emulsion, s
χ = tortuosity factor in the emulsion, dimensionless

Subscripts

b = bubble phase
de = dense phase
di = dilute phase
e = emulsion phase
f = gas
s = solid

Superscripts

d = descending zone
u = ascending zone

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Digital Monitoring and Estimation of Polymerization Reactors

A free-radical polymerization with kinetic equations taking into account monomer, polymer, and solvent transfer and initiation, termination, propagation, and inhibition reactions was studied both experimentally and by simulation to determine the performance of various Kalman filters, with feasible measurements used.

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SCOPE

Kalman filtering theory has been fully described in several books (Bryson and Ho, 1968; Aoki, 1967; Jazwinski, 1970), including applications in the aerospace field. Applications in the chemical process field have frequently been limited to computer simulation studies (Wells, 1970, 1971; Goldman and Sargent, 1971; Joffe and Sargent, 1972; Gavalas and Seinfeld, 1969; Seinfeld, 1970; Coggan and Noton, 1970), where encouraging results have, in general, been reported. A few applications to experimental data have been reported (Hamilton, Seborg, and Fisher, 1973; Hanzevack and Bankoff, 1975) resulting, respectively, from mass and heat balances on a double-effect pilot plant evaporator and sulfur dioxide measurements in an urban air shed. Markedly improved estimation times and accuracy were obtained, but the basic models were linear and low order. Some nonlinear high-order processes, with direct measurement of a single state variable, have been studied (Lynch and Ramirez, 1975; Ajinkya, Ray, and Froment, 1974; Mehra and Wells, 1971). However, with many complex reactions, the state variables must be inferred from multiple on-line measurements, so that both the state and measurement equations contain appreciable modeling errors. In the present work, a free-radical polymerization with kinetic equations taking into account monomer, polymer, and solvent transfer; initiation, termination, propagation, and inhibition reactions was studied both experimentally and by simulation to determine the performance of various Kalman filters, with feasible measurements used. Experimental polymerizations of vinyl acetate were carried out in a small glass CSTR, equipped with a continuous recording refractometer and specially designed viscometer. During the reaction period the impurity concentration in the feed was intentionally varied. Samples of the product were also periodically taken from the reactor and analyzed for conversion and weight-average molecular weight. For the system model of the polymerization process, the kinetic scheme proposed and studied experimentally by Graessley and co-workers, as noted below, was employed, with some slight modifications and parameter adjustments.

CONCLUSIONS AND SIGNIFICANCE

The Kalman filter, in a variety of forms, was used to obtain estimates of conversion and weight-average molecular weight, which were then compared with results obtained through sample analysis. The augmentation of one parameter was effective in improving the filter performance. However, the use of adaptive, exponential and/or iterative schemes did not markedly improve the filter performance, in view of the relatively long residence time. In fact, the quasi steady state assumption was shown to be acceptable. As with previous studies, poor initial estimates of the state variables or of the state covariance matrix could easily be tolerated, but too small estimates of the process noise covariance matrix caused the filter to diverge. To remedy this defect, a fictitious process noise, which actually compensated for model uncertainties, had to be inserted. Similarly, to obtain smooth filter operation, some fictitious measurement noise was desirable to compensate for errors in the empirical correlations between measured and state variables. One concludes that simulation studies of Kalman filtering on complex systems with detailed descriptive equations may easily lead to overoptimistic conclusions. It would appear that a Kalman filter used in the estimation of such processes is best justified when the model errors, by batch processing of experimental data, have been made comparable to the measurement errors.

KALMAN FILTER THEORY

The Kalman filter is an on-line computer algorithm which is intended to give better estimates of the state variables than can be obtained by direct solution of the measurement equations. In addition, if observability conditions are satisfied (Jazwinski, 1970), it is possible to obtain optimal estimates of unmeasured state variables, or variables which cannot be obtained directly from the measurements.

Consider a linear n-dimensional system in which the random-variable state vector x_k, at time t_k, evolves by means of a deterministic (and known a priori) transition matrix $\Phi(k+1, k)$ to a new value, x_{k+1}, at time $t_{k+1} = t_k + \Delta t$ (where Δt is a fixed sampling interval), subject to an additive zero-mean Gaussian disturbance w_k, while an m-dimensional vector y_k is obtained, subject also to a zero-mean Gaussian measurement error v_k. The Kalman filter for this system can be summarized by the following equations:

Prediction between observations

$$\hat{x}^{k}_{k+1} = \Phi(k+1, k)\,\hat{x}^{k}_{k} \tag{1}$$

$$P^{k}_{k+1} = \Phi(k+1, k)\,P^{k}_{k}\Phi^{T}(k+1, k) + \Gamma(k)Q(k+1)\Gamma^{T}(k) \tag{2}$$

Estimation at observations

$$\hat{x}^{k+1}_{k+1} = \hat{x}^{k}_{k+1} + K(k+1)\,\{y_{k+1} - M(k+1)\,\hat{x}^{k}_{k+1}\} \tag{3}$$

$$P^{k+1}_{k+1} = \{I - K(k+1)M(k+1)\}\,P^{k}_{k+1}\{I - K(k+1)M(k+1)\}^{T} + K(k+1)R(k+1)K^{T}(k+1) \tag{4}$$

$$K(k+1) = P^{k}_{k+1}M^{T}(k+1)\,\{M(k+1)P^{k}_{k+1}M^{T}(k+1) + R(k+1)\}^{-1} \tag{5}$$

$$P_o^{o} = P_o \quad \text{and} \quad \hat{x}_o^{o} = x_o \quad \text{at} \quad k = 0$$

The filter algorithm can be processed as follows:

1. Obtain $\hat{x}_o^o = x_o$ and $P_o^o = P_o$ at time t_o from previous knowledge of the system or by guessing.
2. Set $k = 0$.
3. Calculate $\hat{x}^{k}_{k+1}$ and P^{k}_{k+1} at t_k from Equations (1) and (2). These are the a priori estimates of x_{k+1} and P_{k+1} at t_k.
4. Calculate the Kalman gain matrix at t_{k+1}, $K(k+1)$

from Equation (5), determining M and R from the measurement equations and noise properties.

5. Once the measurement y_{k+1} is available at time $t = t_{k+1}$, calculate the a posteriori estimates $\hat{x}_{k+1}^{k+1}$ and P_{k+1}^{k+1} from Equations (3) and (4).
6. Increment k by 1, go back to step 3, and repeat.

The linear filter may be applied to nonlinear systems by linearizing the equations around some reference trajectory.

Suppose the nonlinear dynamic system is described by the stochastic n-vector differential equation

$$\frac{dx}{dt} = f(x, t) + G(t)\, w_t \tag{6}$$

with measurements

$$y = h(x, t) + v_t \tag{7}$$

where the definitions and statistics of x, w, and v are the same as in the linear case.

By using a deterministic reference trajectory $\bar{x}(t)$ generated with a given $\bar{x}_o = \bar{x}(t_o)$, these equations are linearized and discretized as follows:

$$\delta x_{k+1} = \Phi(k+1, k)\delta x_k + \Gamma(k) w_{k+1} \tag{8}$$

$$\delta y_{k+1} = M(k+1)\delta x_{k+1} + v_{k+1} \tag{9}$$

where

$$\delta x_k = x(t_k) - \bar{x}(t_k) \tag{10}$$

$$\delta y_k = y(t_k) - E(y(t_k)) = y(t_k) - h(\bar{x}(t_k), t_k) \tag{11}$$

$$M(k) = h_x(\bar{x}(t_k), t_k) \tag{12}$$

and Φ is a transition matrix which can be obtained from

$$\dot{\Phi}(t, \tau) = f_x(\bar{x}, t)\, \Phi(t, \tau) \tag{13}$$

with the initial condition $\Phi(\tau, \tau) = I$. (14)

The linear filter is then directly applicable to the linearized system, providing that the difference between the reference and actual trajectories is never large. To reduce this difference, one can reestimate $\bar{x}_o$ backwards whenever new observations are available. This procedure, known as global iteration, is repeated until there is no change between two successive reference trajectories at each time step. However, this procedure loses the advantage of the filter as a recursive structure. Furthermore, there is no guarantee that this iteration will converge. Alternatively, one can go only one step backward to t_{k-1}, reestimate $\bar{x}_{k-1}$, and relinearize the trajectory around $\bar{x}_{k-1}$ whenever a new observation is available. As a consequence, large initial estimation errors are less likely to propagate.

One obtains

$$\hat{x}_{k+1}^{k} = \hat{x}_{k}^{k} + \int_{t_k}^{t_{k+1}} f(\hat{x}_{t}^{k}, t)dt \tag{15}$$

$$\hat{x}_{k+1}^{k+1} = \hat{x}_{k+1}^{k} + K(k+1)\,(y_{k+1} - h(\hat{x}_{k+1}^{k})) \tag{16}$$

Replacing Equations (1) and (3) by (15) and (16), one finally obtains the extended Kalman filter for the nonlinear system.

One can additionally obtain an iterated Kalman filter by locally iterating at the interval (t_k, t_{k+1}) to improve the reference trajectory. Thus, rather than relinearizing about $\hat{x}_{k+1}^{k}$ as in the extended Kalman filter, one can relinearize about $\hat{x}_{k+1}^{k+1}$ and recompute the estimate. This procedure can be repeated until there is no significant change in two consecutive iterates. This implies that the Kalman gain matrix K is reevaluated at each iteration. Even so, if the filter is constructed on an erroneous model, it may diverge. The problem is particularly serious when the noises are small. To ameliorate this problem, one can increase the covariance matrix P in order to compensate for model errors. This can be accomplished by adding a fictitious noise to the system. Alternatively, one can limit the filter memory by overweighting the most recent data.

To determine the amount of fictitious noise to be added, one can utilize the concept of the predicted measurement residual:

$$r_{k+1}^{k} \overset{\Delta}{=} y_{k+1} - E(y_{k+1} \mid y^k) = y_{k+1} - h(\hat{x}_{k+1}^{k}, t_{k+1}) \tag{17}$$

It is desired to minimize the probability density of the residual. Omitting the detailed derivation (Jazwinski, 1970), one obtains

$$\hat{Q}(k+1) = \begin{cases} \dfrac{(r_{k+1}^{k})^2 - E\{(r_{k+1}^{k})^2 \mid q \equiv 0\}}{H(k+1)H^T(k+1)} & \text{if positive} \\ 0 & \text{if negative} \end{cases} \tag{18}$$

where

$$E\{(r_{k+1}^{k})^2 \mid q \equiv 0\} = M(k+1)$$

$$\Phi(k+1)P_k^k\, \Phi^T(k+1)M^T(k+1) + R(k+1)$$

The limited-memory (exponential) filter is obtained by substituting the following equations:

$$K(k) = P_k^{k-1} H^T(k)\,(H(k)P_k^{k-1} H^T(k) + cR(k))^{-1} \tag{19}$$

$$P_k^k = \frac{1}{c}\,(P_k^{k-1} - K(k)H(k)P_k^{k-1}) \tag{20}$$

where $c = \exp(-(t_{k+1} - t_k)/\tau)$, and τ represents an effective memory period.

To estimate uncertain parameters, one can augment the state vector with these parameters and estimate them together with the state. This approach increases the dimension of the state vector and thereby the amount of required computation and memory storage. The choice of parameters to estimate in a given problem has to be made by experimentation under actual conditions.

POLYMER KINETICS

The polymerization kinetics of vinyl acetate in t-butanol solvent in a continuous stirred tank reactor have been extensively studied by Graessley et al. (Mittelhauser, 1966; Nagasubramanian, 1970; Kathju, 1970; Hartung et al., 1969; Chatterjee, 1975; Hyun et al., 1975).

The resulting equations are summarized in Table 1 where the starred terms are additional terms due to inclusion of initiation and termination reactions. These equations were solved numerically with and without the starred terms to determine their effect. There was no substantial difference, indicating that the initiation and termination reactions are indeed negligible, as originally proposed. Therefore, only the model without the starred terms were used in this study. It is also possible that partially segregated reactor kinetics should be considered, owing to the high viscosity of the products. However, in view of the relatively long residence time, it seems unlikely that there exists any large-scale segregation in the

TABLE 1

Summary of kinetic equations

$$\frac{dQ_1}{dt} = \frac{k_pY_t}{a}\{(1-x)\,(C_pQ_1 + C_m\,(1-x)) - KQ_1\,(C_pQ_1' + C_sS + {}^*T)\} \quad (1\text{-}1)$$

$$+ {}^*k_pY_tC_m\,(1-x) - \frac{Q_1}{\theta} \quad (1\text{-}2)$$

$$\frac{dQ_1'}{dt} = \frac{k_pY_t}{a}(1 - x + KQ_1)\,(C_pQ_1' + C_sS + {}^*T) + {}^*k_pY_tC_sS + {}^*2fk_dI - \frac{Q_1'}{\theta} \quad (1\text{-}3)$$

$$\frac{dQ_2^T}{dt} = \frac{2k_pY_t}{a}(1 - x + KQ_1)\,(1 - x + KQ_1 + C_pQ_2^T + {}^*C_m\,(1-x) + {}^*C_sS + {}^*T) \quad (1\text{-}4)$$

$$+ {}^*k_pY_tC_m\,(1-x) + {}^*k_pY_tC_sS + {}^*2fk_dI - \frac{Q_2^T}{\theta} \quad (1\text{-}5)$$

where

$$a = C_m\,(1-x) + C_px + C_sS + {}^*T \quad (1\text{-}6)$$

$$k_pY_t = \left\{ \frac{fk_dI_o}{r}\left(1 - \frac{\tau}{\theta}\right) \right\}^{1/2} \quad (1\text{-}7)$$

$$T = \frac{2fk_dI}{k_pY_t} \quad (1\text{-}8)$$

$$I = I_o \quad (1\text{-}9)$$

$$r = k_t/k_p^2 \quad (1\text{-}10)$$

$$C_m = k_{tr,m}/k_p \quad (1\text{-}11)$$

$$C_p = k_{tr,p}/k_p \quad (1\text{-}12)$$

$$C_s = k_{tr,s}/k_p \quad (1\text{-}13)$$

$$K = {}^*k_p/k_p \quad (1\text{-}14)$$

reactor. A study (Chatterjee, 1975) of the mixing pattern of the reactor and comparison of experimental data with micromixing and segregated models did not provide any concrete evidence that such segregation exists.

PARAMETER ADJUSTMENT

The values of C_m, C_p, and K used in earlier studies lie reasonably well in the ranges reported in the literature (Lindemann, 1967; Matheson et al., 1949; Schultz and Stein, 1962) and were retained for this study: $C_m = 2.43 \times 10^{-4}$; $C_p = 2.36 \times 10^{-4}$; $K = 0.66$. This leaves two parameters, $\lambda = (fk_d/r)^{1/2}$ and C_s, to be chosen. λ is a function of several other parameters, all of which are uncertain, while C_s is a parameter which should be determined for each individual solvent. λ can be determined from conversion data and C_s from molecular weight data.

λ was determined by fitting the experimental conversion data for a CSTR to

$$\frac{x_s}{1 - x_s} = \lambda\sqrt{I_o\theta} \quad \text{for} \quad \tau = 0$$

The resulting fit is shown in Figure 1. To determine C_s, the experimental steady state molecular weight data for a CSTR were fitted to the model by a least-squares approach, as shown in Figure 2. The parameter values thus determined were: $C_s = 6.884 \times 10^{-5}$; $\lambda = 1.793 \times 10^{-3}$.

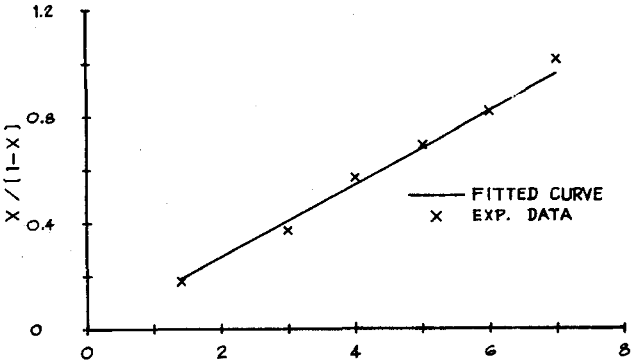

Fig. 1. Conversion data fitting.

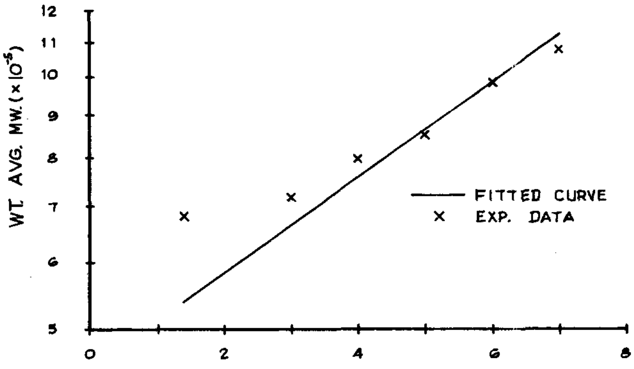

Fig. 2. Molecular weight data fitting.

APPARATUS

The experimental apparatus consisted of a feed unit, continuous flow reactor, viscosity and refractive index transducers, and auxiliary equipment. The feed tank was a 5.0 l flat-ground-flange, glass resin reactor flask connected to a positive-displacement metering pump with a stainless steel diaphragm. Problems of erratic delivery at low flow rate, caused by sticky check valves and entrained gas in the pump, were relieved by cleaning or replacing valve sets, gaskets, and balls.

The reactor was a 1 l glass resin reaction flask with bottom outlet and a stainless steel cover. Details of the argon purge system, temperature control, stirring, pumping, and measuring devices are available (Jo, 1975; Chatterjee, 1975).

MEASUREMENTS

In this work, the refractive index and viscosity were taken as the measurement variables. The choice of refractive index is obvious. It is a very accurate measure of concentration of polymer present in the reactor effluent and hence of the conversion. The choice of viscosity is less obvious. It is well known that the viscosity of linear polymer solutions has some relationship with the molecular weight of the polymer (Flory, 1953). A similar relationship may exist for branched polymers as well, because the contribution to viscosity by branching is generally not large. Furthermore, in this particular case, analysis of the data (Chatterjee, 1975) indicates that the degree of branching is small. This point was also confirmed in a study (Jo, 1973) where the constant flow pressure drop through a glass capillary was measured for a broad range of molecular weights and plotted against $x_1x_2^{1/4}$. The lines could be fairly well superimposed, indicating that the viscosity is primarily a function of conversion and molecular weight only. The viscosity measurement was made on-line and continuously by monitoring the torque exerted on the split impeller shaft by the deformation of a stainless steel torsion spring. Two stainless steel disks with 180-deg semicircular slots were attached to the upper and lower shaft members with their slots opposed by 180 deg., and the

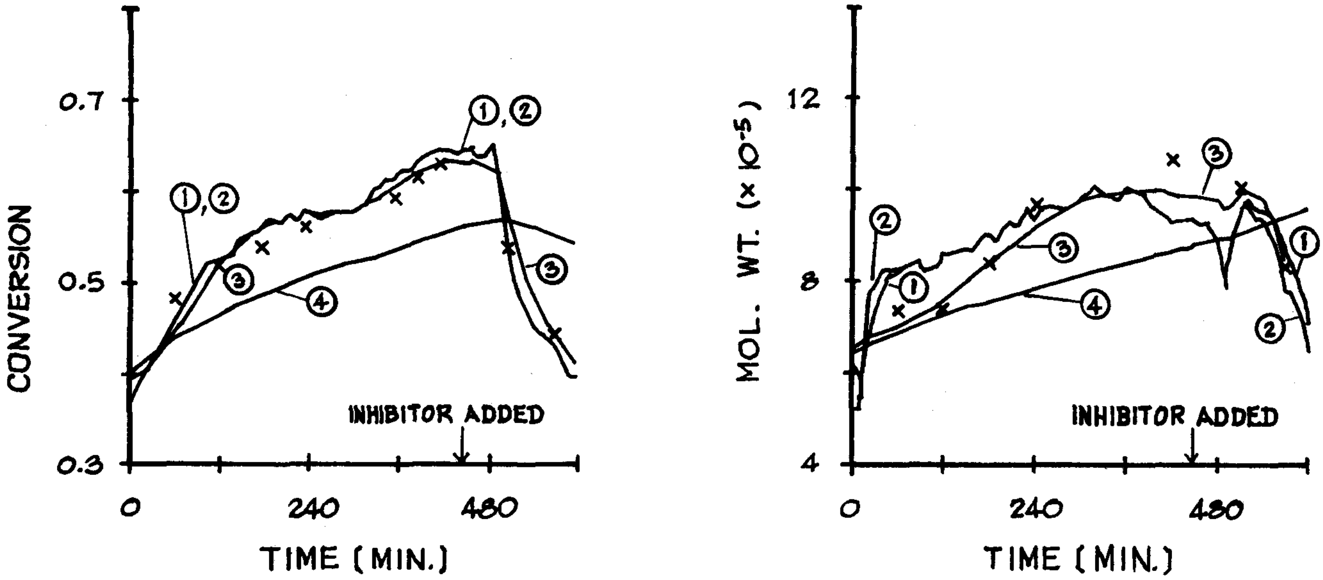

Fig. 3. Effect of covariance of measurement noise (R). x Experimental data. 1) $P = P_0$, $Q = Q_0$, $R = R_0$; 2) $P = P_0$, $Q = Q_0$, $R = 10^{-4}R_0$; 3) $P = P_0$, $Q = Q_0$, $R = 10^2R_0$; 4) $P = P_0$, $Q = Q_0$, $R = 10^4R_0$.

angular displacement at 300 rev./min. was sensed by two internally mounted glass fiber optic bundles to detectors consisting of a light source and phototransistor. Refractive index was measured by a commercial in-line critical angle refractometer, modified to increase the turbulence in front of the prism and thus prevent buildup of polymer on the surface.

The model for the refractive index is straightforward, since it is well known that the relationship of the refractive index with solution concentration can be very closely approximated by a linear model over a broad range of concentration:

$$\bar{y}_1 = f_1(x) = a_1 + a_2x_1 \qquad (21)$$

No definite relationship between molecular weight and viscosity is known. One expression relates the solution viscosity (Huggins, 1942; Flory, 1953) to the concentration c and $[\eta]$, the intrinsic viscosity, by a function at the form

$$\eta = f(c[\eta]) \qquad (22)$$

where $[\eta] = KM^n$, $0.5 < n < 1.0$. Based on this, the following model was chosen to correlate the viscometer data:

$$\ln \bar{y}_2 = b_1 + b_2\,(x_1x_2{}^n) \qquad (23)$$

where x_1 = conversion, x_2 = weight-average molecular weight, and b_1, b_2, and n are constants.

The logarithmic function was taken because the data of $\ln \eta$ plotted against cM^n show a close resemblance to a linear model for $0.5 < n < 1.0$. The logarithmic model has another advantage in that it deals with the relative error rather than the absolute error. The problem of finding the best choice of the exponent n is complicated by the fact that experiments with different conditions generated similar molecular weights at comparable conversions. Thus, the individual effects of conversion and molecular weight on the viscometer were not readily separable. The best fit was, in fact, obtained when $n = 0.3$, whereas theory indicates that n should not be less than 0.5. However, the least-squares error did not increase very much between $n = 0.3$ and $n = 0.7$. Therefore, the value of 0.5 was taken for this study.

The final values of other coefficients were

$$a_1 = 1.38090 \qquad a_2 = 0.02113$$
$$b_1 = 5.009 \qquad b_2 = 0.129$$

STEP INPUT OF INHIBITOR

To study the Kalman filter estimation under changing parameter conditions, the inhibitor concentration in the feed mixture was intentionally changed during a polymerization reaction. An accurately weighed trace amount of hydroquinone mixture with a known amount of feed mixture was prepared. The reactor was taken up to steady state operation, and a predetermined amount of impure mixture was added to the feed mixture in the feed tank. The reaction was further carried out and terminated when the viscometer reading was out of range. Conversion and molecular weight were determined by weight of residue after evaporation and by GPC (Chatterjee, 1975; Jo, 1975). The parameter values were: θ = 5.0 hr; I_o = 0.0015 g mole/l initiator, Z_i = 11.8 p.p.m. hydroquinone.

RESULTS

Several variants of the Kalman filtering algorithm were applied to the experimental data with different combinations of initial estimates, statistics (covariance matrices of system model and measurement), and parameter augmentation. The values of P, Q, and R used in the study were based on the real system (Jo, 1975).

Effect of Initial Estimates

It was found that the initial state variable estimate does not have a significant effect on the estimates of the system variables (conversion and molecular weight), although some notable differences in the estimates of the parameters (τ and θ) could be seen. Usually the filter brought the estimates back to a reasonable range very quickly. This is to be expected, since with the large covariance matrices for the dynamic system (Q) compared to the smaller measurement covariance (R) in this particular problem, the filter did not give much weight to the initial values and depended more on the observations. Similarly, the results showed that the estimates of the system variables were not greatly affected when P_o, the initial state covariance matrix, was varied by a factor of 10^4. Again, this result can be attributed to the large covariance matrix assigned to the model error.

Effect of *R*

The effect of the measurement covariance matrix R on the filter performance was more significant (Figure 3).

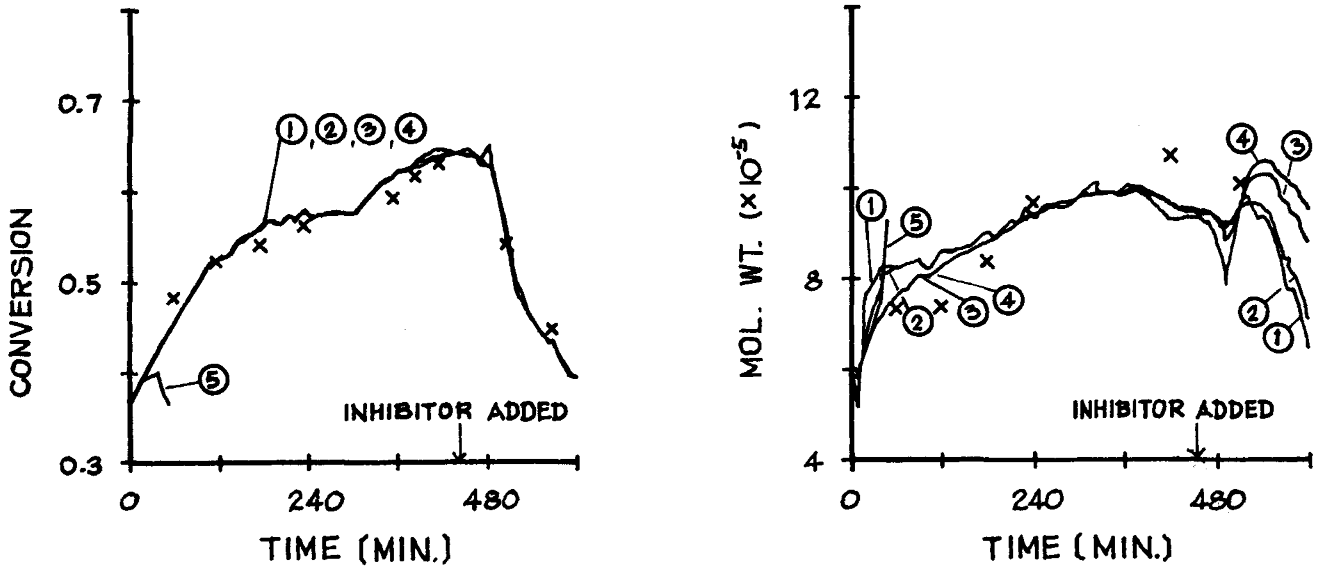

Fig. 4. Effect of covariance of system noise (Q). x Experimental data. 1) $P = P_0$, $Q = 10^4Q_0$, $R = R_0$; 2) $P = P_0$, $Q = Q_0$, $R = R_0$; 3) $P = P_0$, $Q = 0.1Q_0$, $R = R_0$; 4) $P = P_0$, $Q = 0.05Q_0$, $R = R_0$; 5) $P = P_0$, $Q = 0.01Q_0$, $R = R_0$.

Decreasing R from its nominal value R_o did not significantly change the results, but large increases in R resulted in significant deviations in the estimates of the state variables from the experimental values, while the parameter estimation responded more slowly, indicating that the filter was almost wholly dependent on observations. Better filter performance was obtained at $R = 100\ R_o$, indicating that the model errors in the measurement equations themselves were not insignificant.

Effect of Q

No appreciable change was observed in filter performance at a larger Q (Figure 4), which is equivalent to higher uncertainty in the dynamic system model. As Q decreased somewhat ($Q = 0.05\ Q_o$), little change was shown in the estimation of system variables. However, when Q decreased beyond that point ($Q = 0.01\ Q_o$), the filter diverged rather rapidly and failed after a few observations owing to the presence of imaginary numbers in the system equations.

Kalman Filter Variations

The iterated extended Kalman filter was applied to the data with two different R matrices, and hence two levels of model dependence. In both cases, essentially no difference was observed in filter performance, indicating the absence of a serious nonlinearity problem, perhaps due to the slow system response.

Several other techniques, such as adaptive and exponential versions of extended Kalman filter and the method of adding fictitious noise, were tested with this problem, but only the addition of fictitious noise was found to be effective. When adaptive or exponential filters were applied, they immediately started moving in the wrong direction, and after a few observations the filter broke down, again due to the presence of imaginary numbers. In adding fictitious noise (Figure 4), some minimum Q was necessary to make the filter operate properly. With a larger Q, no substantial improvement of filter performance was achieved.

Steady State Filter

Since we have a relatively large model uncertainty error compared to measurement error and the system is very slow, it can be expected that a steady state model for the dynamic system, which essentially eliminates the prediction step, may be used without much effect on filter

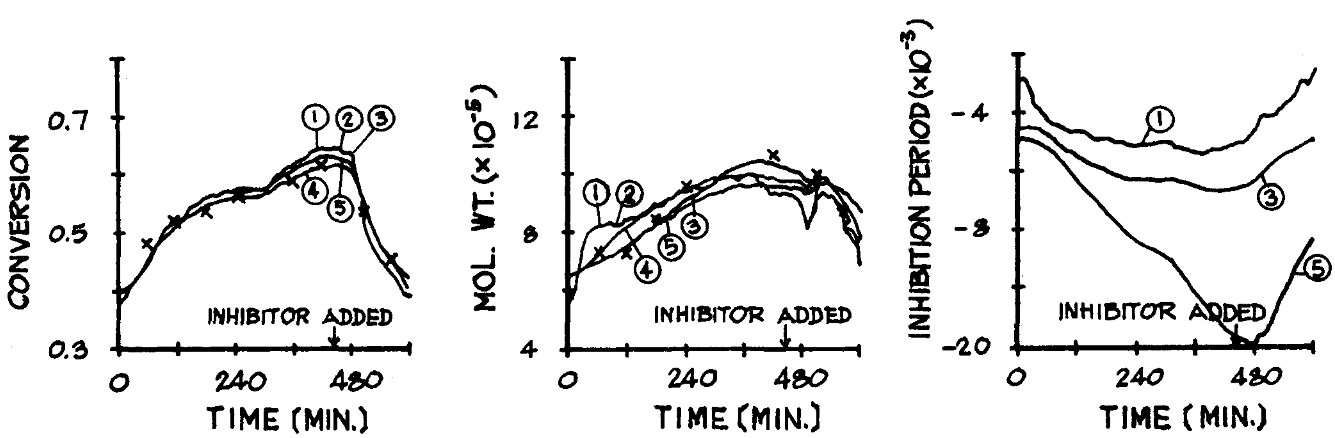

Fig. 5. Effect of number of augmented parameters. x Experimental data. 1) $R = R_0$, 2 parameters (τ and θ) augmented; 2) $R = R_0$, no parameters augmented; 3) $R = 10^2R_0$, 2 parameters (τ and θ) augmented; 4) $R = 10^2R_0$, no parameters augmented; 5) $R = 10^2R_0$, 1 parameter (τ) augmented.

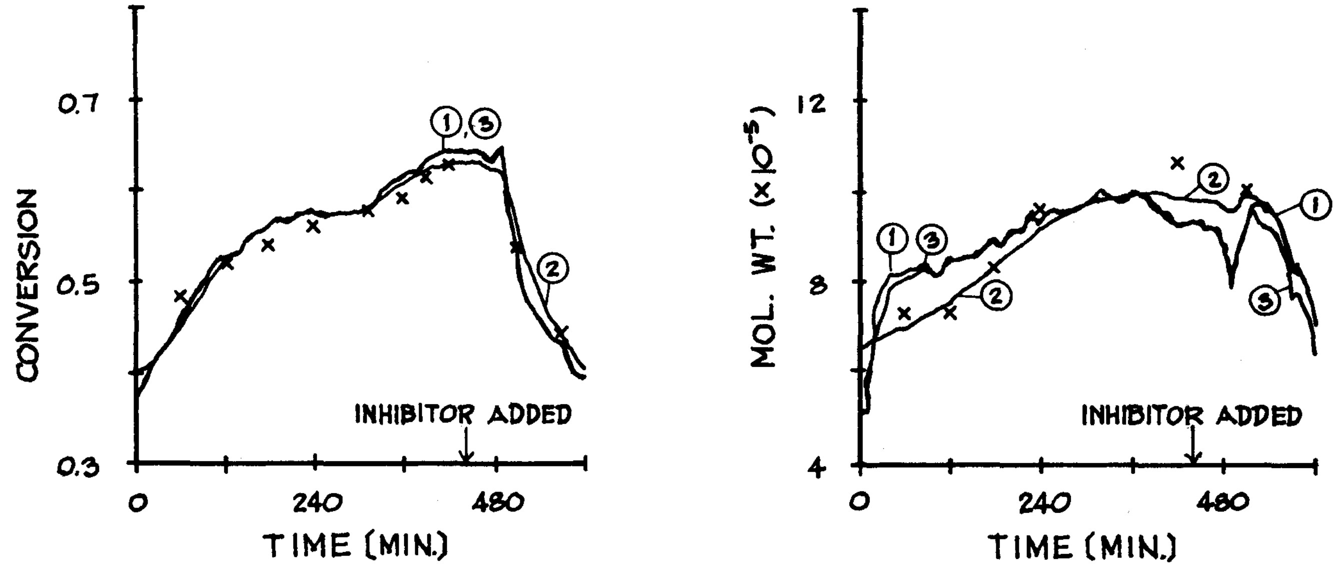

Fig. 6. Comparison of filter estimate with estimate by measurement only. x Experimental data. 1) Estimation by filter, $P = P_0$, $Q = Q_0$, $R = R_0$; 2) Estimation by filter, $P = P_0$, $Q = Q_0$, $R = 10^2 R_0$; 3) Estimation by measurement only.

performance. This study showed that this was indeed true, suggesting that a steady state filter could be recommended whenever a large dynamic system error and slow system are involved. The steady state filter reduced the calculation time by a factor of about 3.

Parameter Augmentation

The filter was tested with different numbers of parameters augmented to the state variables. The result (Figure 5) shows some improvement of filter performance on the state variables when one parameter (τ in this case) was augmented, with $R = 100\ R_o$, although no appreciable change was observed when more than one parameter was augmented. Since parameter augmentation markedly increases the calculational load of the filter, a decision should be made for each individual case whether the improvement is worth the increased calculation. In this case the best compromise was the augmentation of the one most uncertain parameter.

An interesting point was that faster changes for τ were observed when τ only was augmented, as compared to τ and θ together. This behavior is to be expected, but since θ can drift slowly, there may be some advantages in estimating both θ and τ together. In this case the filter re-estimates τ more rapidly than θ, in view of the larger uncertainty in τ, but not as rapidly as if τ only is being estimated. The choice, therefore, depends on the desired speed with which unforeseen changes in inhibitor concentration in the feed are to be detected for control purposes. Parameter augmentation did not provide any difference in the case of a steady state filter, regardless of R, as expected, because updating the parameters does not have any direct effect on the steady state dynamic equations. Therefore, parameter augmentation need not be considered for the steady state filter.

Comparison of Filter Results with Deterministic Solution of Measurement Equations

In this system there are two system variables and two relatively accurate measurements. This suggests that one can obtain an estimate of state variables directly from the measurements by solving the deterministic equations at each time step. Figure 6 shows that close agreement was obtained between the arithmetic solution and the filter with $R = R_o$, justifying the earlier observation that the filter is almost wholly dependent on the observation at this condition. However, it can be also seen that markedly improved performance of the filter was achieved with $R = 100\ R_o$. This result is important, since physically one does not expect a sudden reduction, followed by an increase, of molecular weight after addition of inhibitor, but rather a monotonic decrease in the output molecular weight. This can be explained by modeling errors in the measurement equation itself, which implies that the covariance matrix R should be artificially increased, in a similar fashion to the process covariance matrix Q, in order to compensate for modeling errors and to prevent overreaction on the part of the controller.

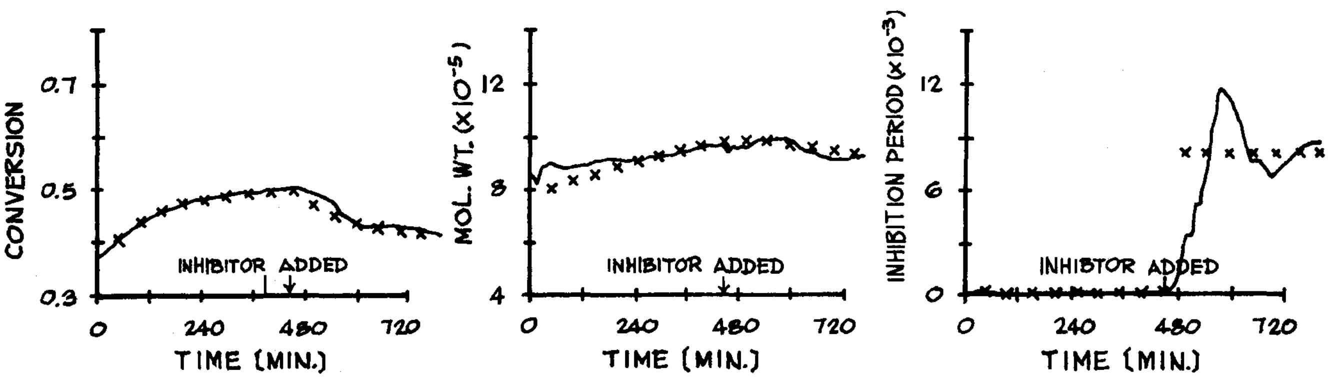

Fig. 7. Filtering with simulated data x Reference trajectory on which the simulation was based. — Estimation by filter, $P = P_0$, $Q = Q_0$, $R = R_0$.

Comparison with Simulation Study

The filtering algorithm was applied to the simulated data generated by computer for the same system. In the simulation study, the covariance matrices which were used for the actual system were employed to generate the simulated data for the refractive index and viscometer. As shown in Figure 7, a considerably improved estimation can be obtained in the simulation study over that obtained with *experimental* data, despite the fact that the same covariance matrices were used in each case. This is an example of overly optimistic filtering results in a simulation study.

The improved results in the simulation study are attributable to the exact model used to generate the data, which cannot be verified without reference to experimental data.

ACKNOWLEDGMENT

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NOTATION

$E(\cdot)$ = expected value of $(\cdot)$
f = efficiency constant of initiation reaction
I_o = initial concentration of initiator
I = current concentration of initiator (Table 1)
I = identity matrix [Equation (14)]
$K(k+1)$ = gain matrix of Kalman filter
k_d = decomposition rate constant of initiator
k_p = propagation rate constant
K_p^* = rate constant of terminal double bond polymerization reaction
k_t = termination reaction constant
$k_{tr,m}$, $k_{tr,p}$, $k_{tr,s}$ = transfer reaction constants of monomer, polymer, and solvent, respectively
k_z = inhibition reaction constant
[illegible] = monomer concentration
$M(k+1)$ = observation matrix
P^k_{k+1} = a priori covariance matrix of x_{k+1}
P^{k+1}_{k+1} = a posteriori covariance matrix of x_{k+1}
$Q(k+1)$ = process noise covariance matrix
Q_n = n^{th} moment of polymer population with double bond
Q_n' = n^{th} moment of polymer population with no double bond
$Q_n^T = Q_n + Q_n'$
$R(k+1)$ = measurement noise covariance matrix
r^k_{k+1} = predicted measurement residual
S = solvent concentration
v_k = measurement error
w_k = process noise
x = conversion (Table 1)
x_1 = conversion
x_2 = weight-average molecular weight
$\bar{x}$ = reference trajectory
x_k = random variable state vector at time t_k
$\hat{x}^k_{k+1}$ = priori estimate of x_{k+1}
$\hat{x}^{k+1}_{k+1}$ = posteriori estimate of x_{k+1}
x_s = steady state conversion in CSTR
y_k = measurement vector
y^k = measurements up to time t_k
Y_t = total radical concentration
Z_i = initial impurity concentration

Greek Letters

Γ = process noise matrix
θ = residence time
τ = inhibition period (Table 1)
τ = effective memory period [Equation (20)]
$\Phi(k+1, k)$ = state transition matrix
η = viscosity of polymer solution
$[\eta]$ = intrinsic viscosity

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Separation of Nonlinearly Sorbing Solutes by Parametric Pumping

A rigorous mathematical analysis shows that parametric pumps can separate, concentrate, and recover in pure form all components of a multisolute mixture. The obtained separation cannot be predicted by existing linear models. Criteria for determining steady periodic separations of binary mixtures are discussed in detail for batch and continuous systems.

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SCOPE

Parametric pumping is a cyclic fixed-bed sorption process for separating and purifying fluid mixtures. Previously, experiments with hydrocarbon mixtures, aqueous solutions of inorganic salts, and other mixtures have shown that parametric pumping can produce very large separations. These separations have been modeled mathematically in two ways. In one method computer solutions of a set of partial differential equations are obtained. This is not easy to implement, and the results apply only to the specific system studied. The other method for modeling is easy to use and is more general, but it is restricted to systems where sorption isotherms are linear, that is, where sorbed phase concentration is directly proportional to fluid phase concentration.

However, in real systems, linear isotherms usually occur only at low concentrations. More likely, the sorption process will follow a Langmuir type of isotherm. In the case of ion-exchange, where sorbing species compete for ion-exchange sites, the isotherms are not linear. Also, when nonionic species compete for sites, sorption is nonlinear. The linear theory cannot adequately treat these cases. A case in point where the linear theory fails is the separation of $K^+ - Na^+ - H^+$ by Butts, et al. (1973), where K^+ and H^+ accumulated at opposite ends of a bed, while Na^+ accumulated in the middle.

In this paper, the theory of nonlinear, multisolute, equilibrium chromatography developed by Rhee, et al. (1970) is used to analyze parametric pumping systems. Using this theory, one can obtain convenient to use algebraic relations for understanding and predicting parametric pumping behavior. The experimental results of Butts, et al. (1973), are predictable from this theory with little effort. The analytical, nonlinear theory also makes the exploration of continuous (that is, not batch) separations much easier.

CONCLUSIONS AND SIGNIFICANCE

A mathematical analysis of parametric pumping separations is presented which rigorously takes into account for the first time realistic nonlinear sorption equilibria.

First, for batch, binary separation, the criteria in Table 2 were developed to determine which type of separation will occur at steady periodic state. The criteria depend on initial loading of the system, sorption isotherm constants, and amount of fluid displaced per half cycle. Transient analysis of this case is also examined.

Second, it was shown how a batch, multisolute parametric pump can separate, concentrate, and recover in pure form all components of a multicomponent mixture. When complete separation occurs, the components will be arranged in the bed in order of their affinity for the sorbent. Criteria for this separation are shown in Equations (21) to (29). The linear theory cannot predict this separation, since the separation is due to nonlinear interactions.

Third, the nonlinear theory applies easily to the two continuous binary separation schemes in Figures 5 and 6, and to a combination of these.

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