Parameter Estimation for Industrial Polymerization Processes

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The parameter estimation problem and its application to industrial data obtained from polymerization processes are analyzed. The polymerization process model consists of the material balances with the polymerization kinetics for the reactor and a simplified dynamic model for the downstream separator. The estimable kinetic parameters in the process model are obtained for plant data by analyzing the associated optimization problem. Two kinetic parameters are estimable for the copolymer data and the homopolymer data based on the information in the available industrial plant data. The identified process model forms the basis for a monitoring and feedback control system for these processes.

Introduction

Physical models can be utilized to gain insight into the ongoing phenomena in polymerization processes. In this article, a detailed process model for a full-scale industrial process is validated from historical plant data using maximum likelihood estimation for the kinetic parameters. The data and parameters shown in this document for the industrial process have been scaled because of proprietary reasons. The model validation problem has not been studied in much detail due to the fact that most researchers do not have access to industrial data sets. Some results on model validation have been obtained for data sets from carefully monitored laboratory experiments that may not show typical behavior of a full-scale industrial process (Soroush and Kravaris, 1992; Crowley and Choi, 1996; Lewin, 1996). Ogunnaike has reported estimating parameters in a fundamental model using plant startup data for an industrial terpolymerization reactor (Ogunnaike, 1994).

The approach taken in this work is to use the available industrial data for model representation without imposing additional requirements on the process measurements or designing extensive, new identification experiments. The modeling objective is to produce the best available model representation with the available process information. The physical nonlinear model framework is chosen to capture the information that is present in the process measurements for the industrial data sets. The alternative approach of local linear models (Banerjee et al., 1997) is not used to avoid extensive bookkeeping arising from numerous grades of the polymer product that rapidly evolve due to the changing needs of the customer and the desire of the manufacturers to find new uses for the polymers. This market scenario imposes new grade requirements for the product, thereby making it harder to maintain a set of linear models that capture the required process features. The approach of empirical models (Yabuki and MacGregor, 1997; MacGregor et al., 1994) also suffers from the same drawbacks. On the other hand, the approaches of linear models and empirical models may perform well when the product requirements are not changing often and the reactor is mostly operated around a fixed operating range without large disturbances or plant–model mismatch.

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Process Description and Model

The industrial polymerization process consists of a well-mixed reactor followed by a product separator, shown in Figure 1. This process is used to make various grades of copolymer and homopolymer. The copolymer grades are characterized by the ratio of comonomer to monomer in the copolymer product. The polymer viscosity is also varied for each copolymer grade, depending upon the market requirements. The homopolymer grades are characterized by the average molecular weight of the product. The hydrocarbon feed consists of monomer, comonomer, and an inhibitor dissolved in a solvent. A cocatalyst is also dissolved in the solvent and fed to the reactor. The transfer agent is used only to make the homopolymer, while the comonomer is used only for the

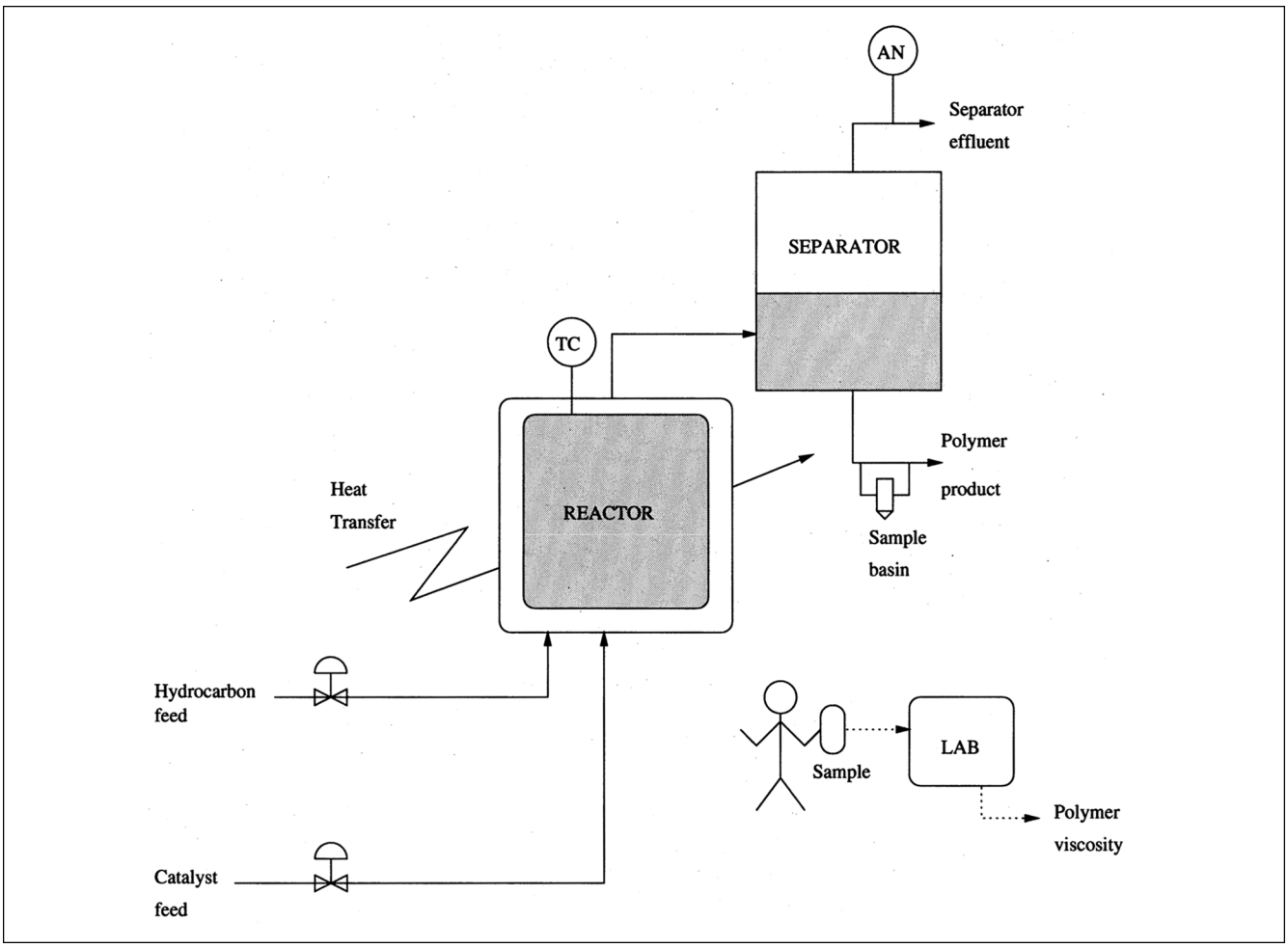

Figure 1. Exxon polymerization process.

copolymer. A coolant is employed for the removal of heat released due to polymerization. The polymer product is separated from the unreacted hydrocarbons in a downstream separator. A physical model based on first principles is proposed to capture the information in the process output measurements and to develop appropriate feedback control strategies. The process model is a quantitative representation of the various reactions taking place in the reactor along with other physical phenomena governing the polymerization process. The flow rate and composition of the feed and product streams are measured along with the reactor temperature. An off-line laboratory measurement is made for the polymer viscosity of copolymer and average molecular weight of homopolymer.

Polymerization kinetics

The copolymerization of monomer (M) and comonomer (C) is carried out at low temperature using an inorganic catalyst (A). The catalyst is accompanied by a cocatalyst (RH) that renders it more reactive. There is no transfer agent (T) for the copolymerization process. An inhibitor (B) that contributes to the termination of active polymer chains also enters the reactor. The reaction mechanism, which is an ideal copolymerization based on the reactivity ratios (Kennedy and Maréchal, 1991), can be divided into the following reactions (Figure 2). The homopolymerization process can be considered as a modification of the copolymerization process that has only one monomer (M) and also has a transfer agent (T).

The reactions are assumed to be irreversible and first order with respect to each reactant. The kinetic rate constants for the reactions are assumed to have a dependence on temperature given by the Arrhenius equation. These rate constants are assumed to be independent of reactor composition or chain length (j) of the active polymer (P_j^+). This simple reaction mechanism is proposed to quantify the information available in the process measurements due to polymerization reactions. A few of the reactions are assumed to be negligible compared to the rest of them based on previous laboratory and simulation studies. The rate constants corresponding to those reactions are set to zero. These reactions are not clearly identified in this report so that the exact proprietary kinetic scheme for the polymerization process is not disclosed.

The differential material balances, including the rate expressions coupled with the equations for the physical phenomena, constitute the dynamic process model. The probability of propagation of active polymer chains (α) can be evaluated for mass fractions (x_i) and molecular weights (M_i)

of reactor constituents i

$$\alpha = \frac{k_{p_M}\frac{x_M}{M_M} + k_{p_C}\frac{x_C}{M_C}}{\left(k_{p_M} + k_{tr_M} + k_{T_M}\right)\frac{x_M}{M_M} + \left(k_{p_C} + k_{tr_C} + k_{T_C}\right)\frac{x_C}{M_C} + k_{tr_T}\frac{x_T}{M_T} + k_{T_B}\frac{X_B}{M_B}} \tag{1}$$

The model is simplified using quasi-steady-state approximations for the active polymer chains because of their rapid equilibration relative to other components. These approximations can be simplified to yield the following algebraic equations for molar concentrations of active polymer chains

$$[P^+] = \sum_{f=1}^{\infty} [P_j^+] \tag{2}$$

$$[P_1^+] = [P^+](1-\alpha) \tag{3}$$

$$[P_j^+] = \alpha[P_{j-1}^+] \tag{4}$$

Moments for the active and dead polymers

The polymer viscosity is measured for the copolymer, and the average molecular weight is measured for the homopolymer. The polymer viscosity is related to the average molecular weight by an empirical formula. The weight-average molecular weight for the polymer is obtained using leading moments for the molecular-weight distribution. Hence, there is no need to evaluate explicitly the entire chain-length distribution of the polymer. The moments for the molecular-weight distribution can be calculated by employing generating functions (Ray, 1972). In this case, the leading moments for the polymer are obtained by explicitly evaluating the series summations involved. The zeroth and first moments for the mass fraction of the dead polymer can be defined as

$$\lambda_k = \sum_{j=1}^{\infty} j^k x_{P_j}, \qquad k = 0, 1 \tag{5}$$

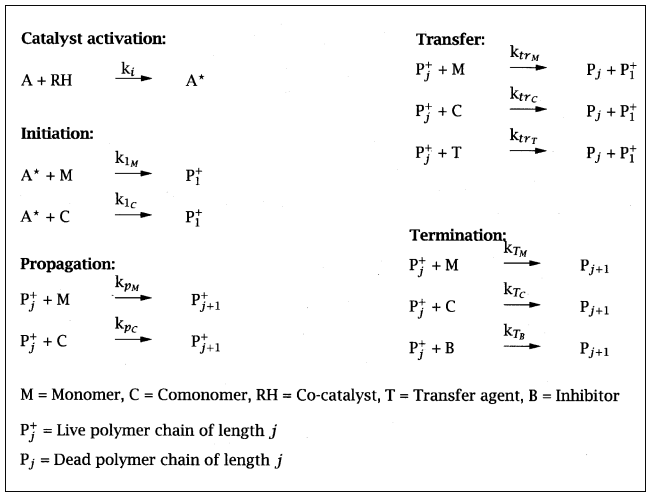

Figure 2. Reaction mechanism for Exxon's polymerization process.

Leading moments of the differential molecular-weight distribution are also used to describe the state of the active polymer chains. The zeroth and the first moments of the number chain-length distribution for the active polymer chains can be defined as

$$\lambda_k^+ = \sum_{j=1}^{\infty} j^k [P_j^+], \qquad k = 0, 1 \tag{6}$$

Using Eqs. 3 and 4 to evaluate the sum to get the first moment (λ_1^+)

$$\lambda_1^+ = \frac{[P^+]}{1-\alpha} \tag{7}$$

The differential component balances for the various species in the reactor are obtained by using the CSTR assumption. The assumption that the species are well mixed in the reactor is justified because of the low Peclet number obtained from dimensional analysis (Bindlish, 1999). An energy balance cannot be closed effectively to obtain a differential equation for the reactor temperature because of a lack of reliable measurements for the reactor coolant flow rate. Hence, the reactor temperature is used as a measured input in the process model. The differential equations for material balances along

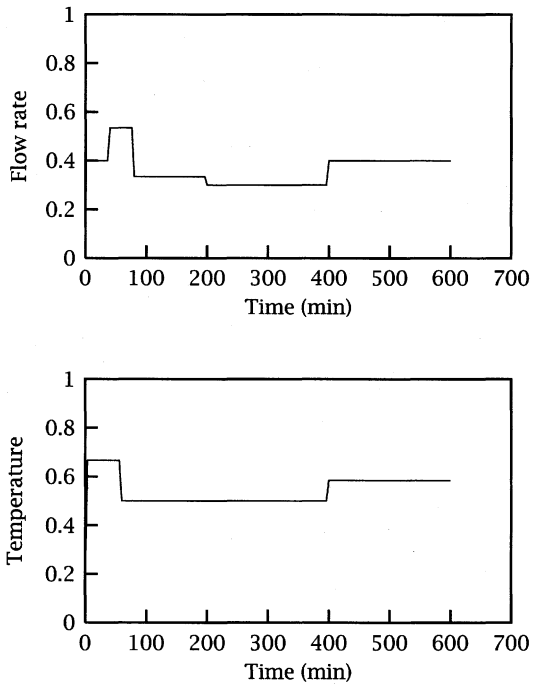

Figure 3. Scaled simulated inputs for copolymer.

with the algebraic equations constitute the dynamic model of the reactor.

The reactor is followed by a separation unit that has dynamics due to mixing. The residence time (τ) of the unreacted hydrocarbon in the separator is expressed as a first-order lag. The mass fraction of monomer in the effluent gas (x_{M_e}) and the mass fraction of comonomer in the effluent gas (x_{C_e}) are evaluated as

$$\frac{dx_{M_e}}{dt} = \frac{1}{\tau}\left[- x_{M_e} + \frac{x_M}{1 - x_S} \right] \tag{8}$$

$$\frac{dx_{C_e}}{dt} = \frac{1}{\tau}\left[- x_{C_e} + \frac{x_C}{1 - x_S} \right] \tag{9}$$

Parameter Estimation

Parameter estimation is carried out for the Exxon polymerization process to validate the process model. Several physical and kinetic parameters appear in the process model developed in the previous section. The physical parameters, like the reactor volume and species densities, are fixed based on process knowledge. Each kinetic parameter has a preexponential factor and an activation energy associated with it

$$k = k_o e^{(-E/RT)} \tag{10}$$

The activation energies (E) have been fixed based on previous simulation and experimental studies. The preexponential factors (k_o) of the kinetic parameters are estimated next from historical plant operating data.

Likelihood function formation

The maximum likelihood estimate (Bard, 1974) is applied to evaluate the parameters (θ) in the process model. The likelihood function, which is the joint probability distribution function of the observations, is maximized with respect to the unknown parameters. The problem is formulated in terms of maximizing the logarithm of the likelihood function ($\ln L$) since it is a simpler expression than the likelihood function (L) itself. The various experiments ($i = 1 \cdots n$) with sensor outputs ($a = 1 \cdots m$) contain the process information that is utilized for parameter estimation. The errors ($e_{ia}(\theta)$) in the sensor outputs are assumed to be independent and normally distributed with a variance υ_a. The logarithm of the likelihood function (L) can be expressed as

$$\ln L = -(nm/2)\ln(2\pi) - (n/2)\sum_{a=1}^{m} \ln(\upsilon_a) - 1/2 \sum_{a=1}^{m} \upsilon_a^{-1}\left(\sum_{i=1}^{n} e_{ia}^2(\theta) \right) \tag{11}$$

Seeking values of error variance (υ_a) that maximize $\ln L$ gives

$$\upsilon_a(\theta) = (1/n)\sum_{i=1}^{n} e_{ia}^2(\theta) \tag{12}$$

The logarithm of L can be reduced to

$$\ln L = \left[(mn/2)\ln(n/2\pi) - 1\right] - (n/2)\sum_{a=1}^{m} \ln\left[\sum_{i=1}^{n} e_{ia}^2(\theta) \right] \tag{13}$$

Maximizing $\ln L$ is equivalent to minimizing

$$\phi(\theta) = (n/2)\sum_{a=1}^{m} \ln\left[\sum_{i=1}^{n} e_{ia}^2(\theta) \right] \tag{14}$$

The preceding objective function (ϕ) is minimized to obtain a maximum likelihood estimate for the kinetic parameters. The confidence intervals are obtained by linearizing the model equations at the values of the estimated parameters. It can be shown (Bard, 1974) for maximum likelihood estimates with normal distributions that the covariance matrix of the sampling distribution of the parameter estimate (V_θ) can be approximated from the Hessian of the logarithm of the likelihood function ($\ln L$) at the optimal parameter estimates (θ^*)

$$V_\theta \approx H^{*-1} = -\left(\frac{\partial^2 \ln L}{\partial\theta\partial\theta} \right)^{-1}_{\theta = \theta^*} \tag{15}$$

If the sampling distribution of parameter estimates (θ^*) is normal and unbiased then

$$(\theta - \theta^*)^T V_\theta^{-1} (\theta - \theta^*) \le \chi^2(l) \tag{16}$$

where l is the number of parameters. The 95% confidence regions for the parameters (Eq. 16) are obtained after computing the covariance of the estimates (V_θ).

Simulated data

The parameter estimation problem is first examined using simulated data corrupted with noise. This study is carried out to determine the kinetic parameters that may be reliably estimated using the available measurements. The pre-exponential factors of the kinetic parameter k_{p_M}, k_{tr_C}, and k_{T_C} are estimated. These parameters are chosen because the singular value decomposition of the Hessian indicates that these three parameters may be estimable. The inputs for the simulation of the reactor are hydrocarbon feed (w_1), catalyst feed (w_2), transfer agent feed (w_T), monomer mass fraction in w_1 (x_{M_1}), comonomer mass fraction in w_1 (x_{C_1}), inhibitor mass fraction in w_1 (x_{B_1}), mass fraction of cocatalyst in w_2 (x_{RH_2}), and temperature of reactor (T). The catalyst feed and reactor temperature (Figure 3) are varied during the polymerization process. The monomer mass percent in the separator effluent (M^{se}), the comonomer mass percent in the separator effluent (C^{se}) and the polymer viscosity (μ) are the available measurements used in parameter estimation. These simulated measurements obtained using nominal parameter values are corrupted with noise (Figure 4) and then used to estimate the kinetic parameters.

Estimation Problem Analysis.. The least-square estimation problem is first analyzed for the linearized model to obtain the well-determined kinetic parameters. The linear least-square problem with process measurements (y) and Jacobian (J) can be written as

$$y = J\theta \tag{17}$$

$$f(\theta) = (y - J\theta)^T (y - J\theta) \tag{18}$$

The Hessian of the least-square objective function (Eq. 18) can be written as

$$H = J^T J \tag{19}$$

The singular-value decomposition gives

$$J^T = u\Sigma v^T, \qquad H = u\Sigma^2 u^T, \qquad \|J\| = \|\Sigma\|, \qquad \|H\| = \|\Sigma^2\| \tag{20}$$

Using the perturbation bound (Lawson and Hanson, 1995) for the case where there are more measurements (y) compared to parameters (θ) results in the following expressions

$$\frac{\|d\theta\|}{\|\theta\|} \le \text{cond}(J) \frac{\|y\|}{\|J\|\|\theta\|} \frac{\|dy\|}{\|y\|} \tag{21}$$

$$\|d\theta\| \le \frac{\text{cond}(J)}{\|J\|} \|dy\| \tag{22}$$

The error bound for the parameters (θ) can be obtained using the norms given in Eq. 20

$$\|d\theta\| \le \sqrt{\frac{\sigma_{\max}(H)}{(\sigma_{\min}(H))^2}}\, \|dy\| \tag{23}$$

This error bound (Eq. 23) gives the well-determined set of parameters based on the process information available in the sensor outputs.

This estimable set of parameters is chosen to avoid saddle points and ill-conditioned solutions. The Hessian of the objective function shown in Eq. 14 is evaluated using second-order finite differences. There are two sources of error in the evaluation of numerical derivatives, truncation error (caused due to neglected terms of the Taylor series), and the round-off error (caused by inaccuracies in computed function values). The truncation error is an increasing function of step size (h), while the round-off error is a decreasing function of h. The step size for the finite differences is chosen using a procedure (Gill et al., 1981) to balance these two sources of error. The Hessian (H) at the optimal parameter values for the simulated data with added random noise is

$$H = \begin{array}{c} \begin{matrix} k_{p_{M_o}} & k_{tr_{C_o}} & k_{T_{C_o}} & k_{p_{C_o}} & k_{i_o} & k_{1_{M_o}} \end{matrix} \\ \begin{bmatrix} 3.49\times10^5 & -1.29\times10^4 & -5.93\times10^5 & 2.56\times10^5 & 1.59\times10^4 & 8.14\times10^2 \\ -1.29\times10^4 & 5.26\times10^4 & -6.29\times10^3 & -3.34\times10^4 & 4.13\times10^2 & 2.26\times10^1 \\ -5.93\times10^5 & -6.29\times10^3 & 1.34\times10^6 & -7.44\times10^5 & -3.61\times10^4 & -1.86\times10^3 \\ 2.56\times10^5 & -3.34\times10^4 & -7.44\times10^5 & 5.21\times10^5 & 1.98\times10^4 & 1.03\times10^3 \\ 1.59\times10^4 & 4.13\times10^2 & -3.61\times10^4 & 1.98\times10^4 & 1.02\times10^3 & 5.35\times10^1 \\ 8.14\times10^2 & 2.26\times10^1 & -1.86\times10^3 & 1.03\times10^3 & 5.35\times10^1 & 3.02 \end{bmatrix} \end{array}$$

The singular-value decomposition of H gives

$$H = u\Sigma^2 u^T$$

where

$$\Sigma^2 = \begin{bmatrix} 2.03\times10^6 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1.71\times10^5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 6.76\times10^4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4.68\times10^1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.50 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1.79\times10^{-1} \end{bmatrix}$$

$$u = \begin{bmatrix} -0.36 & 0.68 & -0.39 & -0.01 & -0.50 & 0.00 \\ 0.01 & 0.13 & 0.86 & -0.01 & -0.50 & 0.00 \\ 0.81 & -0.10 & -0.28 & 0.02 & -0.50 & -0.00 \\ -0.46 & -0.71 & -0.18 & -0.01 & -0.50 & 0.00 \\ -0.02 & 0.00 & 0.01 & 1.00 & -0.00 & -0.07 \\ -0.00 & 0.00 & 0.00 & 0.07 & -0.00 & 1.00 \end{bmatrix}$$

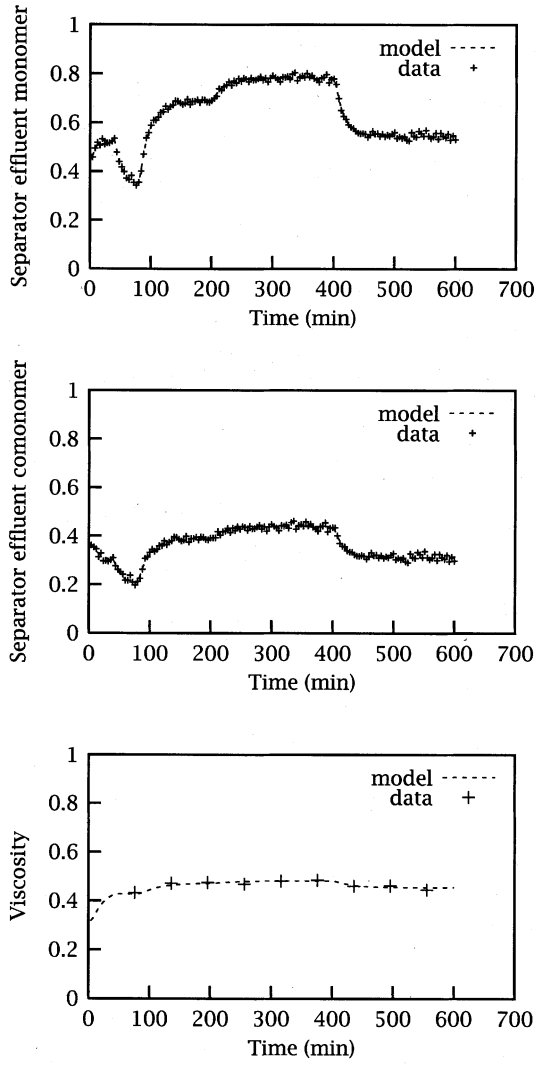

Figure 4. Scaled simulated outputs for copolymer.

The columns of u indicate that only three of the first four parameters can be estimated based on the error bound (Eq. 23). Substituting the appropriate values in Eq. 23 gives

$$\| \Delta\theta \| \leq 0.021 \| \Delta y \|$$

Estimation Results. The maximum likelihood estimates for the three well-determined parameters are obtained by starting at different initial guess values using GREG (Stewart et al., 1999) to test and confirm the conclusion from the Hessian analysis that the parameter estimation problem is well defined for those three parameters. The parameter estimates and the confidence intervals obtained from GREG (Table 1) are identical irrespective of the initial guesses. The sensor measurements corresponding to the estimates in the last row of Table 1 are compared with the simulated data. The predicted responses from the parameter estimates fit the simulated data well (Figure 4).

An attempt to estimate more than three kinetic parameters results in different modal estimate values depending on initial guesses giving identical fits to simulated data. Hence, the analysis indicates that only three parameters (Table 1) are estimable using simulated data with no plant–model mismatch. More parameters can be estimated if the reactor composition is also measured. It is currently not feasible to measure the reactor composition because of the nature of the polymer.

Table 1. Scaled Parameter Estimates Resulting from Simulated Copolymer Data

	$k_{p_{M_o}}$	$k_{tr_{C_o}}$	$k_{T_{C_o}}$	No. of Iter.
Initial guess	30.000	27.700	25.500	
Estimate	30.000	27.709	25.499	4
95% confidence interval	±0.007	±0.009	±0.003	
Initial guess	34.000	27.700	25.500	
Estimate	30.000	27.709	25.499	6
95% confidence interval	±0.007	±0.009	±0.003	
Initial guess	30.000	31.000	25.500	
Estimate	30.000	27.709	25.499	7
95% confidence interval	±0.007	±0.009	±0.003	
Initial guess	30.000	27.700	21.000	
Estimate	30.000	27.709	25.499	6
95% confidence interval	±0.007	±0.009	±0.003	
Initial guess	33.000	31.000	22.000	
Estimate	30.000	27.709	25.499	6
95% confidence interval	±0.007	±0.009	±0.003	

Estimation for copolymer

The parameter estimation results for copolymer plant data are typical of the 13 data sets provided by Exxon. The preexponential factors of the kinetic parameters k_{p_M} (propagation due to monomer) and k_{p_C} (propagation due to comonomer) are obtained using historical plant data. These two parameters are chosen based on the analysis of the Hessian for parameter estimation, as illustrated previously. The analysis indicates that the plant data are informative enough to estimate only two of the six unknown kinetic parameters. The kinetic parameter estimates using historical plant data are given in Table 2. The parameter estimates and the confidence intervals obtained from different data sets are similar. The 95% confidence intervals for the preceding parameters are tight (order of magnitude $= 10^{-3} \sim 10^{-2}$). The predicted measurements corresponding to the estimates in the last row of Table 2 fit the validation data set reasonably well. The predicted responses of the monomer mass percent in the separator effluent, the comonomer mass percent in the separator effluent, and the polymer viscosity are compared with the plant data for the validation data set (Figure 5). The relatively constant bias in the fit to the viscosity measurement

Table 2. Scaled Parameter Estimates Resulting from Copolymer Plant Data

	$k_{p_{M_o}}$	$k_{p_{C_o}}$
Data set 1	30.412±0.027	32.740±0.013
Data set 2	30.296±0.029	32.880±0.018
Data set 3	30.282±0.017	32.676±0.009
Data set 1+2+3	30.348±0.016	32.720±0.008

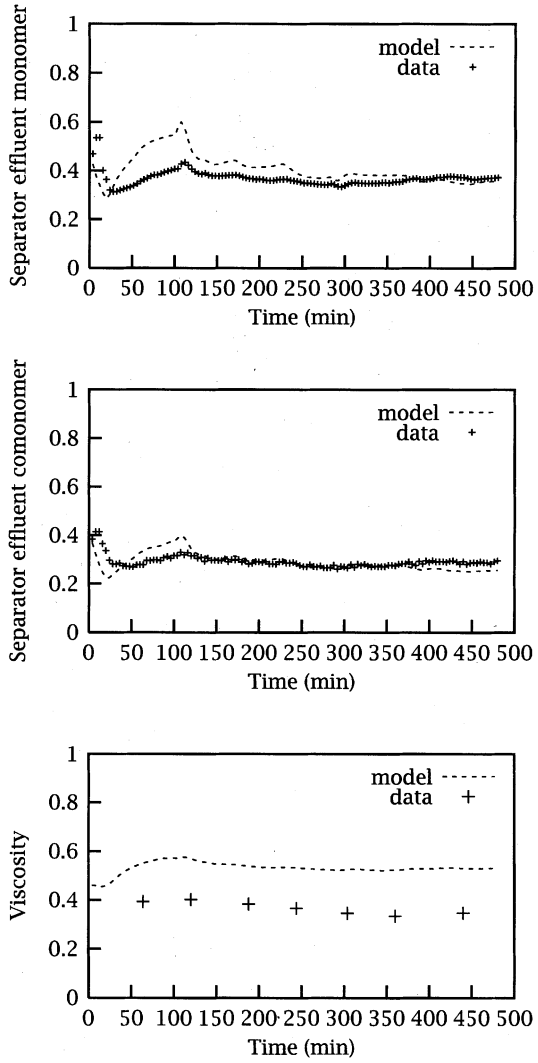

Figure 5. Scaled outputs for copolymer validation plant data.

means that part of the model is a good candidate for an output disturbance model if one employs a feedback-control scheme based on this model.

Estimation for homopolymer

The reactors are also used to make different grades of homopolymer without a comonomer in the process. A transfer agent is also fed into the reactor to make homopolymer. The polymer molecular weight (M_p) and the monomer mass percent in separator effluent (M^{se}) are the available measurements. The maximum likelihood estimates for the kinetic parameters ($k_{p_{M_o}}$ and $k_{tr_{T_o}}$) are obtained using historical plant data. These two parameters are estimable based on the Hessian analysis. The analysis indicates that only two of the four unknown kinetic parameters are estimable. The kinetic parameter estimates are obtained using plant data for different grades of homopolymer from the process (Table 3). Similar parameter estimates are obtained from different data sets. The predicted measurements corresponding to the modal estimates in the last row of Table 3 are compared with the homopolymer validation data set from the reactor. The predicted responses of the monomer mass percent in the separator effluent and the polymer molecular weight match the homopolymer plant data closely (Figure 6).

Table 3. Scaled Parameter Estimates Resulting from Homopolymer Plant Data

	$k_{p_{M_o}}$	$k_{tr_{T_o}}$
Data set 1	33.738 ± 0.262	27.074 ± 0.479
Data set 2	33.126 ± 0.126	25.217 ± 0.188
Data set 1+2	33.550 ± 0.149	26.111 ± 0.337

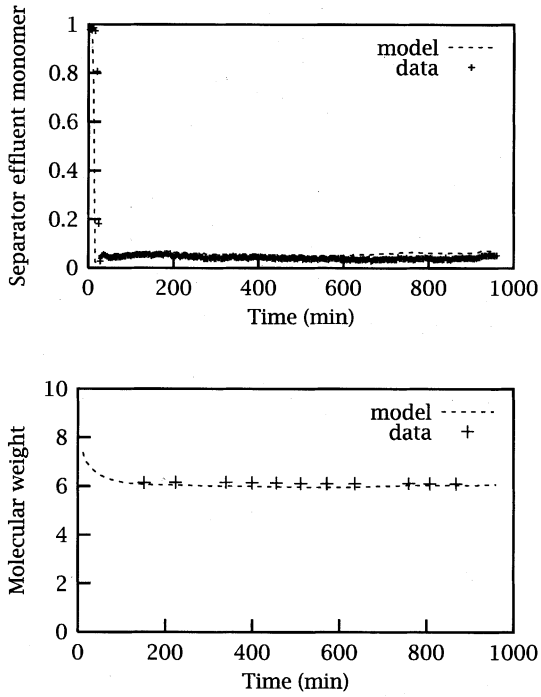

Figure 6. Scaled outputs for homopolymer validation plant data.

Conclusions

The physical nonlinear model framework is chosen to achieve modeling objectives for the polymerization processes. The details of the nonlinear model are tailored according to the available process information. The physical model is validated by using extensive historical data after performing a quantitative analysis to determine the estimability of the kinetic parameters based on the information content in the available industrial data. The numbers of estimable parameters are fewer for real plant data compared to simulated data with noise. Two kinetic parameters are estimable for the copolymer data and the homopolymer data based on the information in the industrial plant data. The identified process model has been used to develop and implement a feedback control and monitoring system for prototypical industrial polymerization processes (Bindlish, 1999).

Acknowledgments

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Literature Cited

Banerjee, A., Y. Arkun, B. Ogunnaike, and R. Pearson, "Estimation of Nonlinear Systems Using Linear Multiple Models," *AIChE J.*, **43**, 1204 (1997).

Bard, Y., *Nonlinear Parameter Estimation*, Academic Press, New York (1974).

Bindlish, R., *Modeling and Control of Polymerization Processes*, PhD Thesis, Univ. of Wisconsin-Madison, Madison, WI (1999).

Crowley, T. J., and K.-Y. Choi, "On-Line Monitoring and Control of a Batch Polymerization Reactor," *J. Process Control*, **6**, 119 (1996).

Gill, P. E., W. Murray, and M. H. Wright, *Practical Optimization*, Academic Press, London (1981).

Kennedy, J. P., and E. Maréchal, *Carbocationic Polymerization*, Krieger, Malabar, FL (1991).

Lawson, C. L., and R. J. Hanson, *Solving Least Squares Problems*, SIAM, Philadelphia, PA (1995).

Lewin, D. R., "Modeling and Control of an Industrial PVC Suspension Polymerization Reactor," *Comput. Chem. Eng.*, **20**(Suppl.), S865 (1996).

MacGregor, J. F., C. Jaeckle, C. Kiparissides, and M. Koutoudi, "Process Monitoring and Diagnosis by Multiblock PLS Methods," *AIChE J.*, **40**, 826 (1994).

Ogunnaike, B. A., "On-Line Modeling and Predictive Control of an Industrial Terpolymerization Reactor," *Int. J. Control*, **59**, 711 (1994).

Ray, W. H., "On the Mathematical Modeling of Polymerization Reactors," *JMS — Rev. Macromol. Chem.*, 1 (1972).

Soroush, M., and C. Kravaris, "Nonlinear Control of a Batch Polymerization Reactor: An Experimental Study," *AIChE J.*, **38**, 1429 (1992).

Stewart, W. E., M. Caracotsios, and J. P. Sørensen, *Computer-Aided Modelling of Reactive Systems* (1999).

Yabuki, Y., and J. F. MacGregor, "Product Quality Control in Semibatch Reactors Using Midcourse Correction Policies," *Ind. Eng. Chem. Res.*, **36**, 1268 (1997).

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