

On-Line Parameter Estimation in a Continuous Polymerization Process

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A large number of high activity catalysts are used to produce different grades of polymers in a continuous olefin polymerization reactor. Often the transition from one grade to another is carried out by changing the reactor operating conditions as well as the catalyst. The major kinetic parameters are seldom known for all the different types of catalysts. The catalyst composition may differ only slightly from each other but enough to result in significant differences in polymer properties. In practice, it is very time consuming and costly to carry out extensive plant tests to identify the kinetics of polymerization for a given catalyst system. In this paper, two different on-line parameter estimation schemes (extended Kalman filtering and nonlinear dynamic parameter estimation) are investigated to estimate key kinetic parameters of transition-metal-catalyzed olefin polymerization. Parameter estimation using an extended Kalman filter is shown to perform robustly even in the presence of substantial measurement noise because of greater flexibility in tuning parameters, while the parameter estimator based on nonlinear programming techniques (nonlinear dynamic parameter estimator) shows a stronger sensitivity to measurement noise due to a lack of sufficient tuning parameters. Both the extended Kalman filter and the nonlinear dynamic parameter estimator give identical results after a sufficient number of measurements have been obtained.

Introduction

Continuous reactors are widely used to manufacture high-volume commodity polymers and some specialty polymers. With a growing demand for consistent and high-quality polymers, there is a strong need to optimize process operations. Tightening economic constraints also force polymer manufacturers to reduce the amount of off-specification products during the normal process operation, startup, and grade transition. For a process that has a large process time constant or residence time, it is particularly important to optimize the transition operations so that minimum transition products or off-specifications are produced. For normal steady-state operation, it is also important to control the effect of process disturbances so that polymers of consistent quality can be produced. Recently, some workers have reported optimal-grade transition control problems in continuous olefin polymerization processes (Ray, 1992, 1994; Debling *et al.*, 1994; McAuley and MacGregor, 1992). In these works, it was shown that the production schedule or cycle can be optimized to minimize the production of transition products and thus maximize the profitability of the process. It was also illustrated that the polymers of different properties or grades can be produced by changing the reactor operating conditions for a given catalyst system. In all these works, the design of optimal-grade transition strategies was based on process models.

In the polymerization process to be considered in this paper, ethylene copolymers are produced in a continuous fluidized-bed reactor with high-activity transition-metal catalysts. Polymer properties can be varied to some extent by changing the reactor operating conditions such as temperature, feed composition, additives, and so forth. However, we consider the case where polymer properties are primarily dictated by the type of catalyst being used. To make polymers of different properties or grades, catalysts of different activity and

selectivity are injected into the reactor. In general, extensive pilot plant and plant testings are necessary to design the reactor operating conditions for a given catalyst system to produce the polymers of certain properties.

Let us assume that there are several catalysts to be used for the production of different grade polymers. For the design of advanced reactor controls and operating conditions, we need a process model based on the chemistry and physics of the process. Such a model contains a large number of kinetic parameters and reactor-specific parameters. However, it is generally very costly and time consuming to characterize the polymerization kinetics for a given catalyst system. Let us suppose that we have conducted an extensive kinetics study to complete a process model for a reference or base catalyst. When there are many other catalysts that give rise to different polymer properties, it is not often economically feasible to carry out similar study for each catalyst system. In olefin polymerization processes, these catalysts are often characterized by similar compositions with the same base transition metal but exhibit distinctly different polymerization performances, as reflected in the polymer properties produced by them. This implies that the kinetics of polymerization can be modeled by a single framework, but each catalyst system may have a different set of kinetic parameters. It must also be pointed out that, in reality, batch-to-batch variations in catalyst composition are not uncommon even for one type of catalyst. Then, the problem is how one can use the information for a certain catalyst system (i.e., base catalyst) that is relatively well understood to quantify the kinetics of polymerization for different but similar catalysts. This is the problem we shall address in this paper. As will be described in what follows, we propose to use an approximate process model with an on-line optimal parameter estimation technique.

Polymerization Reactor Model

The polymerization system we shall consider in this work is a fluidized-bed reactor for ethylene copolymer-

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Table 1. Kinetic Scheme for Copolymerization Reaction^a

initiation	$C^* + M_1 \xrightarrow{k_{i1}} P_{1,0}$
	$C^* + M_2 \xrightarrow{k_{i2}} Q_{0,1}$
propagation	$P_{n,m} + M_1 \xrightarrow{k_{11}} P_{n+1,m}$
	$P_{n,m} + M_2 \xrightarrow{k_{12}} Q_{n,m+1}$
	$Q_{n,m} + M_1 \xrightarrow{k_{21}} P_{n+1,m}$
	$Q_{n,m} + M_2 \xrightarrow{k_{22}} Q_{n,m+1}$
chain transfer	$P_{n,m} + H_2 \xrightarrow{k_h} M_{n,m} + C^*$
	$Q_{n,m} + H_2 \xrightarrow{k_h} M_{n,m} + C^*$
catalyst deactivation	$C^* \xrightarrow{k_d} D^*$
	$P_{n,m} \xrightarrow{k_d} M_{n,m} + D^*$
	$Q_{n,m} \xrightarrow{k_d} M_{n,m} + D^*$

^a See notations for symbols.

ization. The polymerization is catalyzed by solid catalysts of high activity. Feed monomer mixture, hydrogen (chain-transfer agent), and catalyst are supplied to the reactor. The heat of polymerization is removed by the fluidizing gas and the reactor residence time is on the order of 3–5 h. Since the polymer is formed on the solid catalyst, the catalyst particle increases in its volume as polymerization continues. Thus, polymers are withdrawn from the reactor to maintain a constant reactor volume. Table 1 shows the kinetic scheme used in the reactor modeling. The key polymer property parameters are melt index and polymer density that can be correlated to molecular weight and copolymer composition, respectively.

To start the grade transition, the supply of old catalyst is stopped and new catalyst is injected. During the transition period, the reactor has a mixture of old and new catalysts. Here, our objective is to extract kinetic information from the dynamic process data during the transition period to estimate principal kinetic parameters for the new catalyst. The kinetic parameters for each catalyst are unique and constant. Before the grade transition, the kinetic parameters of the old catalyst are known with good certainty. The true kinetic parameters of the new catalyst are not known but are reasonably close to the parameters of the old catalyst. The delayed (ca. 2 h) measurements of polymer properties and slow process dynamics (residence time of ca. 4 h) make the on-line parameter estimation task difficult and challenging.

Let us first briefly review the various parameter estimation schemes available which can be used for on-line calculations using a process model.

Parameter Estimation

The continuous polymerization reactor system is represented by a system of ordinary differential equations. The cost function to estimate parameters in a mathematical model of a dynamic system is formulated in terms of an error function $\epsilon(t)$ which reflects the discrepancy between the model and the real system (plant). The most common cost function is a weighted integral squared error:

$$J = \int_{t_0}^{t_f} [\epsilon^T(t) \mathbf{W}(t) \epsilon(t)] dt \quad (1)$$

where \mathbf{W} is a positive definite weighting matrix and $t_f - t_0$ is the time period over which data are available. There are two basic methods of data processing by minimizing cost functions. These are “off-line” or batch processing and the “on-line” or recursive approach. In off-line processing the computational operations are carried out on the complete set of data as a whole. In the recursive or on-line approach the parameter estimate vector is updated continuously while working serially through the data. The most common recursive algorithm is a gradient algorithm of the form (Young, 1981)

$$d\beta(t)/dt = -\mathbf{G}\nabla_{\beta} J_1\{\beta(t)\} \quad (2)$$

or its discrete-time equivalent,

$$\beta_k = \beta_{k-1} - \mathbf{G}\nabla_{\beta} J_1\{\beta_{k-1}\} \quad (3)$$

where \mathbf{G} is a positive definite gain matrix which may be time variable. The parameter estimate $\beta(t)$ is updated continuously according to the gradient ($\nabla_{\beta} J_1$) of the instantaneous cost function $J_1\{\beta\}$. Given the labyrinthine nature of parameter estimation classification, the same method can be known under different names depending on the model structure it is applied to. Different algorithms may result depending on the approach used in the derivation. Different approximations and tricks for performance improvement also lead to a myriad of algorithms that, in fact, are closely related (Eykhoff, 1974; Young, 1981; Ljung and Söderström, 1983; Unbehauen and Rao, 1990). For the polymerization process system considered, we will investigate two different methods.

A. EKF (Extended Kalman Filter). A Kalman filter is used to optimally estimate the state vector in linear systems. For nonlinear systems EKF is used which linearizes the nonlinear system around the current time. The applications of an extended Kalman filter to polymerization systems have been investigated by many workers for state estimation and controller design (Jo and Bankoff, 1976; Hyun and Bankoff, 1976; Kiparissides and MacGregor, 1981; Schuler and Suzhen, 1985; Schuler and Papadopolou, 1986). Delayed off-line measurements can be incorporated using two time-scale filters (Ray, 1984, 1986; Papadopolou and Gilles, 1986; Taylor *et al.*, 1986; Ellis *et al.*, 1988; Choi and Khan, 1988; Adebekun and Schork, 1989; Dimitratos *et al.*, 1989; Kim and Choi, 1991). EKF can also be used for on-line parameter estimation (Adebekun and Schork, 1989; Li and Olson, 1991; Kim *et al.*, 1992). In such a case, the state vector is extended by adjoining it with the vector of unknown parameters β . Identifying constant parameters (β) in a system is a special case of the general state estimation problem:

$$\dot{\beta} = 0 \quad (4)$$

The dynamic model of a polymerization reactor system is given by

$$\dot{\mathbf{x}}(t) = f(u(t), \mathbf{x}(t), t, \beta) \quad (5)$$

In order to estimate the states (\mathbf{x}) and the parameters (β) in real time, an extended state vector (\mathbf{z}) becomes

$$\mathbf{z}(t) = \begin{bmatrix} \mathbf{x} \\ \beta \end{bmatrix} = \begin{bmatrix} f(u(t), \mathbf{x}(t), t, \beta) \\ 0 \end{bmatrix} = F(u(t), \mathbf{z}(t), t, \beta) \quad (6)$$

EKF was selected over other on-line recursive methods because (a) it makes full use of all the states of detailed first principles model (the model being open-loop stable), (b) it provides tuning parameters for all the variables, and (c) there is a negligible effect of colored noise in closed-loop operation. The sluggish convergence of parameters during on-line use of EKF can be expedited by overweighing the most recent data (Jazwinski, 1969), though it was not attempted in this paper. If the model is open-loop unstable, then a reduced-order estimator can be constructed (Berstein and Haddad, 1989; Bequette, 1991). The computations in EKF are fast due to its recursive nature, and this aspect makes it suitable for on-line applications.

B. NDPE (Nonlinear Dynamic Parameter Estimator). In this method, the parameters are estimated by solving the estimation problem as a nonlinear programming problem (NLP). The objective function is formulated as the sum of squared error between the plant and model output. This method is similar to the off-line least-squares method. Since it is known when a new batch/type of catalyst is introduced to the reactor, the measurements since then are used to minimize the weighted least-squares objective function. NDPE is a deterministic estimation method when compared to EKF. As measurements become available, the model represented by eqs 7 and 8 is integrated from t_0 to t_i , where t_i is the current time and t_0 is the time when a new batch/type of catalyst was introduced:

$$\dot{\mathbf{x}}(t) = f(u(t), \mathbf{x}(t), t, \beta) \quad (7)$$

$$\text{I.C.} \quad \mathbf{x}(t_0) = \mathbf{x}_0 \quad (8)$$

The solution of the differential equations will strongly depend on the initial condition \mathbf{x}_0 . Sistu and Bequette (1991) have discussed the effects of various choices for the initial conditions. They conclude that setting the initial conditions for the model equal to the process measurements can yield poor performance in the presence of a model-plant mismatch. They found that the initial conditions for an open-loop stable system can be obtained from the solution of the model over the previous time step. For an open-loop unstable system they recommended using a state variable identification procedure so that model states do not diverge significantly from the actual state variables. For an on-line parameter and state estimation Jang and co-workers (1986) found the approach based on nonlinear programming to be superior to an extended Kalman filter. The nonlinear programming approaches are computationally intensive and have been used in designing nonlinear model predictive controllers (Ramamurthi *et al.*, 1993). The problem of data reconciliation and parameter estimation accounting for errors in both the input and output variables was formulated as a nonlinear dynamic error-in-variables method (NDEVM) by Kim *et al.* (1991). Numerical integration was nested within a nonlinear programming algorithm for on-line and off-line parameter estimation. They defined a moving data window (or horizon) which extended back certain time steps from the current time. At current time, all the measurements within this data horizon are available to estimate the parameters or reconcile the data. As a new measurement is included in the data horizon, the oldest measurement is dropped from the data window, thus keeping the horizon size fixed.

The parameter estimation problem in the polymerization process being considered in this paper is of a

different nature. The time and the type of major disturbance (i.e., change of feed catalyst type) are known with reasonable accuracy. Once acceptable estimates of the new parameters (i.e., kinetic parameters) are obtained, the nonlinear dynamic parameter estimator (NDPE) is switched off. The initial states play a very important role in solving the model differential equations. We have used EKF to provide for optimal model state estimates at time t_0 to NDPE since EKF is assumed to have reached steady state and provides good estimates. A combination of NDPE and EKF to estimate the parameters utilizes the well-developed theory of nonlinear optimization and optimal state estimation. After NDPE is started, the data set continues to grow, and each successive calculation takes longer to complete. If satisfactory parameter estimates are not available before the data set becomes too large, then a moving window or a horizon approach may be used. The model used in this paper to represent an industrial reactor model consists of 17 state variables. Using computationally intensive approaches which take into account errors in all the variables is not warranted for our model at this moment.

Plant and Model

Since no actual polymerization plant data are available, the plant will be simulated by a mathematical model which is referred to as *Plant Model* (PM). PM is a detailed first-principles fluidized-bed copolymerization reactor model. This model is an extension of the two-phase fluidized-bed reactor model proposed by Choi and Ray (1985). The monomers used are ethylene and butene-1. Inert nitrogen is also used along with the monomers to achieve the high flow rates required for fluidization and heat removal. Hydrogen is used as a chain-transfer agent to control the molecular weight. The details of the fluidized-bed olefin polymerization process are also described by McAuley and MacGregor (1992). PM acts as a plant in which pressure, gas compositions, and bed weight (or level) are controlled by manipulating bleed flow rate, makeup flow rates, and product withdrawal rate, respectively. Since the goal of this study is not controller design, hence PI controllers are used in all the loops. A schematic of the polymerization reactor is shown in Figure 1.

The choice of model for on-line estimation which will be referred to as *Simulation Model* (SM) is a difficult one. In this work, the actual polymerization reactor is modeled as a continuous stirred-bed reactor (CSBR). In practice, PM approaches a CSBR model if the reactor is very well mixed (i.e., no distinction between the phases) and conversion per pass is very small. The simplified CSBR model is selected as SM. SM has only one perfectly backmixed phase. It is very obvious that there will be some model-plant (SM-PM) mismatch. In industrial practice, when an available model is to be used on a plant, it is first modified or adjusted to that particular plant to remove any mismatch before using it for any on-line estimation and control purposes. We call this procedure a customization process. The customization (removing mismatch) of SM to PM can be carried out by updating certain kinetic parameters. The results of the customization will be shown later. The rate constant values and typical reactor conditions for ethylene-butene-1 copolymerization are taken from Hutchinson *et al.* (1992) and are shown in Table 2. The CSBR model is shown in the appendix.

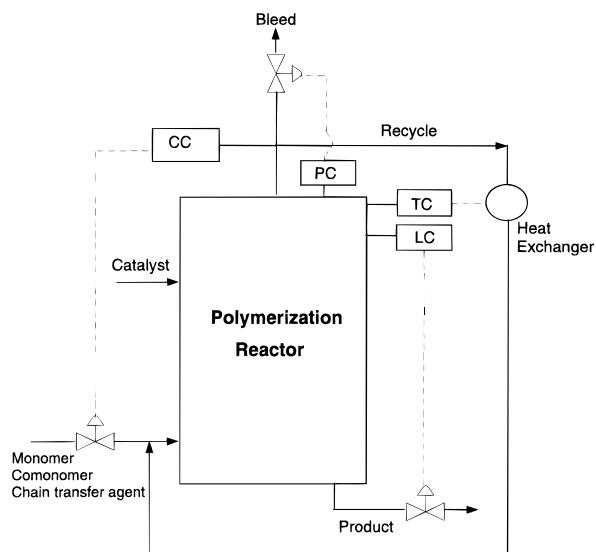


Figure 1. Schematic of a continuous polymerization reactor (CC, composition controller; LC, bed level controller; PC, pressure controller; TC, temperature controller).

Table 2. Simulation Conditions

Kinetic Parameters	
$k_{11} = 4.49 \times 10^{10} \exp(-7000/RT) \text{ L/mol}\cdot\text{s}$	
$k_{12} = 1.50 \times 10^9 \exp(-7000/RT) \text{ L/mol}\cdot\text{s}$	
$k_{21} = 4.49 \times 10^9 \exp(-7000/RT) \text{ L/mol}\cdot\text{s}$	
$k_{22} = 5.96 \times 10^8 \exp(-7000/RT) \text{ L/mol}\cdot\text{s}$	
$k_h = 1.60 \times 10^9 \exp(-8000/RT) (\text{L/mol})^{1/2}/\text{s}$	
$k_d = 1.6 \times 10^{-4} \exp(-1000/RT) 1/\text{s}$	
Simulation Parameters	
$T(^{\circ}\text{C})$	80.0
$P(\text{atm})$	35.0
U_0 (gas velocity, cm/s)	50.0
catalyst flow rate (g/h)	10.0
solid-phase residence time (h)	4.0

Selection of Key Parameters

The four most important plant outputs required for off-line estimation of rate constants are reactor temperature, production rate, polymer density, and melt index (or molecular weights). The reactor temperature affects the polymer properties (density and M_w), while bed weight affects the production rate. In our simulations, temperature and bed weight are maintained constant using PI controllers. Time-varying values of these four plant outputs during the reactor transients give information about the major kinetic parameters which control the reactor behavior and product properties. Most of the other input variables do not directly affect the kinetic rate constants. It is not possible to carry out off-line parameter estimation studies for each and every catalyst since they are often expensive and time consuming. Moreover, as described earlier, it is not easy to estimate all the kinetic parameters in the model for a new catalyst system using the kinetic information for the base catalyst.

Our approach is first to identify a small number of key kinetic parameters that have the strongest effects on the major output variables. Thus, we carry out a perturbation test (step test) on the process originally at steady state. Then, each kinetic parameter in the plant model (PM) is increased by 10%, and the corresponding changes in production rate, density, and molecular weight are observed. Only the propagation, deactivation and chain transfer to hydrogen rate parameters are selected since they are the dominant ones.

Table 3. Steady-State Sensitivity Analysis

parameter (10% change)	output properties (% changes)		
	$\Delta Q/Q$	$\Delta \rho/\rho$	$\Delta M_w/M_w$
k_{11}	5.53	0.18	9.21
k_{12}	0.25	-0.19	0.47
k_{21}	0.110	9.58×10^{-4}	0.21
k_{22}	9.93×10^{-3}	-1.42×10^{-3}	3.13×10^{-2}
k_h	-2.8×10^{-2}	-7.40×10^{-4}	-9.04
k_d	-2.25	-5.80×10^{-3}	0.47

As the system reaches a new steady state, the resulting percent changes in polymer properties and production rate are measured. The steady-state reactor temperature is 80 °C. When each of the rate constants is increased by 10%, the steady-state reactor temperature changes from 80 °C, which is again brought back to 80 °C by manipulating the reactor feed temperature. The corresponding changes in production rate, density, and molecular weight are noted with respect to original steady-state values and are entered as percentage changes as shown in Table 3. It is quite clear from Table 3 that to capture the deviations in production rate (Q), density (ρ), and weight-average molecular weight (M_w) at least three (minimum possible) kinetic parameters (k_{11} , k_{12} , k_h) need to be updated on-line. The reactor temperature during the transition is relatively constant; hence, it is not possible to uniquely identify both the frequency factor and activation energy of each rate constant. The new catalyst parameters are thus related to the old catalyst parameters at a fixed temperature by introducing simple multiplicative factors (ϕ_{11} , ϕ_{12} , and ϕ_h) in our simulations:

$$K_{11}^{\text{new}} = \phi_{11} K_{11}^{\text{old}}, \quad K_{12}^{\text{new}} = \phi_{12} K_{12}^{\text{old}}, \quad K_h^{\text{new}} = \phi_h K_h^{\text{old}}$$

If more input and output variables are present, then a systematic structural and singular value analysis can be carried out (Krishnan *et al.*, 1992). The selection of parameters is similar to loop pairings used in multi-variable control. Note that the sensitivity analysis in Table 3 is performed at one set of typical reactor operating conditions. The values may be different with a different set of operating conditions (e.g., at different temperatures) and/or kinetic parameters.

Extended Kalman Filter and Estimator Design

The reactor model is in continuous time, and the measurements are obtained at discrete time intervals; therefore, an extended Kalman filter is implemented as a continuous-discrete filter (Gelb, 1982). To estimate the unknown parameters, the state vector of the filter (\mathbf{x}) is augmented by the parameter vector ($\boldsymbol{\beta}$) and the resulting state vector (\mathbf{z}) is solved to obtain optimal estimates of the states and parameters. The algorithm incorporating the delayed measurements is shown in Table 4 (Kim and Choi, 1991). The process model is corrupted by noise $w(t)$. The outputs (y) have measurement errors $v(t)$. \mathbf{Q} is the covariance matrix of model errors, \mathbf{P} the estimation covariance matrix, and \mathbf{R} the covariance matrix of measurement errors. The noise is assumed to be white in nature. τ is measurement delay. The delayed measurements are incorporated as a simple two-step procedure:

(i) When measurements taken at time $t - \tau$ are available at present time t , old state and covariance estimates at $t - \tau$ are updated.

(ii) With updated values of $\mathbf{z}(t - \tau)$ and $\mathbf{P}(t - \tau)$, integration of the process model (SM) is carried out from $t - \tau$

Table 4. Parameter Estimation Algorithm Using EKF

extended model (model states and unknown parameters)

$$\dot{\mathbf{z}}(t) = F(u(t), \mathbf{z}(t), t) + w(t), w(t) \sim N[0, Q(t)]$$

measurement model (with on-line measurements)

$$y_{0k} = h_0(z_k) + v_{0k}, v_{0k} \sim N[0, R_{0k}]$$

measurement model (with off-line measurements)

$$y_{d_{k-r}} = h_d(\mathbf{z}_{k-r}) + v_{d_{k-r}}, v_{d_{k-r}} \sim N[0, R_{d_{k-r}}]$$

state estimate propagation

$$\hat{\mathbf{z}}(t) = F(u(t), \hat{\mathbf{z}}(t), t)$$

error covariance propagation

$$\dot{\mathbf{P}}(t) = F_z(t) \mathbf{P}(t) + \mathbf{P}(t) F_z^T(t) + Q(t)$$

state estimate update at t_k with on-line measurements

$$\hat{\mathbf{z}}_k(+) = \hat{\mathbf{z}}_k(-) + K_k[y_{0k} - h_0(\hat{\mathbf{z}}_k(-))]$$

error covariance update at t_k with on-line measurements

$$P_k(+) = [I - K_k H_0] P_k(-)$$

gain matrix at t_k with on-line measurements

$$K_k = P_k H_0^T [H_0 P_k(-) H_0^T + R_{0k}]^{-1}$$

where

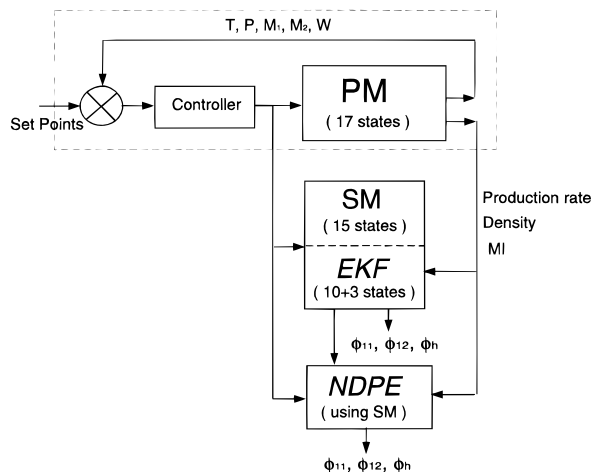
$$F_z(t) = \left. \frac{\partial F(u(t), \mathbf{z}(t))}{\partial \mathbf{z}(t)} \right|_{\mathbf{z}(t)=\hat{\mathbf{z}}(t)}$$

$$H_{0k} = \left. \frac{\partial h_0(z_k)}{\partial z_k} \right|_{z_k=\hat{z}_k}$$

to present time t to provide updated estimates at present time.

Figure 2 schematically shows how EKF is used to estimate the parameters. PM has 17 system states and is the detailed two-phase reactor model with recycle. SM is a simplified 15 state one-phase single-pass open-loop reactor model. It is desired to have a minimum number of states for the filter lest the total number of ODEs should become too large. A few of the model states which do not affect the plant output prediction and parameter estimation (e.g., nitrogen concentration, active site concentrations) are not considered a part of the reduced order filter. The filter is a subset of SM, i.e., it uses only some of SM state equations for parameter and state estimation. The filter state vector is augmented to include the unknown parameters as additional states, resulting in a total of 13(10 + 3) EKF states. PM is operating in a closed loop, with the temperature, pressure, monomer and comonomer concentrations (M_1 , M_2), and bed weight controlled by PI controllers. It is implicit from the model equations that the system is observable. The process outputs that are measured and used to drive the filter and model equations are reactor temperature (T), reactor pressure (P), ethylene (M_1) mole percent at the reactor outlet, butene (M_2) mole percent at the reactor outlet, bed level (W), M_w (weight-average molecular weight), M_n (number-average molecular weight), and polymer density.

Reactor pressure and temperature along with the concentration (mol %) of components at the reactor outlet are used to calculate the concentration (mol/L) values required for the filter and the model solutions. The number- and weight-average molecular weights are calculated using the method of moments (Ray, 1972). To calculate the properties of a polymer mixture produced by two single active sites during the transition period, six molecular weight moments for dead polymers are required. When there is only one type of catalyst active site in the reactor, the molecular weight moments are fully observable. During the transition period two types of catalyst active sites are present in the reactor, and to calculate the average molecular weights, six moment equations need to be solved. The system during the transition time is only partially observable (only two measurements for six molecular weight moments). To solve the filter equations during this time,

**Figure 2.** Information exchange between various models and parameter estimators.

we assume that, as soon as catalyst B is injected and catalyst A feed is stopped, the polymer properties predicted by SM for catalyst A are perfect (i.e., the EKF has converged to true estimates of state variables and kinetic parameters). Therefore, when catalyst B is injected, the filter switches from catalyst A molecular weight moments to catalyst B molecular weight moments. The system becomes fully observable with the above assumption.

Polymer density is empirically correlated to weight percent comonomer incorporated in the polymer. Measurement of the copolymer density makes the copolymer composition in the reactor observable. SM and EKF are run in an open loop at each iteration. The predicted state variables and the filter covariances are updated at each iteration using on-line measurements. The results of off-line analysis are available after some delay which is included in the filter as discussed before. In this estimator design tuning of the filter parameters plays a very important role. To use the extended Kalman filters, extensive trial and error effort is often required to tune the filter to obtain satisfactory performance. As shown in Table 6, we select measurement noise for PM based on our experience. Covariance matrix \mathbf{R} of EKF is then fixed based on the noise level selected. \mathbf{Q} is the covariance matrix of model errors, and it acts as a tuning parameter to obtain desired estimator speed and robustness. We have shown later that once the estimator is tuned satisfactorily it performs well in other similar cases too.

NDPE Design

Parameter estimation using EKF formulation has been discussed in the previous section. Estimation using NLP techniques uses the initial states from EKF just before the new catalyst is introduced. Figure 2 shows how NDPE exchanges information with other models. There is some model-plant mismatch at the initial starting time for NDPE. The initial estimates of parameters (when only a few data points are available) would be in error if initial SM-PM prediction mismatch is not removed in NDPE formulation. As in model predictive control (MPC) (Bequette, 1991), the prediction step in NDPE assumes that process disturbance (model error) during integration from past to present is equal to the additive disturbance at the time (t_0) when new catalyst is injected:

$$d(t_0) = y(t_0) - y_m(t_0)$$

$$\hat{y}(t) = y_m(t) + d(t_0); \quad t > t_0$$

where y_m is the measured output and \hat{y} is the predicted output. This assumption becomes insignificant after a large number of data points are obtained but is significant when the process outputs and the operating conditions do not change much. This assumption is used to make the estimator more robust to measurement noise especially when the properties have not deviated significantly from their steady state and only a few polymer property measurements are obtained. If this assumption is not used, then NDPE estimation is expected to be noisy (at the beginning) until a sufficient number of measurements become available. The following objective function is minimized by NDPE:

$$J = \sum_{i=1}^N \sum_{j=1}^3 w_j (y_i - \hat{y}_j)^2$$

subject to

$$\dot{\mathbf{x}}(t) = f(u(t), \mathbf{x}(t), t, \beta)$$

$$\mathbf{x}(t_0) = \mathbf{x}_0$$

where N is the number of data points available, w_j are the weights, y_i are the measured plant outputs, and \hat{y}_j are the model predicted outputs. The three outputs used in the objective function are melt index, polymer density, and production rate. The measurements are obtained every half hour with a delay of 2 h. There will be only 4 data points available after 4 h and 16 data points after 10 h. The evaluation of the objective function (J) of the NLP problem requires the solution of model ODEs. Since the model is very nonlinear, the gradient of the objective function is calculated using finite differences. Figure 3 shows how the NDPE algorithm works. The NLP problem is solved sequentially by successively integrating the ODEs as new measurements become available. There are several other ways to solve the above problem (Bequette, 1991), but a successive integration technique keeps the detailed first-principles process model structure intact.

FSQP (feasible sequential quadratic programming) algorithm (Panier and Tits, 1993) is used to solve the optimization problem. FSQP minimizes the maximum of a smooth objective function subject to general smooth constraints. The FSQP algorithm is based on a modified sequential quadratic programming (SQP) so as to generate feasible iterates. If the initial guess provided by the user is infeasible for some inequality constraint or some linear equality constraint, FSQP first generates a feasible point for these constraints and all successive iterates generated by FSQP satisfy these constraints. Nonlinear equality constraints are converted to inequality constraints. The software implements two algorithms. The first one is a monotone line search in which a certain Armijo type arch search is used with the property that the step of one is eventually accepted, which is a requirement of superlinear convergence. In the second algorithm the same effect is achieved by means of a nonmonotone search along a straight line.

NDPE uses SM to successively integrate the model equations to evaluate the objective function. The optimal values of the states at time t_0 are supplied by EKF for the solution of model equations. Tuning NDPE is

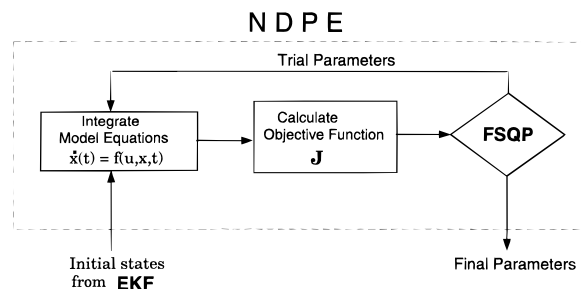


Figure 3. Formulation of NDPE algorithm.

much easier and less time consuming than EKF. The weights w_j are selected based on how much of each variable in the objective function is expected to change. By trial and error it was fairly simple to fix the weights for a broad operating range. The results using the two estimators will be discussed and compared in the next section.

Results and Discussion

Model-Plant Customization. The two different types of models (PM for plant simulation and SM for on-line estimation) have been described earlier. EKF is used to minimize the model-plant mismatch by updating certain model parameters. As mentioned earlier, only three kinetic parameters are updated on-line to remove any model-plant mismatch if it results because of catalyst disturbances only. When the simplified simulation model (SM) is force fitted to the detailed plant model (PM), one more parameter is required to be updated because of inherent differences between the model and the plant. The simplified model assumes that the reactor has only one perfectly backmixed phase, while the detailed model contains two separate bubble and emulsion phases. There is a substantial amount of heat transfer between the phases. The amount of heat transfer between the emulsion and bubble phases depends on various fluidization parameters, the most important being the average bubble size in the reactor. For the operating conditions chosen the simplified model estimates a higher reactor temperature for a given input feed temperature and catalyst injection rate. To fit the model to the plant, the temperature, production rate, melt index, and density should match. An additional parameter chosen is the wall heat-transfer coefficient (h_w).

It is assumed that the rate constants obtained for SM from PM data have 5–10% error in estimation. Figure 4 shows the temperature, melt index, and density profiles for SM and PM. Notice that the plant is at its steady state. The EKF is started at 5 h. All the input conditions are the same for both SM and PM. Random noise has been included in manipulated makeup component feed flow rates and measurements as shown in Table 6. A random walk model is used when estimating the kinetic parameters in EKF formulation. PM measurements are represented by open circles (○). As seen in Figure 4 there is substantial SM-PM mismatch before EKF is started ($t < 5$ h). The solid phase residence time in the reactor is 4 h. It is seen in Figure 4 that the estimated reactor temperature converges to the actual temperature in about one residence time, whereas the polymer property parameters (melt index and density) converge rather slowly. Figure 5 shows the parameters which are updated. The kinetic parameters and wall heat-transfer coefficient have been scaled

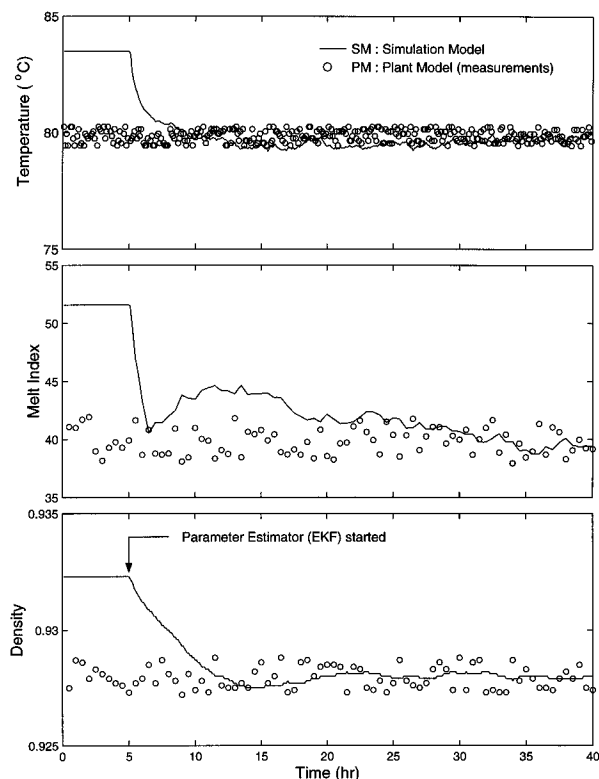


Figure 4. Reactor properties during model-plant customization. The parameter estimator (EKF) is started at 5 h. No delay is present in this off-line processing.

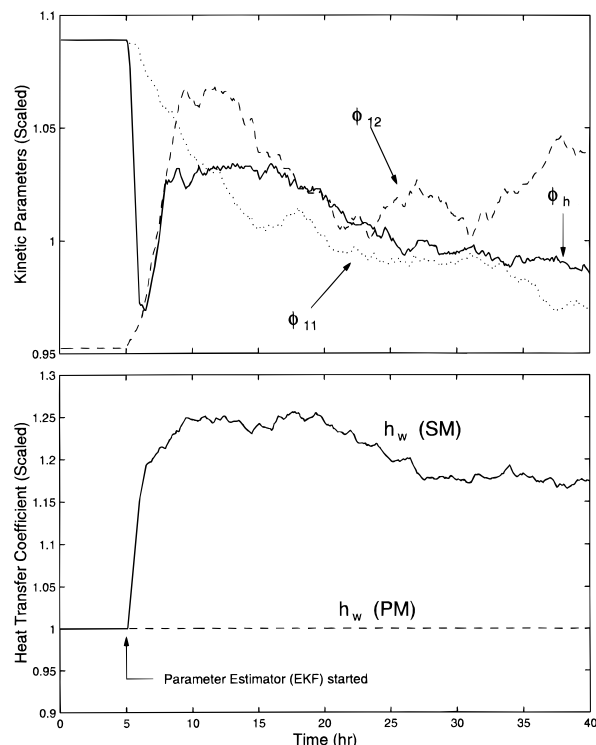


Figure 5. SM parameters during model-plant customization. The parameter estimator (EKF) is started at 5 h. No delay is present in this off-line processing.

with reference to parameters in PM. The wall heat-transfer coefficient for the simplified model is about 15% higher than for the two-phase model (PM). Recall that the wall heat-transfer coefficient (h_w) estimated by SM is not necessarily the true wall heat-transfer coefficient for the plant. The h_w value is used to match the predicted reactor temperature with the actual reactor

Table 5. Relative Catalyst Parameters

catalyst type	in relation to old parameters					
	$\times k_{11}$	$\times k_{12}$	$\times k_{21}$	$\times k_{22}$	$\times k_h$	$\times k_d$
catalyst A (base)	1.0	1.0	1.0	1.0	1.0	1.0
catalyst B (case 1)	0.9	1.4	2.0	2.5	0.8	1.67
catalyst B (case 2)	1.1	0.7	9.0	0.1	1.2	0.71
						half-life = 5 h
						half-life = 3 h
						half-life = 7 h

Table 6. System and Measurement Noise

monomer flow rate (kg/h)	$\pm(0-2)\%$
comonomer flow rate (kg/h)	$\pm(0-5)\%$
hydrogen flow rate (g/h)	$\pm(0-2)\%$
temperature ($^{\circ}\text{C}$)	$\pm(0-1)^{\circ}\text{C}$
production rate (kg/h)	$\pm(0-3)\%$
M_w	$\pm(0-3)\%$
M_n	$\pm(0-3)\%$
density (g/cm^3)	$\pm(0-0.001)$

temperature. Note that the updated parameters should stay at 1.0 if SM models PM perfectly. It is interesting to observe that the estimated melt index profiles are very similar to the profiles of ϕ_h (correction factor for hydrogen chain-transfer constant).

Comparison of NDPE and EKF. After SM has been customized to PM, the simulation model is used to estimate the catalyst disturbances when a new type/batch of catalyst is injected. Since the strategy is to be applied on-line, it is not known which parameters are going to change in the new catalyst, but it is known that the new catalyst exhibits polymerization kinetics similar to that of the old catalyst. The old catalyst (catalyst A) is in the reactor initially. At 5 h the feed rate of the old catalyst is stopped and the new catalyst (catalyst B) is injected. The kinetic parameters of catalyst B are different from catalyst A as shown in Table 5 for two different cases to be considered. Catalyst A refers to the parameters of the old catalyst in PM. The second and third rows are the two cases showing how the kinetic parameters for catalyst B will be changed with reference to that of catalyst A. Notice that the catalyst deactivation parameter (k_d) is also changed, but this value is not updated by the estimator. Thus, any effects due to the variation in catalyst deactivation characteristics will be indirectly reflected in the three kinetic parameters to be estimated.

EKF estimates both the states and the parameters, while NDPE estimates only the parameters. It should be pointed out that, for $t < 5$ h, EKF has already reached the steady state. The simulation model (SM) predictions in the following figures use the updated parameters from EKF. NDPE only estimates the parameters for comparison and does not feed back the values to SM (see information flow in Figure 2). The following simulation cases are investigated to compare the two parameter estimation strategies.

Case 1. Random noise has been added to all the measurements and the makeup feed flow rates used to control the gaseous composition in the reactor. Table 6 shows the amount of noise added to the feed flow rates and the measurements. Figure 6 shows the profiles of melt index and density of the polymer mixture. The measurements are represented by open circles (\circ). The instantaneous polymer properties produced from each site are also plotted. The melt index and density measurements are taken every 2 h before catalyst B is injected. Catalyst B is injected at 5 h, and thereafter the measurements are taken every 30 min and again are available after a delay of 2 h.

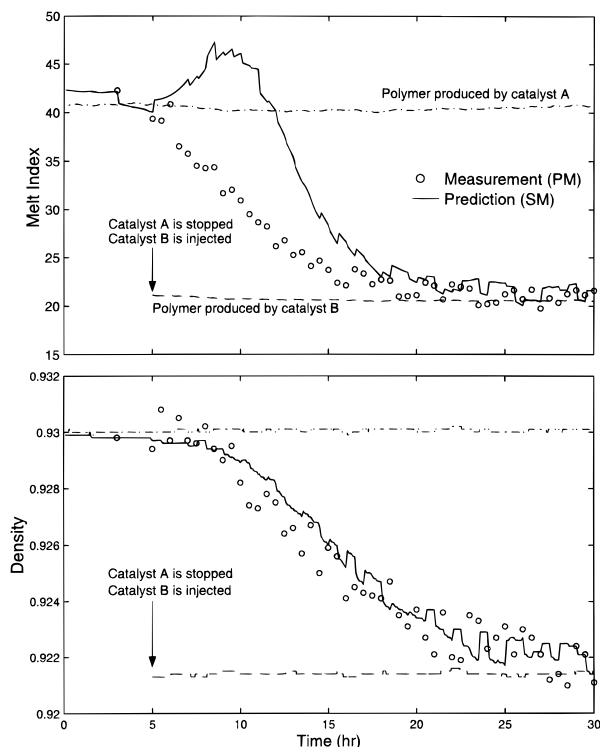


Figure 6. Polymer properties when catalyst A is stopped and catalyst B is injected at 5 h (case 1, Table 5). Measurements are available every 2 h before 5 h and every 30 min after 5 h. The measurement delay is 2 h.

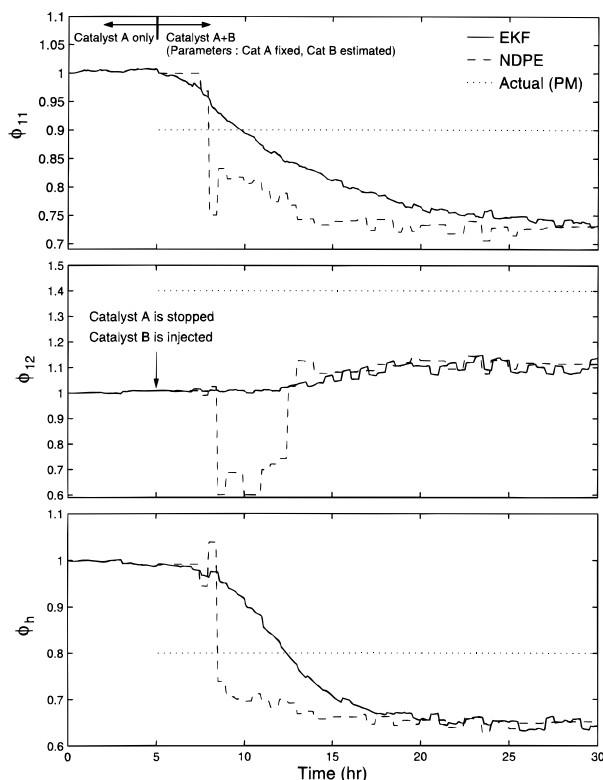


Figure 7. Estimated kinetic parameters when catalyst A is stopped and catalyst B is injected at 5 h (case 1, Table 5). Measurements are available every 2 h before 5 h and every 30 min after 5 h. The measurement delay is 2 h.

The estimated parameters are shown in Figure 7. It is observed that EKF estimates the parameters conservatively. As the reactor approaches a new steady state, the filter also converges very closely to actual reactor states. NDPE predictions of kinetic parameters suc-

cumb to the measurement errors and give wrong predictions until a substantial number of data points are available. Finally the predictions of kinetic parameters by both NDPE and EKF converge to the same value, which is quite different from the true values of the kinetic parameters. Recall that not only these three kinetic parameters but also other parameters including a deactivation rate constant have been changed for the plant model. The SM model is used in conjunction with the parameter estimator to *force fit* the model to the plant data by updating only three key kinetic parameters. Therefore, discrepancies in the three estimated kinetic parameters from their true values are the result of "lumping" the variations in all other parameters into these three key kinetic parameters.

As shown in Tables 3 and 5 the change we have considered in the deactivation parameter is substantial enough to change output properties. We included the deactivation parameter as a fourth parameter in our estimation. With four parameters to be updated the estimated values of the four parameters are not unique and are dependent on tuning parameters. The deactivation rate constant is very difficult to estimate. Carefully designed experiments should be performed to obtain information about the deactivation rate parameter. For example, the effect of deactivation is best observed when data at different residence times are obtained. Often it is not possible to carry out such tests during a plant's production schedule. During shutdown the catalyst flow rate is stopped and the production rate trickles down to zero. The dynamic data obtained during this time provide a very broad range of residence times. Such data may be used to estimate the deactivation rate constant for that particular catalyst. Estimating the deactivation parameter on-line along with other parameters provides nonunique values as discussed above, so we decided to estimate only three parameters. If additional polymer property measurements (e.g., polydispersity, etc.) are included, then a greater number of kinetic parameters can be estimated on-line.

It is also interesting to observe that the polymer properties (melt index and density) reach their new steady states in about 20 h, whereas the kinetic parameters, particularly ϕ_{11} and ϕ_h , converge to new stationary values in about 10 h. Note that ϕ_{12} (correction factor for the cross-polymerization rate constant) converges rather slowly and so does polymer density. As is seen in Figure 6, several reactor turnovers are required to reach a new steady state, suggesting that certain optimal-grade transition controls may have to be required to reduce the time for grade changeover.

The scaled rates of polymerization (or production rate) from each catalyst type, total rate of polymerization (or product withdrawal rate), and weight fraction of polymer produced by catalyst A are shown in Figure 8. The scaling of production rates is done with reference to the steady-state production rate. This figure gives an insight as to what is happening inside the reactor during the transition period.

As shown in Figure 7 the estimated values of the parameters are quite different from the actual ones because we did not estimate the deactivation parameter. This may mean that SM may not be valid beyond this operating region. We did perturbation tests for PM and SM to see how much they differ. Figure 9 shows how much PM and SM differ for step changes in hydrogen setpoint concentration, butene setpoint concentration, and catalyst flow rate. Here, the kinetic parameters in

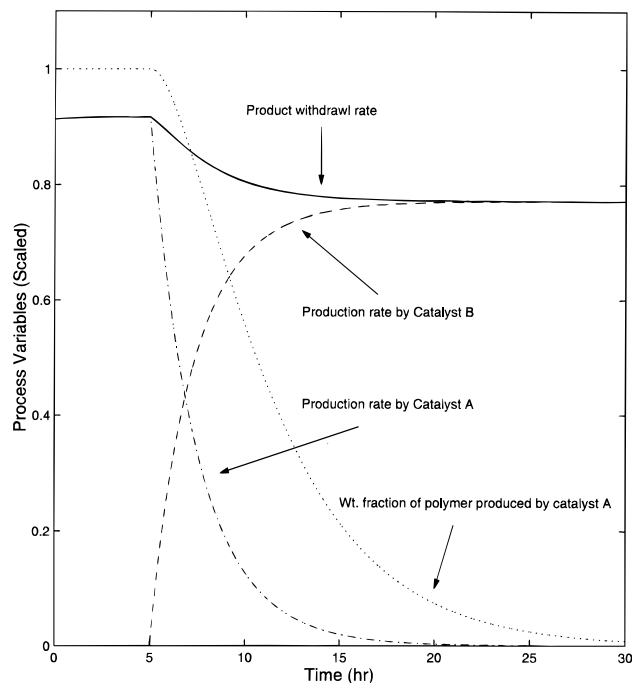


Figure 8. Profiles of process variables during the grade transition (plant model PM) when catalyst A is stopped and catalyst B is injected at 5 h (case 1, Table 5).

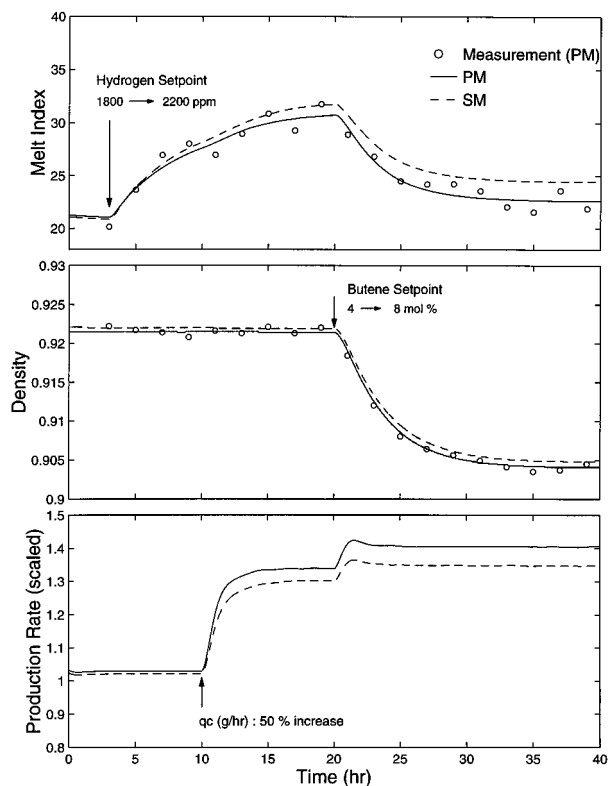


Figure 9. Response of PM and SM to step changes after the transition is complete (parameters converge for case 1, Table 5).

SM are those obtained from the previous on-line estimation. We selected these setpoint variables because these are the manipulated variables that can be used in on-line optimization. As seen in Figure 9 the deviations between the plant and model are not significant; hence, SM can be confidently used for optimization purposes.

Case 2. As seen in the above case, both EKF and NDPE methods converge to the same values. In this

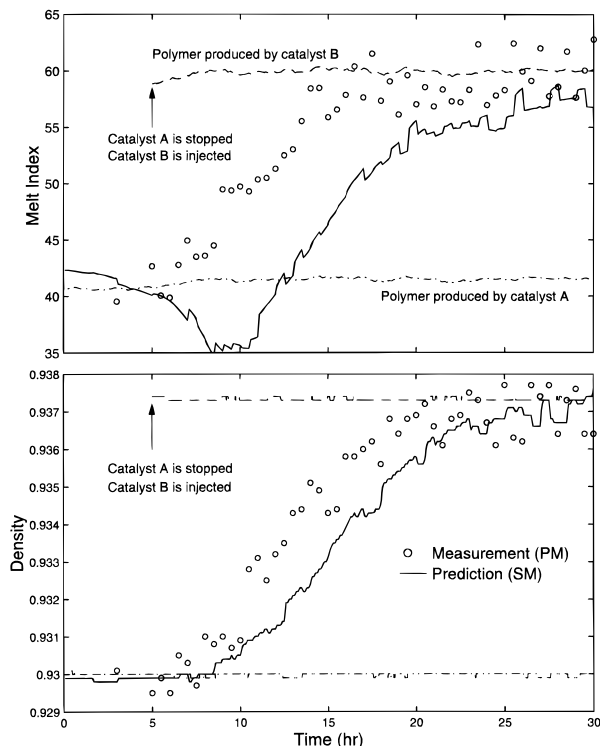


Figure 10. Polymer properties when catalyst A is stopped and catalyst B is injected at 5 h (case 2, Table 5). Measurements are available every 2 h before 5 h and every 30 min after 5 h. The measurement delay is 2 h.

case we will carry out a robustness test for the two methods. Let us suppose that the parameters change as shown in Table 5. The tuning parameters (matrices Q and R in EKF and weights w_i in NDPE) are kept the same as for case 1. The results are shown in Figures 10 and 11. Figure 11 shows that NDPE gives erroneous prediction of parameter values when a sufficient number of data points are not available. After 15 h, however, both NDPE and EKF converge to the same values. Initial NDPE predictions seem to be a strong function of measurement noise.

In the above two examples, we have shown that changes in all the kinetic parameters can be captured in three key parameters which are updated on-line. It is expected that disturbances other than catalyst change would be reflected in the updated key parameters. Let's consider case 1 in Table 5 when the new catalyst B is slightly less active (lower k_{11} value) than the old catalyst A. When the plant operator notices a decrease in plant productivity (Figure 8) at 10 h, he increases the catalyst flow rate by 20% but forgets to input this information in the simulator running on the computer. This mistake would be similar to a disturbance in the total number of catalyst active sites in the reactor. Figure 12 shows the estimated parameter values in this case. Notice that the final values of parameters are different from those shown in Figure 7. One may expect that other types of disturbances may have a similar effect.

Since NDPE is based on a nonlinear programming approach, it usually takes more computational time than on-line recursive methods. When delayed measurements are incorporated in EKF, the estimator has to go backward in time and integrate from the time when measurements were obtained. If measurements of melt index are taken every half hour and the results are available after a delay of 2 h, EKF has to integrate for 2 h from the time measurement was obtained to the

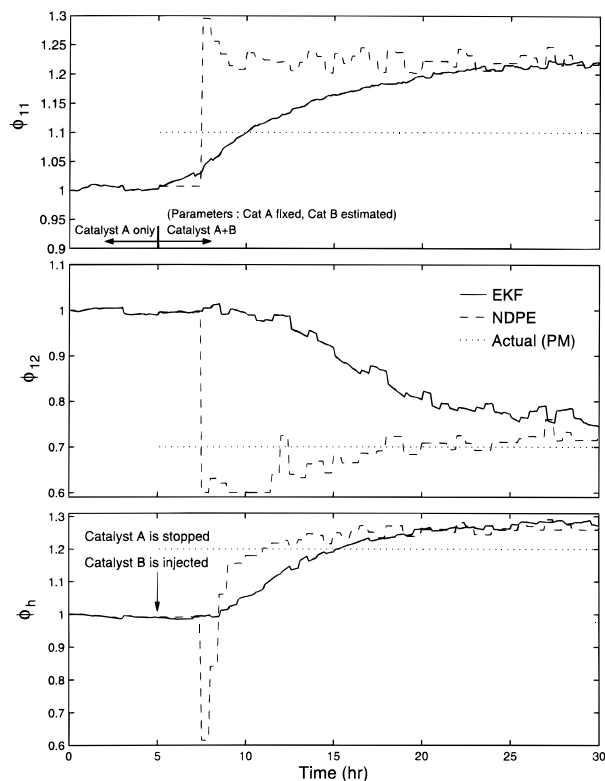


Figure 11. Estimated kinetic parameters when catalyst A is stopped and catalyst B is injected at 5 h (case 2, Table 5). Measurements are available every 2 h before 5 h and every 30 min after 5 h. The measurement delay is 2 h.

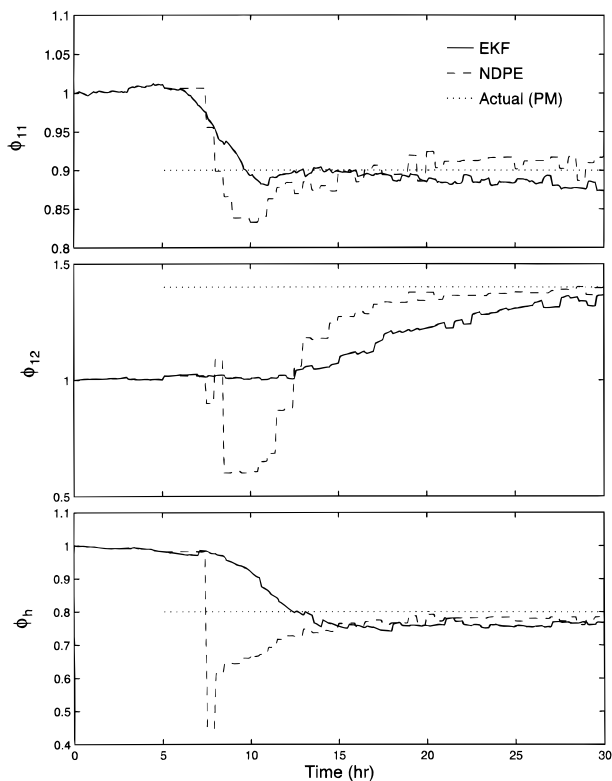


Figure 12. Updated parameters when a disturbance occurs at 10 h. Catalyst active sites in catalyst B increase in PM by 20% at 10 h.

current time. This has to be repeated every 30 min whenever a new measurement is available. Incorporating very frequent measurements in EKF can slow down the filter calculations to the point that its advantage as a recursive algorithm may be lost. Figure 13 shows

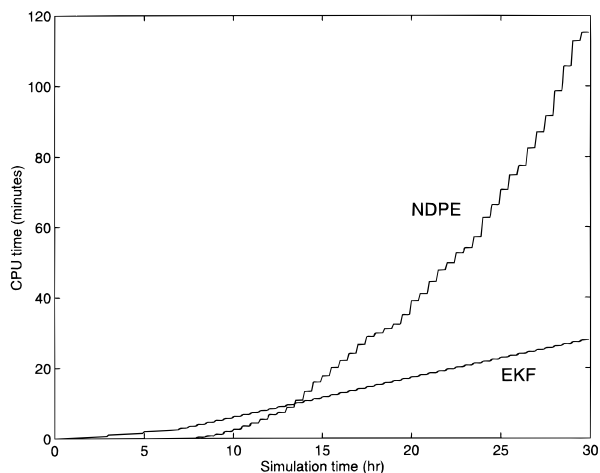


Figure 13. Comparison of cumulative computational times for two different strategies.

the cumulative computational time for both the strategies. A DEC Alpha 3000 computer was used in all the calculations. The slope of cpu time taken by EKF is constant and is smaller before 5 h when less frequent measurements are incorporated. If measurements are obtained every 15 min as opposed to every 30 min, then the slope will be steeper. As expected the cpu time taken by NDPE keeps on increasing as the data set keeps on growing. The cpu time shown in Figure 13 is for a fixed set of tuning parameters. The speed of the estimators can be increased by lowering the tolerance values for the estimators. Measurement noise plays a very important role in NDPE. When the simulation was carried out in the absence of measurement noise, NDPE results were better than EKF. In the presence of substantial measurement noise, EKF performs better than NDPE. The computational time required to execute NDPE depends strongly on the optimization algorithm used. Tuning EKF is somewhat more difficult than NDPE. When a lot of good (less noise) measurement data and faster computers are available, NDPE may prove advantageous to use for on-line optimization. Certainly, NDPE can also be used for off-line parameter estimation.

Concluding Remarks

In this paper, we have presented two on-line parameter estimation methods applied to a continuous fluidized-bed olefin copolymerization process. In view of the fact that a large number of high activity catalysts are used to produce polymers of different grades, it is of practical interest to develop an on-line parameter estimation technique in the most economical way. In general, it is very costly and time consuming to determine the major kinetic parameters for a given catalyst using either pilot plant or plant data. Once a *good* estimate of catalyst parameters becomes available for such a catalyst (i.e., reference catalyst), our question is how we can use the information for the reference catalyst system to estimate the parameters for other catalysts of similar characteristics. In this work, the extended Kalman filter and the nonlinear dynamic parameter estimation technique have been used. The main idea is that dynamic process data during a grade transition, by switching the catalyst type, are used to estimate several key kinetic parameters for the new catalyst which is assumed to exhibit similar polymerization characteristics. Our simulation results show that

both methods yield quite acceptable performance. It was also shown through simulations that an extended Kalman filter is a robust parameter estimation algorithm even in the presence of substantial measurement noise. The nonlinear dynamic parameter estimation technique which utilizes nonlinear programming (NLP) can be made robust to measurement noise by taking frequent samples of the polymer properties. The parameters take a relatively long time to converge because the polymer phase residence time is large (4 h) and polymer properties are available after a delay of 2 h. The conservative parameter estimates by EKF during the transition period will be useful when rejecting the effect of catalyst disturbances even before parameters converge to their final values.

Finally it should be noted that the proposed methods can also be used for off-line computations after a complete set of plant data (including measured polymer properties) become available. However, the use of these methods for on-line estimation has a unique merit: not only the new kinetic parameters but also other process output parameters, particularly polymer properties, are predicted during the transition operation.

Acknowledgment

This work has been supported in part by the industrial sponsors of the Chemical Process Systems Laboratory at the Institute for Systems Research, University of Maryland, College Park, MD.

Nomenclature

C^* = vacant active sites
 D^* = permanently deactivated sites
 \mathbf{d} = disturbance vector
 \mathbf{G} = positive definite gain matrix
 H_2 = hydrogen (chain-transfer agent)
 J = objective cost function
 k_d = spontaneous deactivation rate constant, (1/s)
 k_{ij} = initiation rate constant for j th monomer, $j = 1, 2$ (L/mol·s)
 k_{jk} = propagation rate constants, $j = 1, 2$; $k = 1, 2$ (L/mol·s)
 k_h = chain transfer to hydrogen rate constant (L/mol)^{1/2}/s
 M_1 = monomer (ethylene)
 M_2 = comonomer (butene)
 M_n = number-average molecular weight
 M_w = weight-average molecular weight
 $M_{n,m}$ = the concentration of dead polymer with n units of M_1 and m units of M_2
 N = number of data points
 $P_{n,m}$ = concentration of live polymer with n units of M_1 and m units of M_2 with M_1 attached to a transition-metal site
 $Q_{n,m}$ = concentration of live polymer with n units of M_1 and m units of M_2 with M_2 attached to a transition-metal site
 t_0 = time at which catalyst is changed
 t_f = current (or final) time
 \mathbf{x} = model state vector
 w_i = weights in the nonlinear programming objective function
 \mathbf{W} = positive definite weighting matrix
 y_i = measured plant outputs
 y_m = model predicted outputs (before adding disturbance)
 \hat{y}_i = model predicted outputs (after adding disturbance)
 \mathbf{z} = extended state vector

Greek Letters

β = vector of unknown parameters
 ϕ_{11} = correction factor for k_{11}
 ϕ_{12} = correction factor for k_{12}

ϕ_h = correction factor for k_h

ρ = density

τ = measurement delay.

Appendix A. Continuous Stirred-Bed Reactor Model

Material Balances

Monomers:

$$\frac{dC_{M_1}}{dt} = \frac{U_0}{H}(C_{M_1f} - C_{M_1}) - \frac{R_{p_1}}{\epsilon} - \frac{C_{M_1}}{\tau} \quad (A1)$$

$$\frac{dC_{M_2}}{dt} = \frac{U_0}{H}(C_{M_2f} - C_{M_2}) - \frac{R_{p_2}}{\epsilon} - \frac{C_{M_2}}{\tau} \quad (A2)$$

$$\frac{dC_{M_3}}{dt} = \frac{U_0}{H}(C_{M_3f} - C_{M_3}) - \frac{C_{M_3}}{\tau} \quad (A3)$$

$$\frac{dC_{H_2}}{dt} = \frac{U_0}{H}(C_{H_2f} - C_{H_2}) - \frac{R_{hc}}{\epsilon} - \frac{C_{H_2}}{\tau} \quad (A4)$$

Catalyst:

$$\frac{dX_{cat_i}}{dt} = \frac{q_{ci}}{V} - \frac{X_{cat_i}}{\tau} - k_{di}X_{cat_i} \quad (i = 1, 2) \quad (A5)$$

Solid:

$$\frac{dW}{dt} = R_{p_1} + R_{p_2} - Q_0 \quad (A6)$$

Energy Balance

$$\begin{aligned} \frac{d}{dt} [\{ (1 - \epsilon)Q_s C_{ps} + \epsilon C_{M_1} C_{pg_1} + \epsilon C_{M_2} C_{pg_2} \} (T - T_{ref})] = \\ - \frac{U_0}{H} \epsilon (T - T_p) \{ C_{M_1} C_{pg_1} + C_{M_2} C_{pg_2} \} + \{ (-\Delta H_1) R_{p_1} + \\ (-\Delta H_2) R_{p_2} \} (1 - \epsilon) - \frac{(T - T_{ref})}{\tau} \{ (1 - \epsilon) Q_s C_{ps} + \\ \epsilon C_{M_1} C_{pg_1} + \epsilon C_{M_2} C_{pg_2} \} - \frac{\pi D}{A} h_w (T - T_w) \end{aligned} \quad (A7)$$

where R_{hc} = rate of hydrogen consumption, R_{p_1} = rate of polymerization of monomer 1 (ethylene), R_{p_2} = rate of polymerization of monomer 2 (butene), Q_0 = production rate, W = bed weight, V = total volume of the reactor, ϵ = void fraction in the reactor, and τ = polymer phase residence time.

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Received for review August 4, 1995

Revised manuscript received December 11, 1995

Accepted January 8, 1996*

IE950487Y

* Abstract published in *Advance ACS Abstracts*, March 15, 1996.