, 1964) to become

$$U(Z,\tau) = \sum_{i=1}^{n} f_i G_i(Z,\tau_n) \qquad (15)$$

where

$$G_i(Z,\tau_n) = \int_{\tau_{i-1}}^{\tau_i} d\tau' \frac{1}{(\tau_n - \tau')^{0.5}} \times \left\{\exp\left[\frac{-(Z - 1)^2}{4(\tau_n - \tau')}\right] - \exp\left[\frac{-(Z + 1)^2}{4(\tau_n - \tau')}\right]\right\} \qquad (16)$$

and f is assumed to be piecewise constant.

Equation 15 can be written as

$$\overline{Y}(\tau_n) = 3\sum_{i=1}^{n} f_i G_i(\tau_n) \qquad (17)$$

Similarly, $Y(\tau_{n-1})$ is obtained, and subtracting

$$\overline{Y}(\tau_n) - \overline{Y}(\tau_{n-1}) = \frac{3K_f R(\tau_n - \tau_{n-1})}{D_p \rho(1 - \epsilon)}[C(\tau_{n-1}) - C_s(\tau_{n-1})] \qquad (18)$$

Method of Solution

1. From the initial condition $C_s(\tau_0) = \overline{Y}(\tau_0) = 0$ and $C(\tau_0) = C_0$, it is possible to calculate $\overline{Y}(\tau_1)$ from Eq. 18.
2. Using this result and combining it with Eq 17 for $n = 1$, and coupling this with the solute mass balance as shown in Eq. 19

$$C = C_0 - \frac{W}{V}\overline{Y} \qquad (19)$$

then f_i and $C(\tau_1)$ are obtained.

3. Substitution of $f_1$1 into Eq. 15, followed by substitution of 15 into 12, gives

$$Y_s(\tau_1) = f_1 G_1(1,\tau_1) \qquad (20)$$

4. Consequently, Newton's rule (HMSO, 1961) uses Eq. 20 to obtain $C_s(\tau_1)$.

These four steps give the relevant quantities—Y, C, Y_s, C_s—at the appropriate τ values.

DISCUSSION

The model has been developed to evaluate the integral in Eq. 16 and to give the theoretical concentration decay curve with corresponding surface equilibrium conditions using the two-resistance approach. Initially, the value of the surface mass transfer coefficient was taken from single resistance and analysis values. Using this and an estimate of the surface diffusivity—together with particle radius, solution volume, adsorbent mass, particle porosity, adsorbent density, isotherm constants, the time value relating to the extent of time allowed for adsorption, and data relating to step length for integration—it is possible to obtain a theoretical decay curve. By iterating between the external mass transfer coefficient

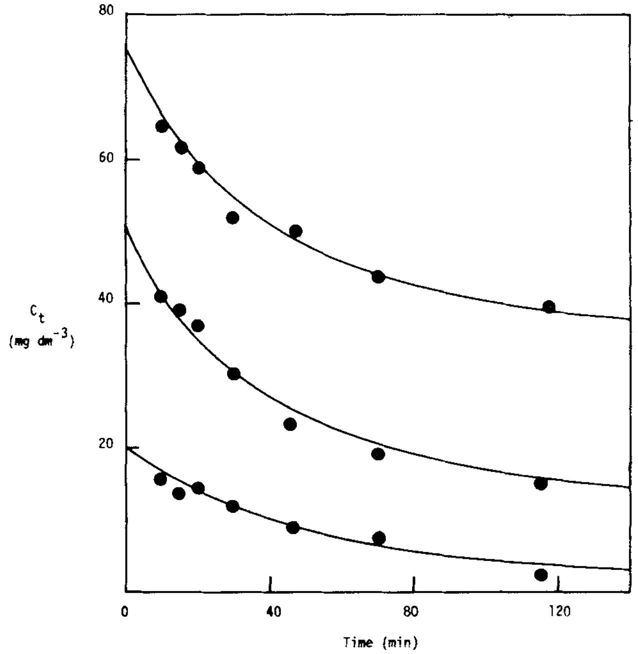

Figure 1. Effect of initial dye concentration for the adsorption of telon blue on carbon.

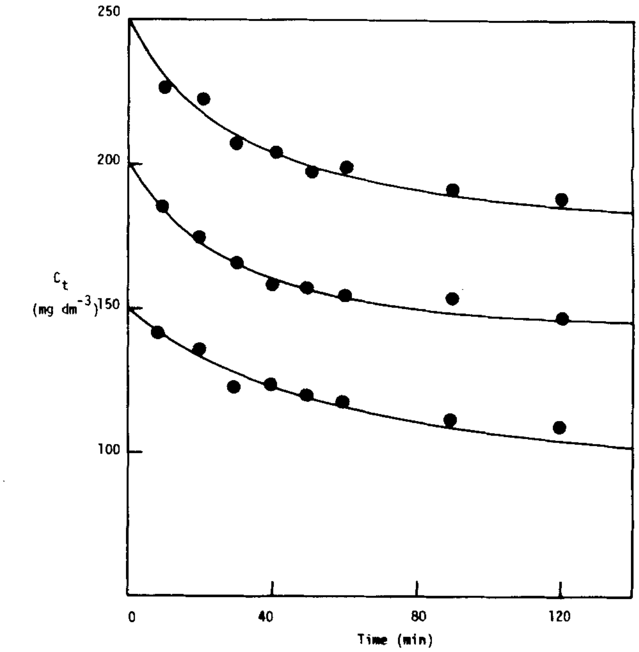

Figure 2. Effect of initial dye concentration for the adsorption of deorlene yellow on carbon.

and diffusivity, it is possible to obtain a "best" fit to the experimental decay curves for batch adsorption.

The dimensionless time variable can now be solved using numerical techniques to give the model greater stability over a given increment. Three important factors were observed in the application of the model: (1) the value of the external mass transfer coefficient and surface diffusion coefficient, (2) the surface concentration, and (3) solid-liquid equilibrium solute distribution.

If the value of the external mass transfer coefficient is relatively large, about 0.5×10^{-2} cm·s^{-1}, and solid phase diffusivity is relatively small, $D_p < 0.5 \times 10^{-8}$ cm^2·s^{-1}, then small integration increments are required and large computer times are incurred. The surface concentration is also very important, since not only is it part of the resistance for mass transfer from liquid to solid phase but it also leads to numerical instabilities when the concentration in the solid and liquid phases become comparable. If the solid has a high solid-liquid equilibrium distribution, the solution to the model becomes less rigid.

The effect of initial dye concentration is shown in Figure 1 for a range of concentrations for the adsorption of telon blue dye on carbon. Figure 2 shows concentration time curves for the adsorption of deorlene yellow dye on carbon. In the case of telon blue, the external mass transfer coefficient and diffusion coefficient are 2.0×10^{-3} cm·s^{-1} and 2.0×10^{-9} cm^2·s^{-1}, respectively, while for deorlene yellow, the external mass transfer coefficient and diffusion coefficient are 1.0×10^{-3} cm·s^{-1} and 3.0×10^{-10} cm^2·s^{-1}, respectively.

Correlation between experimental and theoretical data is not as good at low and high concentrations, although the deviation is only small. At low concentrations the isotherm is not completely described by the modified isotherm Eq. 21.

$$Y_e = \frac{K_m C_e}{1 + b_m C_e^{\beta m}} \tag{21}$$

Furthermore, at low concentrations, as at high concentrations the mechanism might not be one of complete surface/homogeneous solid phase diffusion. There is a possibility of some pore diffusion and desorption processes occurring.

The accumulation of telon blue dye in the carbon is controlled by the isotherm, which for this system is given by Eq. 22.

$$Y_e = \frac{18.5 C_e}{1 + 0.80 C_e^{0.99}} \tag{22}$$

Similarly, Eq. 23 represents a modified isotherm expression for the adsorption of deorlene yellow on carbon.

$$Y_e = \frac{100 C_e}{1 + 0.80 C_e^{0.92}} \tag{23}$$

The rapid buildup of the solid surface concentration with time highlights the problems of previous two resistance models in ac-

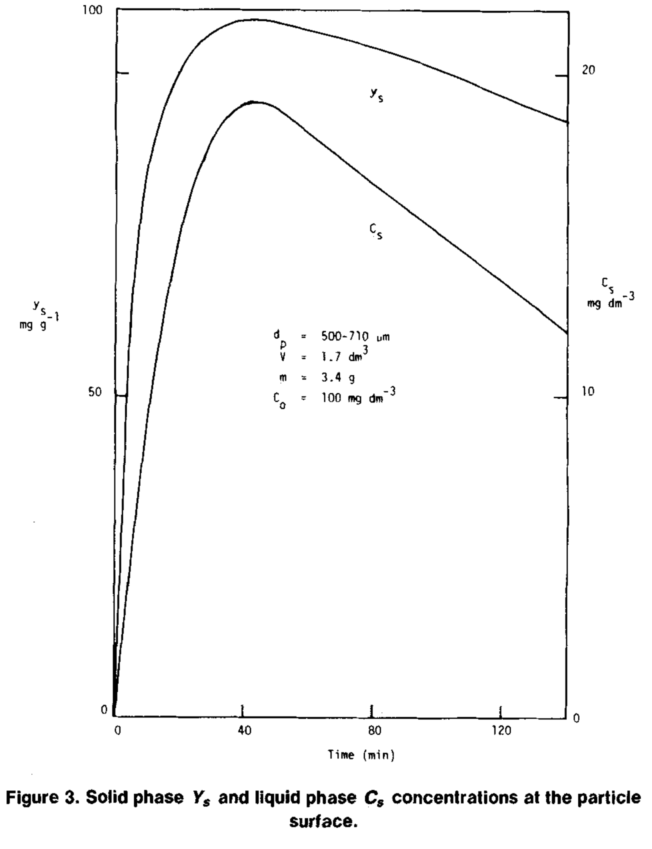

Figure 3. Solid phase Y_s and liquid phase C_s concentrations at the particle surface.

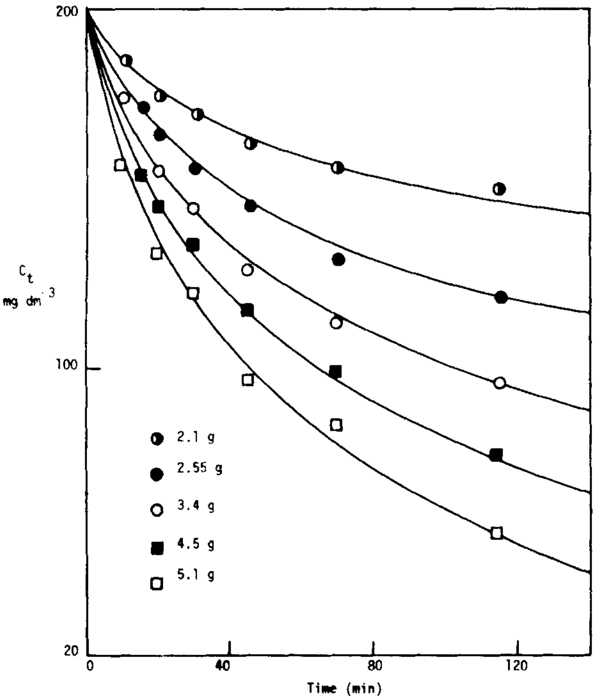

Figure 4. Effect of carbon mass for the adsorption of telon blue on carbon.

commodating small increments in the driving force for mass transfer. For high initial dye concentrations the surface solid phase concentration rises very rapidly, and Figure 3 shows the variation of surface solid phase concentration with the liquid phase concentration at the surface. The plots are for the adsorption of telon blue dye, initial concentration 100 mg·dm^{-3}, onto carbon, mass 3.4 g.

In a previous paper on two resistance the integration of Eq. 9 became unstable when applied to several experiments reported in this paper and produced an oscillating effect as the surface concentrations varied with time. This problem was overcome by the analytical solution reported, and for high liquid concentrations the method predicted the surface concentration on the solid will rise to the equilibrium value and then slowly fall due to the inward diffusion of the dye into the carbon particle.

Initially, the method of Matthews and Weber (1976) was adopted and it was found to work for the types of systems they had studied. However, applying this procedure to several of the experimental conditions reported in this paper it was found that the computer program ran into problems. The source of the difficulty was the numerical solution of Eq. 9. A procedure was sought, therefore, that avoided direct numerical solution of Eq. 9. Other solutions were available to test the system (Huang, 1974; Rasmuson and Neretnieks, 1980; Wang and Tien, 1982), but it was decided to attempt a semianalytical solution for dimensionless distance using Eq. 18. The technique enabled experimental data to be analyzed successfully even in those cases where the Matthews and Weber technique did not work. The precise limits of stability of the model compared with other relevant literature models is currently under investigation in our department.

The effect of varying carbon mass is shown in Figure 4 for telon blue. The same external mass transfer coefficients and homogeneous diffusivities were used as in the concentration results, and, again, the correlations between experimental and theoretical results are excellent. The model predicts a constant external mass transfer coefficient independent of all system parameters except agitation, which will influence the film resistance around the carbon particle. The model also predicts a constant homogeneous solid phase diffusion coefficient for the variation of initial dye concentration and carbon mass variation.

CONCLUSIONS AND SIGNIFICANCE

A homogeneous solid phase diffusion model has been developed for the adsorption of dyes onto carbon. The model includes an analytical solution for a two-resistance model based on external mass transfer and homogeneous solid phase diffusion. The solution has been successful over a wide range of dye concentrations and liquid/solid ratio. The adsorption of telon blue dye onto carbon was described using an external mass transfer coefficient of 2.0×10^{-3} cm·s^{-1} and a homogeneous solid phase diffusion coefficient of 2.0×10^{-9} cm^2·s^{-1}. The adsorption of deorlene yellow dye onto carbon was described using an external mass transfer coefficient of 1.0×10^{-3} cm·s^{-1} and a homogeneous solid phase diffusivity of 3.0×10^{-10} cm^2·s^{-1}.

The mathematical model developed in this work, incorporating an analytical component for the solution of dimensionless distance, represents a more practical alternative to previous solutions. The only problem is in the selection of dimensionless time increments to give numerical stability. The method offers a more general and rapid solution than earlier numerical techniques for the calculations of liquid phase adsorption in agitated batch adsorbers.

NOTATION

b_m = isotherm constant in modified isotherm expression
C = liquid phase concentration (mg·dm^{-3})
C_s = concentration of solute in liquid at the outer surface of the particle (mg·dm^{-3})
C_t = liquid phase concentration at time t (mg·dm^{-3})
D_p = homogeneous solid phase diffusion coefficient (cm^2·s^{-1})
f_i = average value of $f(\tau')$
$f(\tau)$ = function of τ' as defined in Eq. 14
G_i = constant in the complementary solution to the second-order differential equation
K_f = liquid phase mass transfer coefficient (cm·s^{-1})
K_m = reaction rate at OK
R = particle radius (cm)
r = radial distance from the center of the particle, $0 \leq r \leq R$ (cm)
S_p = particle surface area (cm^2)
t = time (s)
$u, U(Z,\tau)$ = transformed solid phase concentration $Y_r(r/R)$ (mg·g^{-1})
V = volume of batch reactor (dm^3)
V_p = volume of adsorbent particle (cm^3)
W = weight of adsorbent (g)
Y = solid phase dye concentration (mg·g^{-1})
Y_r = concentration of adsorbed solute at radius r of particle (mg·g^{-11})
Y_s = concentration of adsorbate at the surface of a particle (mg of adsorbate/g of dry adsorbent)
$\bar{Y}_t$ = average solid phase concentration at time t (mg·g^{-1})
z, Z = dimensionless radial distance (r/R)

Greek Letters

β_m = isotherm constant in modified isotherm expression
ϵ_p = particle voidage
ρ = density of particles (g cm^{-3})
τ = dimensionless time $(D_p t/R^2)$

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Use of a Distributed Computer System for Tubular Reactor Profile and Catalyst Activity Identification

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INTRODUCTION

In the last decade or so, a relatively complete theory of sequential distributed parameter filtering theory has appeared in the literature (Tzafestas, 1978). All of the distributed parameter filters described to date are dynamic in nature. The dynamic feature of these filters adds considerable complexity, making them very difficult to implement on-line. In fact, applications of these fully dynamic filters are scarce and are limited to rather simple systems (Ray, 1978). Fortunately, the full complexity involving dynamic modeling and filtering of all process states and parameters is not required for many processes that are characterized by certain fast dynamic modes and also long-term, slowly varying effects.

A quasi-steady state approach is suitable for these industrial processes. This approach allows one to decompose the full dynamic distributed filter into two simpler ones: a steady state distributed parameter filter that can be used for the fast dynamic states and a simpler dynamic filter that can track the slower modes or parameters. The on-line implementation of two such filters, which are developed to estimate the states and to identify the catalyst activity of a packed-bed styrene monomer reactor, is presented here.

PROCESS DESCRIPTION, MATHEMATICAL MODEL, AND FILTER EQUATIONS

The process considered here is the thermal dehydrogenation of ethylbenzene to form styrene. Ethylbenzene is passed through a tubular reactor packed with an iron oxide catalyst and dehydrogenation takes place. There are ten distinct chemical species associated with this process. Since the main dehydrogenation reaction is strongly endothermic, a 50°C temperature drop down the reactor is typical. A two-dimensional, heterogeneous mathematical model is derived and presented elsewhere (Kuruoglu, 1977). A general model is simplified via order-of-magnitude scaling arguments. The final mathematical model is summarized in Table 1. This model is further simplified to allow for convenient on-line implementation. By assuming the gas phase temperature to be that of the catalyst phase, the two energy balance equations may be combined. Then the method of orthogonal collocation (Kuruoglu, 1982) is used to eliminate radial partial derivatives. Jacobi polynomials for a single interior collocation point are used to approximate the radial profiles. After these simplifications the mathematical model has the form, when expressed at a collocation point

$$\frac{\partial x}{\partial t} = F\left(x, \frac{\partial x}{\partial z}\right) \tag{1}$$

with $x(0,z)$ and $x(t,0)$ given. Here, x is the process state vector of temperature and nine compositions; F is a set of nonlinear differential expressions corresponding to the deterministic model of the process; t is time; and z is the axial location in the reactor from the entrance.

For identification purposes, the states of the process are augmented by a catalyst activity parameter related to the main dehydrogenation rate by

$$r = \alpha k e^{-E/RT} \tag{2}$$

where r is the reaction rate, α is the catalytic activity parameter, k is a frequency factor, E the activation energy, R the gas law constant, and T temperature. The state equation for the augmented parameter is postulated to be

$$\frac{d\alpha}{dt} = -\frac{\alpha}{\tau} \tag{3}$$

where τ is a first-order time constant.

Since the typical dynamic range of the state variables is on the order of 1 sec (or 1 min for temperature), while the activity decay time constant is of the order of hours or even days, a quasi-steady state assumption is used and the process dynamics are assumed to be instantaneous. Hence, the steady state form of Eq. 1 is used to describe the process state profiles. This is a set of ordinary differential equations, and white noise with a priori statistics is added to the right-hand side of Eqs. 1 and 2 in order to introduce model

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