

State Estimation in a Batch Suspension Polymerization Reactor

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ABSTRACT

This paper concerns non-linear state estimation in a batch polymerization reactor where suspension polymerization of methyl methacrylate takes place. A kinetic model proposed in the literature is selected and its validity has been verified through an experimental set-up. Based on this model monomer conversion and average molecular weights of the polymer are estimated using only one output measurement (reactor temperature). The performance of the estimator, which has the structure of an extended Kalman filter, is examined through simulation and experimental studies in the presence of different levels of parameter uncertainties. The effects of adding 'fictitious noise' and parameter state' to the estimation algorithm are also investigated. To find the best fictitious state, the main parameters of polymerization model are divided into three groups. The parametric study of the MMA polymerization model indicates that, when the source of parameter uncertainty is unknown, the best selection of parameter state is the initial mass of monomer.

Key Words: extended Kalman filter, state estimation, suspension polymerization, dynamic modeling, batch reactor

INTRODUCTION

In the polymerization industry there is considerable economic incentive to produce polymers with desired end-use properties. The development of operating policies that will result in the production of polymers with desired end-use properties is called "quality control". However, the final polymer properties (e.g. melt index, impact strength, tensile strength, chemical resistance, thermal stability, etc) can be related, through empirical relationships, to the molecular properties of polymers such as molecular weight distribution (MWD) [1,2].

Therefore, the main objective in control of polymerization reactors is to maintain the molecular properties at some desired values.

A major problem in control and monitoring of polymer quality in industrial polymerization reactors is the lack of suitable on-line molecular property measurements. Although instruments for measuring the MWD are available, these instruments are very expensive and possess substantial measurement delays [3]. By using state estimation techniques, some of these difficult-to-measure variables can be estimated with aid of certain easily measurable variables such as temperature, viscosity and density of the reaction

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mixture.

The problem of state estimation for non-linear processes has been studied extensively in the literature and has been reviewed in many papers such as Embirucu et al. [4] and Soroush [5]. These studies can be divided into three main classes.

In the first class, different types of neural networks are used for state estimation. When the process modeling is complicated and a suitable model is not available, especially in industrial polymerization, neural network models based upon monitored reactor data can be developed. Using the learning capability of a neural network, the relationship between polymer quality variables and the on-line measured variables can be identified [6–8].

The second class includes the estimator design methods whose derivations are based on the notion of linearization through coordinate transformation, adopted from non-linear control theory. Examples include the method of output injection [9], and the Luenberger-like observer design methods [10–17]. In these methods, a non-linear process model, without any linearization, is used directly for estimator design.

The third class includes those non-linear estimator design methods which are a result of a straightforward extension of Luenberger observer or Kalman filter (KF) to non-linear processes. Examples of this class are extended Luenberger and EKF. The state estimation techniques mostly used in polymerization reactors are those based on the EKF [18–31].

In this paper, the difficulties and different modifications of EKF for state estimation in batch polymerization reactors are studied. A batch polymerization reactor, in which suspension polymerization of MMA takes place, is selected for this investigation. It is assumed that the only available measurement is the reactor temperature.

The kinetic model proposed by Chiu et al. [32] is selected and its validity has been verified through data obtained from an experimental set-up. Based on this model an EKF is designed to estimate the average molecular weights.

The performance of the estimator is examined through experiments and simulation studies. The effects of adding 'fictitious noise' and 'parameter

state' to the estimator have been investigated. Simulation results indicate that the best selection for parameter state is the initial mass of monomer.

EXPERIMENTAL SYSTEM

Figure 1 depicts the schematic diagram of experimental system. The reactor is a 5L stainless steel jacketed vessel. The reacting mixture is mixed by a three paddle agitator at 600 rpm during the polymerization.

The heating/cooling system of the reactor consists of an electrical heater with power of about 6.0 kW, a shell and tube heat exchanger, a motorized three-way control valve, a circulating pump and temperature sensors (four 0–100 °C resistance temperature detectors, RTD). The reactor temperature is measured by a RTD of the same type. The circulating pump maintains a constant jacket-side heat transfer coefficient. The temperature of the heater is controlled by an on/off controller at about 80 °C.

The experimental system is connected to a computer by an I/O interface board (Axiom, Inc.; model AX5411).

Experimental Procedure

To verify the model, the experimental system of Figure 1 is used for suspension polymerization of MMA with benzoyl peroxide initiator. The loading amounts of monomer, initiator and distilled water in each batch are 1.4, 0.018 and 2.0 kg, respectively. The

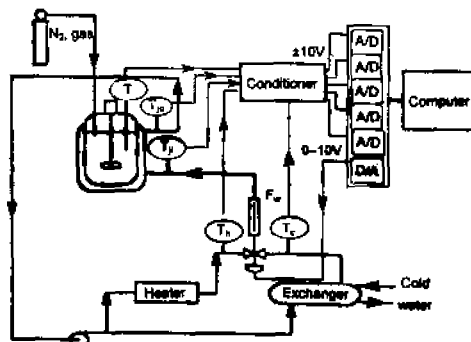


Figure 1. Experimental system.

quantities of trisodium phosphate (TSP), calcium chloride and SDBS (used for producing suspending medium), are 0.0191, 0.1315 and 0.0168, respectively.

These quantities are found by trial and error for obtaining small size pellets of polymer (50–200 μm), at agitation rate of 600 rpm.

The procedure used in each batch has the following steps:

- Preparation of materials using the given loading conditions.
- Dissolution of the TSP in distilled water and loading it into the reactor vessel.
- Loading the monomer into a vessel and stirring it by an agitator, followed by introduction of nitrogen gas into the monomer for 1 h to purge any dissolved oxygen.
- Preheating the reactor to the desired temperature and loading the calcium chloride.
- Loading the SDBS into the reactor vessel within about 10 min.
- Removing about 150 mL of the monomer and loading it into a 250 mL beaker and then heating the remaining monomer in the vessel to the desired temperature.
- Dissolving the initiator in the beaker containing monomer.
- Loading the solution prepared in step 7 into the monomer vessel and mixing it properly. Then loading the mixture into the reactor vessel and controlling its temperature. In the experimental set-up the reactor temperature is controlled by manipulating the jacket inlet temperature using a conventional PID controller.
- Purging the reacting medium with nitrogen gas to keep oxygen out of the reactor.
- During the polymerization, samples were taken and conversion is determined gravimetrically, while the average molecular weights are determined by the gel permeation chromatography (GPC; model 150-C, Waters).

MATHEMATICAL MODEL

The kinetic mechanism for free radical polymerization

Table 1. Free radical polymerization mechanism.

Steps	Mechanisms
Initiation	$I \xrightarrow{k_d} 2R_0$ $R_0 + M \xrightarrow{k_i} R_1$
Propagation	$R_n + M \xrightarrow{k_p} R_{n+1}$
Chain transfer	$R_n + M \xrightarrow{k_{ct}} P_n + R_1$
Termination	$R_n + R_m \xrightarrow{k_{tc}} P_n + P_m$ $R_n + R_m \xrightarrow{k_{tm}} P_{n+m}$

of MMA initiated by benzoyl peroxide is given in Table 1 [33–35]. In order to obtain average molecular weights of the growing radicals and resulting polymers the method of moments is used. These moments are defined below:

$$\lambda_k = \sum_{n=1}^{\infty} n^k R_n \quad \text{and} \quad \mu_k = \sum_{n=1}^{\infty} n^k P_n \quad (1)$$

where: R_n and P_n are concentrations of live radical and dead polymer chain with n monomer units, respectively.

Using the kinetic mechanism and performing mass and energy balances results the following set of ordinary differential equations:

$$\frac{dx_m}{dt} = (1 - x_m)(k_p + k_m)\lambda_0 \quad (2)$$

$$\frac{dx_i}{dt} = (1 - x_i)k_d \quad (3)$$

$$\frac{dT}{dt} = \frac{(-\Delta H_p)k_p\lambda_0 C_m V + UA(T_j - T)}{mc} \quad (4)$$

$$\frac{d(\mu_0 V)}{dt} = \lambda_0 V(k_m C_m + k_t \lambda_0) - 0.5k_{tc}\lambda_0^2 V \quad (5)$$

$$\frac{d(\mu_1 V)}{dt} = \lambda_1 V(k_m C_m + k_t \lambda_0) \quad (6)$$

$$\frac{d(\mu_2 V)}{dt} = \lambda_2 V(k_m C_m + k_t \lambda_0) + k_{tc}\lambda_0^2 V \quad (7)$$

where:

$$\lambda_0 = \left(\frac{2f k_d C_i}{k_t} \right)^{0.5} \quad (8)$$

$$\lambda_1 = \lambda_0 \left(1 + \frac{k_p C_m}{k_m C_m + k_t \lambda_0} \right) \quad (9)$$

$$\lambda_2 = \lambda_1 \left(1 + \frac{2k_p C_m}{k_m C_m + k_t \lambda_0} \right) \quad (10)$$

$$C_m = \frac{(1-x_m)C_{m0}V_0}{V} \quad (11)$$

$$C_i = \frac{(1-x_i)C_{i0}V_0}{V} \quad (12)$$

$$V = V_0(1 + \varepsilon x_m) \quad (13)$$

In the above equations, x_m and x_i are monomer and initiator conversion, respectively and ε is the volume expansion factor and is given by:

$$\varepsilon = \phi_{m0} \left(\frac{\rho_m}{\rho_p} - 1 \right) \quad (14)$$

To obtain average molecular weights from the moments the following equations can be used:

$$M_n = W_m \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} \approx W_m \frac{\mu_1}{\mu_0} \quad (15)$$

$$M_w = W_m \frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1} \approx W_m \frac{\mu_2}{\mu_1} \quad (16)$$

In the MMA polymerization, termination and propagation reactions can become diffusion-controlled at increased viscosity of reaction medium. These phenomena are called gel and glass effects, respectively. To introduce the gel and glass effects in the model, the correlations proposed by Chiu et al. [32] are used. These correlations are given below:

$$k_t = \frac{k_{t0}}{1 + \frac{\lambda_0 k_{t0}}{Dk_{gt}}} \quad (17)$$

$$k_p = \frac{k_{p0}}{1 + \frac{\lambda_0 k_{p0}}{Dk_{gp}}} \quad (18)$$

where:

$$D = \exp\left(\frac{2.3(1 - \phi_p)}{0.168 - 8.21 \times 10^{-6}(T - T_{gp})^2 + 0.03(1 - \phi_p)} \right) \quad (19)$$

The kinetic constants and other parameters of the mathematical model (for suspension polymerization of MMA with benzoyl peroxide initiator) are given in Table 2 [34, 36, 37]. To calculate UA, the overall heat transfer coefficient, several step changes are introduced in the jacket temperature (while only water is present in the reactor) and reactor temperature is measured. Using these data and least square technique UA has been calculated.

KALMAN FILTERING: A REVIEW

The KF is an optimal estimator for linear processes, which provides estimate of the state vector from measurements containing white noise [38]. A straightforward extension of KF to non-linear processes is called EKF [39]. In the following, an EKF algorithm,

Table 2. Kinetic and other parameters of MMA polymerization.

$k_d = 1.69 \times 10^{14} \exp(-1.2561 \times 10^5/RT)$	$W_m = 100.12$
$k_m = 4.661 \times 10^9 \exp(-7.4479 \times 10^4/RT)$	$f = 0.5$
$k_{p0} = 4.9167 \times 10^5 \exp(-1.8283 \times 10^4/RT)$	$c = 3.2$
$k_{t0} = 9.800 \times 10^7 \exp(-2.9442 \times 10^3/RT)$	$m = 3.585$
$k_{gp} = 3.0233 \times 10^{13} \exp(-1.17 \times 10^5/RT)$	$R = 8.345$
$k_{gt} = C_d \times 1.454 \times 10^{20} \exp(-1.4584 \times 10^5/RT)$	$\rho_p = 1200$
$\rho_m = 968 - 1.225(T - 273.2)$	
$-\Delta H_p = 5.78 \times 10^4, \quad T_{gp} = 387.2, \quad UA = 0.087$	

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based on a continuous-time process model and discrete-time measurements, has been reviewed briefly.

Consider the process described by the following equations.

$$\begin{cases} \frac{dx}{dt} = f(x, u, t) + v(t), & x(0) = x_0 \\ y(k) = h(x) + w(k) \end{cases} \quad (20)$$

where: v and w is uncorrelated white noise vectors with covariance Q and R , respectively. The EKF equations have the following form:

– State and covariance estimate propagation:

$$\hat{x}(k+1/k) = \hat{x}(k/k) + \int_{t_k}^{t_{k+1}} f(\hat{x}, u, t) dt \quad (21)$$

$$P(k+1/k) = \Phi(k)P(k/k)\Phi^T(k) + Q(k+1) \quad (22)$$

– Filter gain calculation:

$$K(k+1) = P(k+1/k)H^T(k+1)\{H(k+1)P(k+1/k)H^T(k+1) + R(k+1)\}^{-1} \quad (23)$$

– State and covariance estimates update:

$$\begin{aligned} \hat{x}(k+1/k+1) &= \hat{x}(k+1/k) + K(k+1)\{y(k+1) - \\ &h[\hat{x}(k+1/k)]\} \end{aligned} \quad (24)$$

$$P(k+1/k+1) = \{I - K(k+1)H(k+1)\}P(k+1/k) \quad (25)$$

$\Phi(\cdot)$ is the state transition matrix and is given by:

$$\Phi(k) = \exp[F(t_k, t_{k+1})] \quad (26)$$

In the above equations the Jacobians F and H are defined as:

$$F = \left(\frac{\partial f}{\partial x}\right)_{\hat{x}}, \quad H = \left(\frac{\partial h}{\partial x}\right)_{\hat{x}} \quad (27)$$

In implementation of EKF to real processes several difficulties and challenging problems are encountered. Firstly, it is well known that the EKF can become unstable, particularly in ill-conditioned problems, when eqns (22) and (25) are used for calculation of the state covariance matrix. To circumvent this difficulty, many methods have been suggested in the literature such as Potter's square root and Bierman's U-D factorization [40]. In the present work special form of the square root method proposed by Kaminski et al. [41] is used.

Secondly, if any of the measurements can be considered as noise-free, the gain of the filter becomes infinite. This failure of KF is attributed to the optimal gain of the filter, and thus, a suboptimal gain should be used [42].

Thirdly, when some of the disturbances are non-stationary or in the presence of modeling errors, the filter may be diverged or provides biased estimates. To overcome these difficulties, one can increase the elements of process noise covariance matrix which is equivalent to adding a fictitious noise to the system. Alternatively, one can calculate the covariance matrix Q in an adaptive manner [24]. Another approach is incorporation of a few non-stationary disturbances and/or parameter states in formulating of EKF [27,43,44].

Finally, in order that the state estimation techniques to be applied successfully, it is necessary for the system to be observable. Unfortunately, in the polymerization reactors, the molecular properties cannot be observed from bulk measurements, such as temperature and concentrations. However, even if the process is not observable, it is usually possible to design a reduced order estimator when the process is detectable (a process is detectable if its unstable modes can be observed) [19,45].

Other difficulties and experiences in real implementation of the EKF have been reviewed by Wilson et al. [46].

Estimator Design for the MMA Polymerization

In the experimental system (Figure 1) the only available output measurement is the reactor temperature. The analysis of the process model (eqns 2-7) shows

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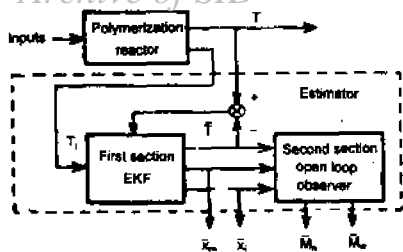


Figure 2. Block diagram of the designed estimator.

that monomer and initiator conversions are observable and dead polymer moments (μ_0, μ_1, μ_2) are not observable from temperature measurements but detectable, and a reduced order estimator can be designed.

The block diagram of the proposed estimator is shown in Figure 2. The states vector to be updated contains only the observable states (x_m, x_i, T). Parallel to this reduced order filter the equations of the moments must be integrated without correcting these variables in the update step. The proposed estimator contains two parts. The first part is an EKF for estimating of the observable states, and the second part is an open loop observer for estimating of the detectable states.

The estimations of the observable and detectable states may have bias in the presence of the

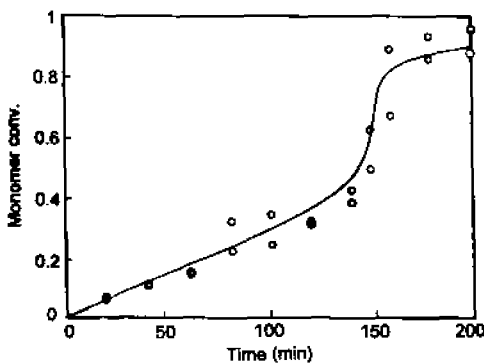


Figure 3. Experimental data and model predictions (solid line) of monomer conversions at 60 °C.

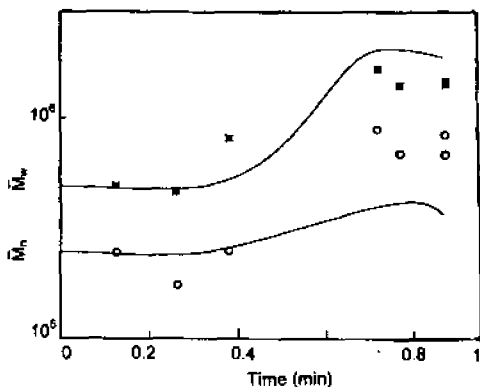


Figure 4. Experimental data and model predictions (solid line) of average molecular weights at 60 °C.

model uncertainties. The bias of the observable states can be reduced by adding a fictitious noise to the system. But the bias of the detectable states can not be reduced by this technique. One approach to overcome this problem is to add all uncertain parameters as fictitious states to the first part of the estimator. For this purpose, the observable state vector can be extended as $x^T = [x^{dT}, x^s]$, where x^d is the vector of deterministic model states (x_m, x_i, T) and x^s is the vector of parameter states. Since the true dynamics of the fictitious states are usually unknown, it is common

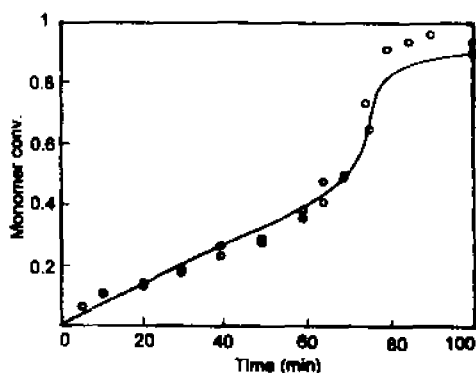


Figure 5. Experimental data and model predictions (solid line) of monomer conversions at 70 °C.

Table 3. Diagonal elements of Q and P₀ in each case.

case	q ₁₁	q ₂₂	q ₃₃	q ₄₄	p ₁₁	p ₂₂	p ₃₃	p ₄₄
I	5×10 ⁻⁹	8×10 ⁻¹¹	3×10 ⁻⁶	—	0.01	1×10 ⁻⁴	1.0	—
II	5×10 ⁻⁴	8×10 ⁻⁶	3×10 ⁻¹	—	0.01	1×10 ⁻⁴	1.0	—
III	5×10 ⁻⁷	8×10 ⁻⁸	3×10 ⁻⁴	3×10 ⁻⁵	0.01	1×10 ⁻⁴	1.0	0.5 for w _{m0} 0.1 for f
IV	5×10 ⁻³	8×10 ⁻⁵	3.0	—	0.01	1×10 ⁻⁴	1.0	—

to assume that these states follow a simple non-stationary random walk behaviour:

$$\frac{dx^s}{dt} = v^s \quad (28)$$

where: v^s represents a white noise vector.

In general, the maximum number of fictitious states that can be estimated is equal to the number of independent measurements. Therefore, in the experimental system with one independent measurement (T), one fictitious state can be added to the estimation algorithm. For this limitation, it is favorable to select a parameter state that provides a better estimate, when the source of uncertainty is unknown.

To find the best fictitious state, the main parameters of the MMA polymerization model are divided into three categories, according to their qualitative effect on the system states:

- In the model equations the parameters w_{i0} , k_d and f are usually appeared as $f k_d w_{i0}$, therefore, the uncertainties in these parameters can be lumped into one parameter.
- UA and $-\Delta H$: These parameters are appeared only in energy balance equation, and therefore their uncertainties can be lumped into one parameter.
- w_{m0} , k_t and k_p : These parameters are appeared in different forms in the model equations. Therefore, the effects of these parameters are studied separately.

The effect of adding any of the aforementioned parameter as parameter state will be discussed later.

Kinetic Model Validation

To verify the model used for the suspension polymerization of MMA several experiments have been performed.

To achieve better agreement between model predictions and experimental results, the chain transfer to monomer and termination by combination reactions are ignored. Experimental data of the monomer conversion and the average molecular weights are compared with the model predictions at 60 °C in Figures 3 and 4, and at 70 °C in Figures 5 and 6, respectively. As can be seen from the results, the model successfully predicts the monomer conversion. In addition, the model predicts the average molecular weights satisfactory except for the region of rapid polymerization. Discrepancies that exist in the average molecular weights are unavoidable, and similar weaknesses have been reported by other researchers [32].

STATE ESTIMATION RESULTS

In this section the performance of the proposed estimator has been examined under different levels of

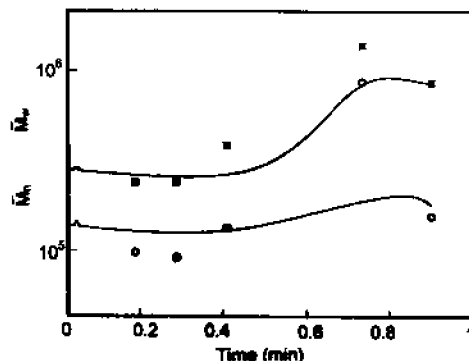


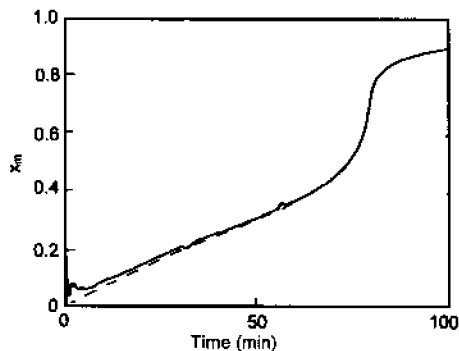
Figure 6. Experimental data and model predictions (solid line) of average molecular weights at 70 °C.

parameters' uncertainties. In all runs the sampling period takes 5 s and covariance of output measurement (R) is 0.0015. In addition, the covariance matrices Q and P_0 are assumed diagonal.

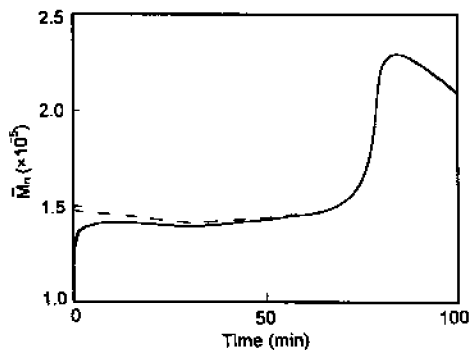
The diagonal elements of Q and P_0 for each case are given in Table 3.

Case I: Nominal

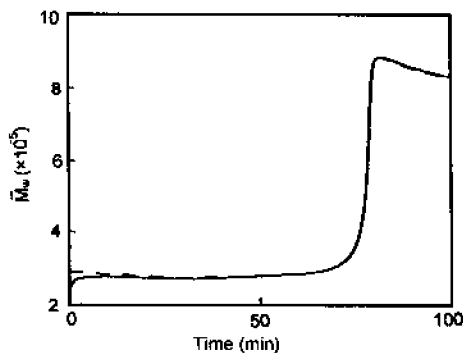
If all model uncertainties can be described as white noise, then the state estimates will be converged without any bias. For example in Figures 7 (a), (b) and (c) the estimated values of monomer conversion, weight and number average molecular weights are compared with their real values in the presence of 20% error in the initial value of monomer conversion.



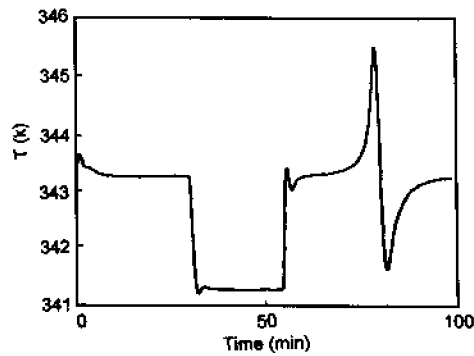
(a)



(c)



(b)



(d)

For this case the corresponding variation of the reactor temperature is shown in Figure 7 (d).

Case II: Using Fictitious Noise

In the presence of parameter uncertainties and/or non-stationary disturbances, the state estimates may have bias or diverge. As mentioned earlier, one way to overcome this difficulty is adding a fictitious noise to the system. For example the estimated values of x_m , x_n , \bar{M}_w and \bar{M}_n in the presence of 20% error in the w_{m0} are shown in Figure 8. The variation of the reactor temperature is similar to Figure 7 (d). In these Figures the covariance matrix Q was increased by a factor of 10^5 , comparing to case I. The filter will diverge, if the covariance matrix Q of the case I is used.

Figure 7. State estimations of case I (solid line: estimated values; dash line: real values).

Case III: Using Fictitious State

In the following the effect of selecting any model parameter as a fictitious state has been examined. For all cases, the variation of the reactor temperature is the same as Figure 7 (d).

If the uncertain parameter is known, it can be added to the estimation algorithm as a parameter state. In this case the filter will converge with approximately bias-free estimated states.

For finding the best parameter state, when the source of uncertainty is unknown, many simulations have been performed on the basis of three model parameter categories defined before. For example in Figures 9–11 the estimated values of \bar{M}_w and \bar{M}_n are compared for two cases where w_{m0} or f has been

selected as a fictitious state. In these cases the estimated values of x_m were approximately the same, and therefore, they are not shown. The performances of the other cases (selecting w_{j0} and UA as a fictitious state) can be examined in a similar way.

The results can be summarized as follows:

- When the uncertainty exists in the first group of the model parameters (w_{i0} , k_d , f), the best selection of the parameter state is f . In addition, the selection of w_{j0} or w_{m0} gives satisfactory results, but filter may diverge, if UA is selected.
- When the uncertainty exists in the second group of parameters (UA and $-\Delta H_p$), the best selection of the parameter state is w_{m0} or UA.
- When the uncertainty exists in the third group of

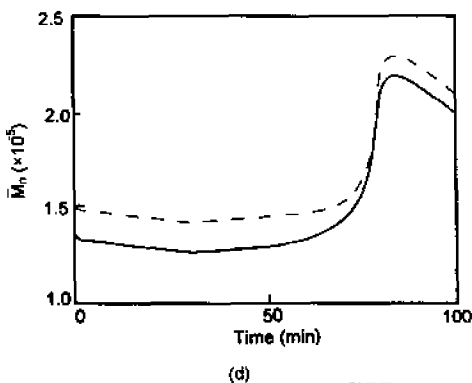
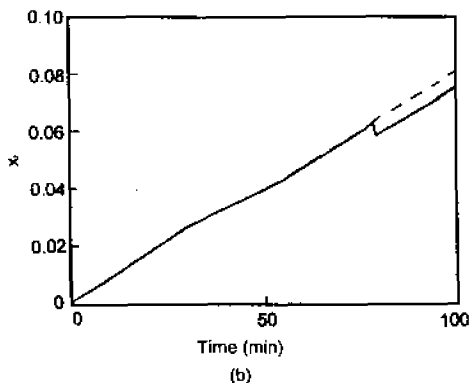
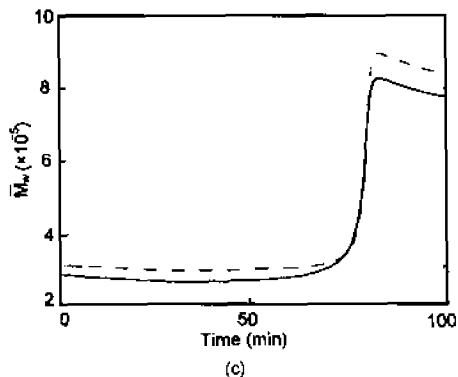
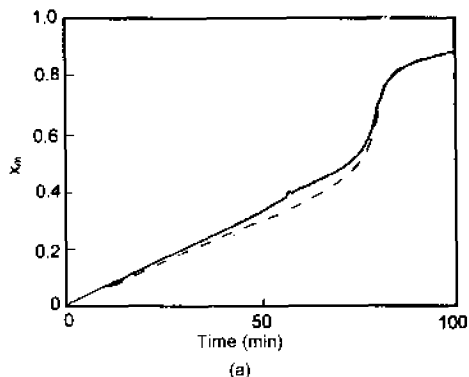


Figure 8. State estimations of case II for 20% error in w_{m0} (solid line: estimated values; dash line: real values).

- parameters (k_{10} , k_{p0} , w_{m0}), the best selection of the parameter state is w_{m0} . In addition, the selection of w_{10} or f is acceptable, but if UA is chosen, the filter may diverge.

Case IV: Experimental Results

In this section the experimental data obtained at 70 °C are used to check the performance of the proposed estimator. The estimated values of x_m , \bar{M}_w and \bar{M}_n are compared with experimental results in Figures 12 and 13. The results show that the monomer conversion and average molecular weights have been estimated successfully. It should be stated that the proper value of matrix Q found by trial and error is given in Table 3.

CONCLUSION

In this paper the state estimation of a batch suspension polymerization reactor of MMA with only one measurement (reactor temperature) was studied through simulations and experiments. For this purpose an estimator consisting of two parts has been proposed. The first part is an EKF which estimates the observable states and the second part estimates the detectable states (open loop observer).

The simulation results indicate that, in the presence of parameter uncertainties and/or non-stationary disturbances, the estimations of observable states can be improved by adding a fictitious noise

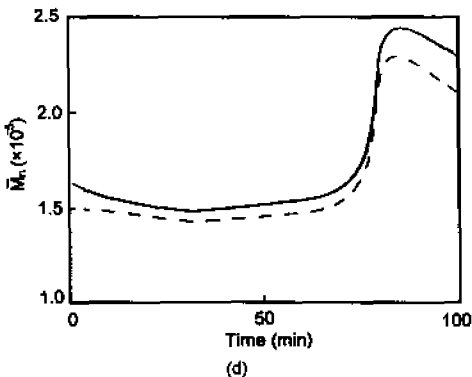
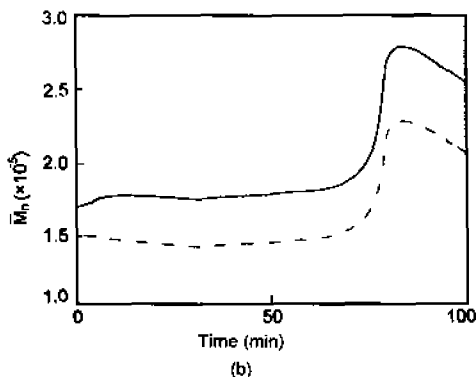
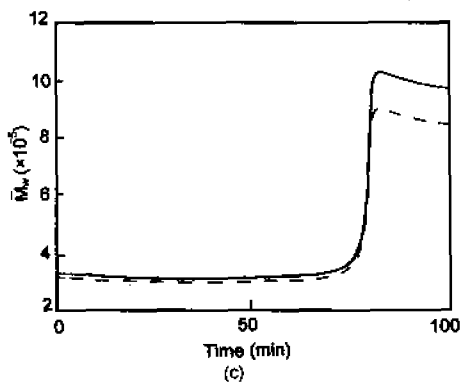
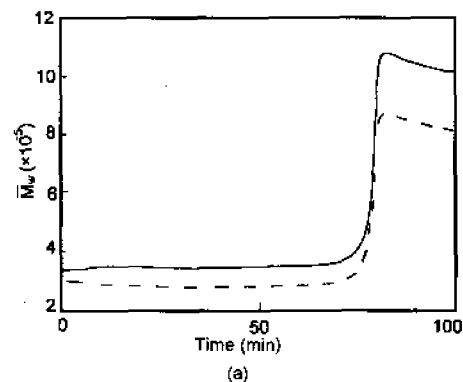


Figure 9. State estimations for 20% error in k_d or w_d ; (a,b) selecting w_{m0} and (c,d) selecting f as a parameter state (solid line: estimated values; dash line: real values).

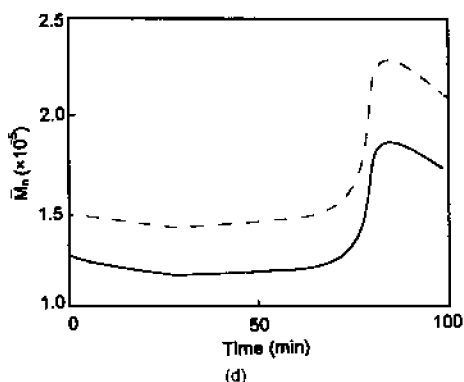
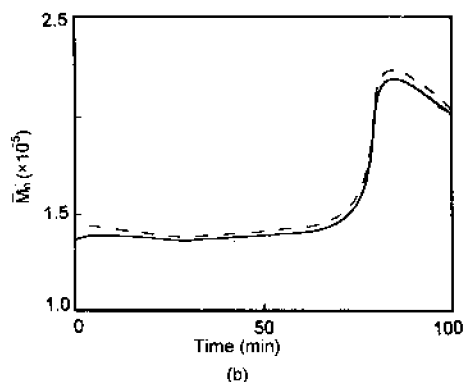
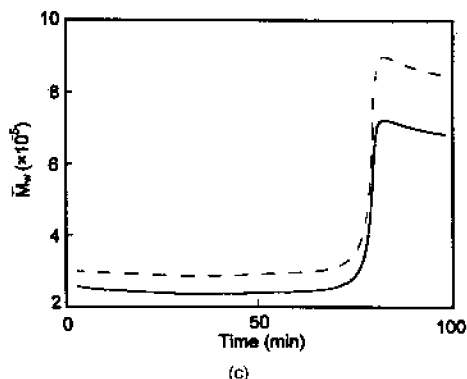
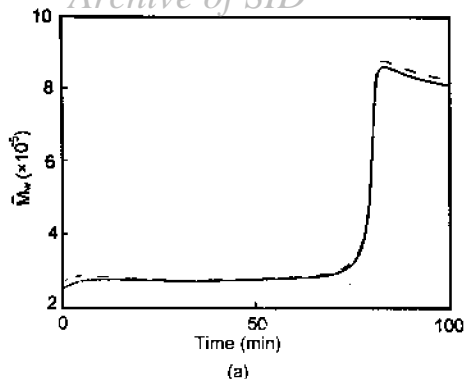


Figure 10. State estimations for 20% error in k_{p0} and k_{t0} ; (a, b) selecting w_{m0} and (c, d) selecting f as a parameter state (solid line: estimated; dash line: real values).

and/or a parameter state to the system. In addition, in many special cases, adding a parameter state will improve the state estimations of detectable states. A parametric study of the MMA polymerization model indicates that, when the source of parameter uncertainty is unknown, the best selection for the parameter state is the initial mass of monomer (w_{m0}).

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SYMBOLS AND ABBREVIATIONS

- A reactor-jacket heat transfer area, m^2
- c heat capacity of reactor contents, $kJ \cdot kg^{-1} \cdot K^{-1}$
- C_i, C_{i0} concentration of initiator and its initial value, $kmol \cdot m^{-3}$
- C_m, C_{m0} concentration of monomer and its initial value, $kmol \cdot m^{-3}$

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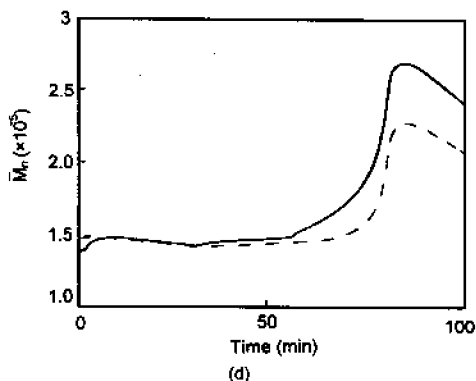
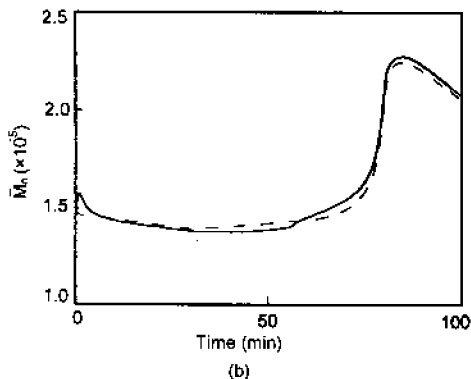
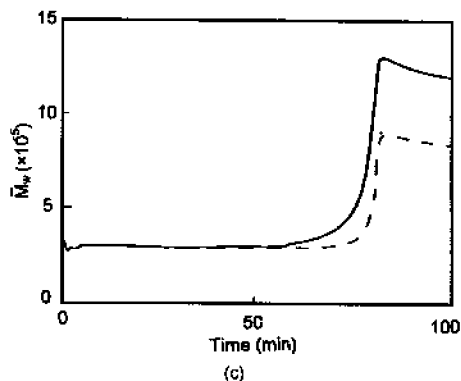
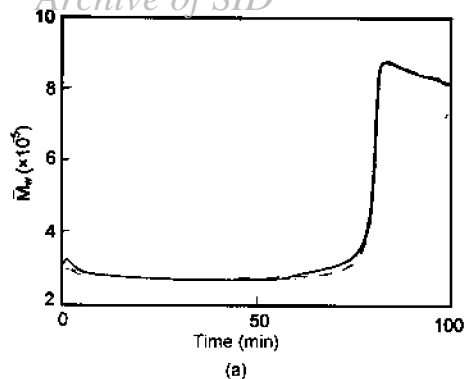


Figure 11. State estimations for 20% error in UA or $-\Delta H_p$: (a,b) selecting w_{m0} and (c,d) selecting f as a parameter state (solid line: estimated; dash line: real values).

f	initiator efficiency	k_{p0}, k_{t0}	true propagation and termination rate constant, $m^3 \cdot kmol^{-1} \cdot s^{-1}$
$f(.)$	vector of system equations	k_{ep}, k_{et}	parameters of gel and glass effect model
k	number of sampling	K	filter gain vector
k_d	rate constant for initiation reaction, s^{-1}	m	mass of reactor contents, kg
k_m	rate constant for chain transfer to monomer, $m^3 \cdot kmol^{-1} \cdot s^{-1}$	\bar{M}_n, \bar{M}_w	number and weight average molecular weights, respectively
k_p	rate constant for propagation reaction, $m^3 \cdot kmol^{-1} \cdot s^{-1}$	P_n	dead polymer chain consisting of n monomer units
k_{tc}	rate constant for termination by combination, $m^3 \cdot kmol^{-1} \cdot s^{-1}$	P, P_0	state covariance matrix and its initial value
k_{td}	rate constant for termination by disproportionation, $m^3 \cdot kmol^{-1} \cdot s^{-1}$	Q	covariance matrix of process noise v
k_t	$k_{td} + k_{tc}$	R	covariance of measurement noise w
		R_n	live polymer chain consisting of n monomer

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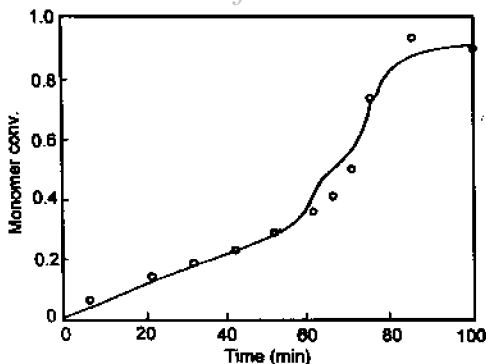


Figure 12. Experimental data and estimated values (solid line) of monomer conversions.

	units
t, t_s	time and sampling time respectively, s
T, T_j	reactor and jacket temperature respectively, K
T_{gp}	glass transition temperature of PMMA, K
U	overall heat transfer coefficient of reactor-jacket, $\text{kW}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
v	vector of the process noise
V, V_0	volume of the reacting mixture and its initial value, m^3
w	vector of measurement noise
w_{i0}, w_{m0}	loading mass of initiator and monomer respectively, kg
W_m	molecular weight of monomer, $\text{kg}\cdot\text{kmol}^{-1}$
x	vector of state variables
x_i, x_m	initiator and monomer conversions, respectively
y	vector of output measurements

GREEK LETTERS

$-\Delta H_p$	heat of propagation reactions, $\text{kJ}\cdot\text{kmol}^{-1}$
ε	polymerization volume expansion factor
λ_k	k th moment of live polymer chains
ϕ_{m0}	initial value of monomer volume fraction
ϕ_p	volume fraction of polymer
Φ	state transition matrix

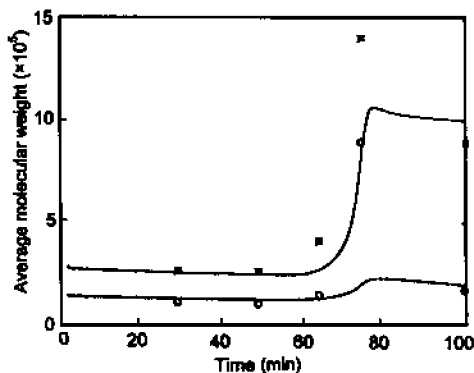


Figure 13. Experimental data and estimated values (solid line) of average molecular weights.

μ_k	k th moment of dead polymer chains
ρ_m, ρ_p	density of monomer and polymer respectively, $\text{kg}\cdot\text{m}^{-3}$

REFERENCES

- Martin J.R., Johnson J.F. and Cooper A.R., "Mechanical properties of polymers: The influence of molecular weight and molecular weight distribution", *J. Macromol. Sci. -Revs. Macromol. Chem.*, **C8**, 1, 57, 1972.
- Nunes R.W., Martin J.R. and Johnson J.F., "Influence of molecular weight distribution on mechanical properties of polymers", *Polym. Eng. and Sci.*, **22**, 205, 1982.
- Chien D.C. and Petlidis A., "On-line sensors for polymerization reactors", *J. Macromol. Sci. -Revs. Macromol. Chem. Phys.*, **C30**, 1, 1, 1990.
- Embrucu M., Lima E.L. and Pinto J.C., "A survey of advanced control of polymerization reactors", *Poly. Eng. and Sci.*, **36**, 433, 1996.
- Soroush M., "State and parameter estimation and their applications in process control", *Comp. Chem. Eng.*, **23**, 229, 1998.
- Zhang J., Martin E.B., Morris A.J. and Kiparissides C., "Inferential estimation of polymer quality using stacked neural network", *Comp. Chem. Eng.*, **21**, Suppl., S1025, 1997.
- Wilson J.A. and Zorretto L.F.M., "A generalized approach to process state estimation using hybrid artificial neural network/mechanistic model", *Comp. Chem. Eng.*, **21**, 951, 1997.

8. Tsen A.Y., Jung S.S., Wong L.S.H. and Joseph B., "Predictive control of quality in batch polymerization using ANN models", *AIChE J.*, **42**, 455, 1996.
9. Krener A.J. and Isidori A., "Linearization by output injection and non-linear observers", *System Control Lett.*, **3**, 47, 1983.
10. Gauthier J.P., Hammouri H. and Othman S., "A simple observer for non-linear systems applications to bioreactors", *IEEE Trans. Autom. Control*, **37**, 873, 1992.
11. Van Dootingh M., Viel F., Rakotopara D., Gauthier J.P. and Hobbes P., "Non-linear deterministic observer for state estimation: application to a continuous free radical polymerization reactor", *Comp. Chem. Eng.*, **16**, 777, 1992.
12. Ciccarella G., Mora M.D. and Germani A., "A Luenberger-like observer for non-linear systems", *Int. J. Control*, **57**, 537, 1993.
13. Valluri S. and Soroush M., "Non-linear state estimation in the presence of multiple steady states", *Ind. Eng. Chem. Res.*, **35**, 2645, 1996.
14. Soroush M., "Non-linear state-observer design with application to reactors", *Chem. Eng. Sci.*, **52**, 387, 1997.
15. Tatrāju S. and Soroush M., "Non-linear state estimation in a polymerization reactor", *Ind. Eng. Chem. Res.*, **36**, 2679, 1997.
16. Kurts M.J. and Henson M.A., "State and disturbance estimation for non-linear systems affine in unmeasured variables", *Comp. Chem. Eng.*, **22**, 1441, 1998.
17. Kazantzis N., Kravaris C. and Wright R.A., "Non-linear observer design for process monitoring", *Ind. Eng. Chem. Res.*, **39**, 408, 2000.
18. Jo J.H. and Bankoff S.G., "Digital monitoring and estimation of polymerization reactors", *AIChE J.*, **22**, 361, 1976.
19. Schuler H. and Suzhen Z., "Real-time estimation of the chain length distribution in a polymerization reactor", *Chem. Eng. Sci.*, **40**, 1891, 1985.
20. Schuler H. and Papadopoulou S., "Real-time estimation of the chain length distribution in a polymerization reactor-ii comparison of estimated and measured distribution functions", *Chem. Eng. Sci.*, **41**, 2681, 1986.
21. Ellis M.F., Taylor T.W., Gonzalez V. and Jensen K.F., "Estimation of molecular weight distribution in batch polymerization", *AIChE J.*, **34**, 1341, 1988.
22. Ellis M.F., Taylor T.W. and Jensen K.F., "On-line molecular weight distribution estimation and control in batch polymerization", *AIChE J.*, **40**, 445, 1994.
23. Dimitratos J., Georgaklis C., El-Aasser M. and Klein A., "Dynamic modeling and state estimation for an emulsion copolymerization reactor", *Comp. Chem. Eng.*, **13**, 21, 1989.
24. Dimitratos J., Georgaklis C., El-Aasser M. and Klein A., "An experimental study of adaptive kalman filtering in emulsion copolymerization", *Chem. Eng. Sci.*, **46**, 3203, 1991.
25. McAuley K.B. and MacGregor J.F., "On-line inference of polymer properties in an industrial polyethylene reactor", *AIChE J.*, **37**, 825, 1991.
26. Gagnon L. and Macgregor J.F., "State estimation for continuous emulsion polymerization", *Can. J. Chem. Eng.*, **69**, 648, 1991.
27. Kozub D.J. and Macgregor J.F., "State estimation for semi-batch polymerization reactors", *Chem. Eng. Sci.*, **47**, 1047, 1992.
28. Mutha R.K., Cluett W.R. and Penlidis A., "A new multirate-measurement-based estimator: emulsion copolymerization batch reactor case study", *Ind. Eng. Chem. Res.*, **36**, 1036, 1997.
29. Chae D.C., Chin I., Lee K.S., Rho H., Rhee H. and Lee J.H., "Integrated quality and tracking control of a batch PMMA reactor using a QBMPC technique", *Comp. Chem. Eng.*, **24**, 953, 2000.
30. Valappil J. and Georgaklis C., "Systematic estimation of state noise statistics for extended kalman filters", *AIChE J.*, **46**, 292, 2000.
31. Oisiovioci R.M. and Cruz S.L., "State estimation of batch distillation columns using an extended kalman filter", *Chem. Eng. Sci.*, **55**, 4667, 2000.
32. Chiu W.Y., Carratt G.M. and Soong D.S., "A computer model for the gel effect in free radical polymerization", *Macromolecules*, **16**, 348, 1983.
33. Penlidis A., Ponnuswamy S.R., Kiparissides C. and O'Driscoll K.F., "Polymer reaction engineering: modeling considerations for control studies", *Chem. Eng. J.*, **50**, 95, 1992.
34. Soroush M. and Kravaris C., "Non-linear control of a batch polymerization reactor: an experimental study", *AIChE J.*, **38**, 1429, 1992.
35. Dotson N.A., Galvan R., Laurence R.L. and Tirrell M., *Polymerization Process Modeling*, VCH Publishers, 1996.
36. Schmidt A.D. and Ray W.H., "The dynamic behavior of continuous polymerization reactors-I", *Chem. Eng. Sci.*, **36**, 1401, 1981.
37. Baillagou P.E. and Soong D.S., "Molecular weight distribution of products of free radical nonisothermal polymerization with gel effect. simulation for polymerization of poly(methyl methacrylate)", *Chem. Eng. Sci.*, **40**, 87, 1985.
38. Kalman R.E. and Bucy R.S., "A new approach to linear filtering and prediction problems", *Trans. ASME J. Basic Eng.*, **83**, 95, 1961.

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39. Gelb A., *Applied Optimal Estimation*, MIT Press, Cambridge, 1974.
40. Blotman G.J., *Estimation Methods for Discrete Sequential Experiments*, Academic Press, 1977.
41. Kambhampati P. G., Bryson A. E. and Schmidt S. F., "Discrete root filtering: a survey of current techniques", *IEEE Trans. Autom. Control*, **16**, 727, 1971.
42. Smith M.W.A. and Roberts A.P., "A study of the kalman filter as a state estimator of deterministic and stochastic systems", *Int. J. Systems Sci.*, **10**, 8, 895, 1979.
43. Semino D., Morretta M. and Scali C., "Parameter estimation in extended kalman filters for quality control in polymerization reactors", *Comp. Chem. Eng.*, **20**, Suppl., S913, 1996.
44. Elicabe G.E. and Georgakis C., "Effect of feed back controllers in state estimation schemes" *Ind. Eng. Chem. Res.*, **39**, 387, 2000.
45. Ray W.H., "Polymerization reactor control", *IEEE Control Systems Mag.*, **6**, 4, 3, 1986.
46. Wilson D.I., Agarwal M. and Ripplin D.W.T., "Experiences implementing the extended kalman filter on an industrial batch reactor", *Comp. Chem. Eng.*, **22**, 1653, 1998.