

Barocalorimetric Technique for Monitoring Pressurized Copolymer Reactors

Ramiro Infante,^{1,2} Arturo Cisneros,¹ Claudia Rivera,¹ Jesús Alvarez²

¹Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna #140, Saltillo, Coahuila, 25198 Mexico

²Depto. de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Apdo. 55534, Distrito Federal, 09340 Mexico

Received 1 October 2003; accepted 26 May 2004

DOI 10.1002/app.21450

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The problem of on-line estimation of the conversion and composition evolutions in a pressurized batch copolymer reactor with temperature and pressure measurements was addressed. The estimation model consisted of mass and energy balances with a pressure equation built from phase-equilibrium considerations. The application of a nonlinear geometric estimation approach yielded the underlying solvability condition with physical meaning, a straightforward estimator construction, and a conventional-like tuning procedure. The resulting barocalorimetric esti-

imator was an on-line dynamic measurement processor with a model-based predictor and a measurement-driven corrector, and whose implementation did not require the polymerization rates and heat-transfer coefficient function dependencies. The technique was tested with a representative laboratory styrene-butadiene system. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 475–482, 2005

Key words: emulsion polymerization; sensors; NMR; monomers; radical polymerization

INTRODUCTION

Originally, the reactor calorimetric estimation and control schemes evolved from laboratory differential estimation techniques: the idea was to draw reaction rate and conversion estimates from mass and energy balances without needing the reaction rate and heat-transfer functions.^{1–4} Motivated by the need to design or redesign industrial batch and semibatch polymer reactors, to attain better compromises between safety, productivity, and quality measures,⁴ the subject of calorimetric estimation and control has been extensively investigated.^{5,6} Diverse nonlinear techniques have been developed and successfully tested in solution and emulsion reactors, including homo-, co-, and terpolymerizations. Recently, a nonlinear geometric estimation approach has provided a unifying design framework for the calorimetric homopolymer case, on the basis of definitions of nonlinear observability and stability for batch motions.^{3,4,7} It has been reported that, in a pressurized copolymer emulsion reactor, the pressure evolution is correlated with the conversion and composition evolutions, depending on the particular reactor, recipe, and kind of (starved or nonstarved) regime.^{8,9} Even though these studies suggest the possibility of a barometric technique for reactor monitoring, its applicability must go beyond case-

specific correlations to a more general-purpose and systematized approach. In this regard, the barometric monitoring approach lags far behind its calorimetric counterpart. These considerations motivated the study on how and when the pressure measurement can be applied to improve the performance of a calorimetric scheme.

The problem of on-line estimation of the conversion and composition evolutions in a pressurized batch copolymer reactor with temperature and pressure measurements is addressed. The point of departure is a model that consists of mass and energy balances combined with a pressure equation drawn from a phase-equilibrium model. The application of the aforementioned nonlinear geometric estimation approach yields the problem solvability conditions with physical meaning, and a straightforward estimator construction-tuning procedure. The resulting barocalorimetric estimator is an on-line dynamic measurement signal processor whose implementation does not require the polymerization rates and heat-transfer coefficient function dependencies. The technique was tested with a representative laboratory styrene-butadiene system.

REACTOR ESTIMATION PROBLEM

Barocalorimetric reactor model

In a typical industrial pressurized free-radical emulsion copolymer batch or semibatch reactor, depicted in

Correspondence to: J. Alvarez (jac@xanum.uam.mx).

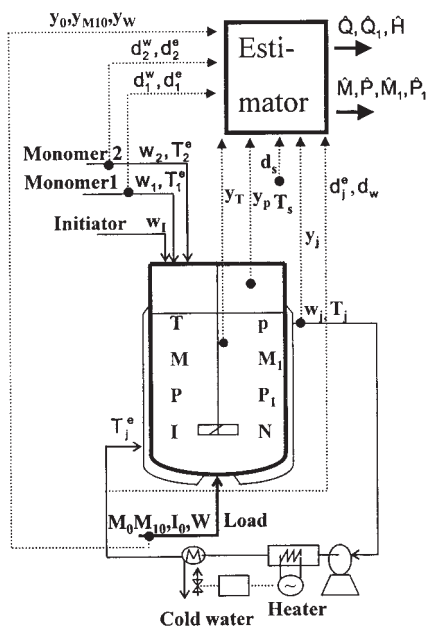


Figure 1 Pressurized copolymer reactor and barocalorimetric estimator.

Figure 1, the loaded and/or fed monomer pair is copolymerized by a pair of strongly exothermic reactions in the presence of radicals generated by an initiator. The reactions occur in particles made of copolymerized material swollen with free monomers. The particle phase is stabilized with a surfactant, and the polymerization rates depend on the free monomers and radical concentrations in the particles. The reactor pressure and the free-monomer partition is set by mass conservation and phase-equilibrium restrictions. The reactor has a heat-exchange system that enables the temperature to be controlled by manipulating the heat-exchange rate.

In the reactor depicted in Figure 1, T is the reacting mixture temperature; p is its pressure; T_j is the jacket fluid temperature; w_1 (or w) is the monomer 1 (or 1 and 2) mass feed rate; T_1^c (or T_2^c) and T_s are the feed monomer 1 (or 2) and surroundings temperatures, respectively; Q_j is the jacket fluid-surroundings heat-exchange rate; M_{10} (or M_0) and W are the monomer 1 (or total monomers) and water-loaded masses at time $t = 0$, respectively; and T_0 is the initial load temperature. M_1 (or M) is the added mass of monomer 1 (or 1 and 2) at time t , and P_1 (or P) is the corresponding mass of monomer 1 (or 1 and 2) in polymer form. The corresponding detailed modeling can be seen elsewhere,¹⁰ and here it suffices to retain the related conservation equations. On the basis of the mass and energy balances, in conjunction with the pressure-dependency function (π , to be determined), the barocalorimetric copolymer reactor model is given by the following system of equations:

$$\begin{aligned} \dot{T}_j &= [H - U_j(T_j - T_s) + Q_j]C_j^{-1} : \\ &= f_j(T_j, H, T_s, Q_j) \quad \dot{H} \approx 0 \quad (1a) \end{aligned}$$

$$\begin{aligned} \dot{T} &= \{Q - H + w_1c_1^m(T_1^c - T) \\ &+ (w - w_1)c_2^m(T_2^c - T)\}f_C^{-1}(P_1, P, M_1, M) \quad (1b) \end{aligned}$$

$$\begin{aligned} \dot{Q} &\approx 0 \quad \dot{P}_1 = \Delta_1^{-1}Q_1 \quad \dot{Q}_1 \approx 0 \\ \dot{P} &= \Delta_2^{-1}Q + (\Delta_1^{-1} - \Delta_2^{-1})Q_1 \quad (1c) \end{aligned}$$

$$\begin{aligned} \dot{M}_1 &= w_1 \quad \dot{M} = w \quad p = \pi(T, P_1, P, M_1, M) \\ T_j(0) &= T_{j0} \quad H(0) = H_0 \quad T(0) = T_0 \quad Q(0) = Q_0 \\ P_1(0) &= 0 \quad M_1(0) = M_{10} \quad M(0) = M_0 \quad P(0) = 0 \quad (1d) \end{aligned}$$

where Q (or Q_1) and H are the total (or attributed to monomer 1) heat generation and exchange rates, respectively; Δ_1 (or Δ_2) is the heat of reaction (per unit mass) of monomer 1 (or 2); U_j is the jacket fluid-to-surroundings heat-transfer coefficient; c_1^m (or c_2^m), c_1^p (or c_2^p), and c_w are the monomer 1 (or 2), polymer 1 (or 2), and water specific heat capacities, respectively. C_j is the cooling-heating system heat capacity and the function f_C is the dependency of the heat capacity on the reactor contents:

$$\begin{aligned} C_j &= C_R + C_F + C_J + C_I \quad C_S = M_S c_S \quad S = R, F, J, I \\ f_C(P_1, P, M_1, M) &= (M_1 - P_1)c_1^m + [(M - M_1) \\ &- (P - P_1)P_2]c_2^m + P_1c_1^p + (P - P_1)c_2^p + Wc_w \end{aligned}$$

where C_R , C_F , C_J , and C_I are, respectively, the reactor wall, jacket fluid, jacket wall, and insulator heat capacities; M_S (or c_S) ($S = R, F, J$, and I) are the corresponding mass and specific heat capacities; and W is the water mass.

The heat generation and reaction rates are related by the following expressions:

$$\begin{aligned} Q_1 &= R_1/\Delta_1 \quad R_1 = f_1(T, P_1, P, M_1, M, I, N) \\ Q_2 &= R_2/\Delta_2 \quad R_2 = f_2(T, P_1, P, M_1, M, I, N) \end{aligned}$$

where R_1 (or R_2) is the monomer 1 (or 2) reaction rate in mass per time units, and f_1 (or f_2) is the corresponding kinetic function, which is assumed to be unknown for the purpose at hand. Thus, the initiator content (I) and number of particles (N) are regarded as unmodeled variables. From a monitoring scheme perspective, the variables to be estimated are the conversion (c) and the accumulated (or instantaneous) copolymer composition (c_1) [or (c)]:

$$c = P/M_L$$

$$= \left\{ \int_0^t [Q(\tau) + (\Delta_2/\Delta_1 - 1)Q_1(\tau)] d\tau \right\} / (M_L \Delta_2)$$

$$M_L = M_0 + \int_0^t w(\tau) d\tau \quad (2a)$$

$$c_1 = P_1/P$$

$$= \frac{1}{1 + (\Delta_1/\Delta_2) \left\{ \left[\int_0^t Q(\tau) d\tau \right] / \left[\int_0^t Q_1(\tau) d\tau \right] - 1 \right\}}$$

$$(2b)$$

$$c_i = R_1/(R_1 + R_2) = Q_1/[(\Delta_1/\Delta_2)Q + (1 - \Delta_1/\Delta_2)Q_1] \quad (2c)$$

These equations say that the conversion (c) and composition (c_1 and c_i) estimates can be drawn from total (Q) and partial (Q_1) heat generation rate estimates.

In the barocalorimetric model [eqs. (1a)–(1d)], $(\cdot) \approx 0$ is a standard assumption made in signal processing and estimation theory to infer (possibly time-varying) model parameters,^{7,11,12} meaning that the variable (\cdot) changes more slowly than the estimator-based predicted measurement convergence rate. The temperature, pressure, and flow measurements are described by the following measurement equations (see Fig. 1):

$$y_T = T + e_T \quad y_j = T_j + e_j$$

$$y_p = \pi(T, P_1, M, P, M_1) + e_p \quad (3a)$$

$$d_1^e = T_1^e + e_1^e \quad d_2^e = T_2^e + e_2^e \quad d_s = T_s + e_s$$

$$d_1^w = w_1 + e_1^w \quad d_w = w + e_1^w + e_2^w \quad (3b)$$

with additive systematic and/or random errors arising from sensor and actuator devices as well as to imperfect mixing and fluctuations in the reacting mixture and jacket fluid. Following standard estimation techniques,^{11,13} the barocalorimetric estimator will be designed by first neglecting these errors, and their presence will be accounted for in the tuning and testing stages.

In compact vector notation, the barocalorimetric reactor model (1) is written as follows:

$$\dot{x}_I = f_I(x_I, x_{II}, d, b) \quad x_I(0) = x_{I0} \quad y = h(x_I, x_{II}, b) \quad (4a)$$

$$\dot{x}_{II} = f_{II}(x_I, x_{II}, d, b), \quad x_{II}(0) = x_{II0} \quad (4b)$$

where y (or d) is the measured output (or input), x_I (or x_{II}) is the innovated (or noninnovated) state:

$$x_I = (T_j, H, T, Q, P_1, Q_1)' \quad x_{II} = (P, M_1, M)'$$

$$y = (y_j, y_T, y_p)'$$

$$d = (d_1, d_w, d_1^e, d_2^e, d_s, d_{Q_i})'$$

$$b = (\Delta_1, \Delta_2, U_j, W, b_j^{c'}, b_p', b_p', b_{Q_i}')'$$

$$b_c = (c_1^m, c_2^m, c_1^p, c_2^p, c_w)'$$

$$(4d)$$

$$b_j^c = (c_R, c_F, c_j, c_V, c_R)'$$

$$b_p = (\rho_1^m, \rho_2^m, \rho_1^p, \rho_2^p, \rho_w)'$$

$$x_{II0} = (0, M_{10}, M_0)$$

where ρ_1^m (or ρ_2^m) and ρ_1^p (or ρ_2^p) are the pure monomer 1 (or 2) and polymer 1 (or 2) densities, respectively; b_p is the vector with the pressure dependency [π in eq. (1)] parameters, and the vector b_{Q_i} (or d_{Q_i}) contains the parameters (or time-varying exogenous terms) associated with the jacket-surroundings heat-exchange system, depending on the particular equipment and temperature control scheme. The model vector functions are given by

$$f_I(x_I, x_{II}, d, b)$$

$$= [f_j(T_j, H, T_s, Q), 0, f_T(H, T, Q, P_1, P, M_1, M,$$

$$w_1, w, T_{1e}, T_{2e}), 0, Q_1/\Delta_1, 0]'$$

$$f_{II}(x_I, x_{II}, d, b) = [f_p(Q, Q_1), w_1, w]'$$

$$h(x_I, x_{II}, p) = [T_j, T, \pi(T, P_1, M, P, M_1)]'$$

where

$$f_j(x_I, d_j, d, p) = [H - U_j(T_j - T_s) + Q_j]C_j^{-1}$$

$$f_p(x_I, x_{II}) = \Delta_2^{-1}Q + (\Delta_1^{-1} - \Delta_2^{-1})Q_1$$

$$f_T(x_I, x_{II}, d, p) = \{Q - H + w_1 c_{m1}(T_{1e} - T)$$

$$+ (w - w_1)c_{m2}(T_{2e} - T)\}f_C^{-1}(P_1, P, M_1, M)$$

Estimation problem

Having in mind the reactor operation (see Fig. 1) and the gravimetric–calorimetric composition equivalences [eqs. (2a)–(2c)], our estimation problem consists of on-line determination of the total (Q) and monomer 1 (Q_1) heat-generation rates on the basis of: (1) the barocalorimetric model [eqs. (2a)–(2c)]; (2) the temperature, flow, and pressure measurements [eqs. (3a) and (3b)]; and (3) the assumption that the reaction rate (f_I and f_2) and heat transfer (f_{II}) dependency functions are unknown. In particular, we are interested in: (1) the identification and interpretation with physical

meaning of the underlying solvability conditions, (2) the development of systematic estimator construction and tuning procedures, and (3) the experimental testing of the technique with the styrene–butadiene copolymerization as a representative case example.

BAROCALORIMETRIC ESTIMATOR

Pressure-dependency function

The reactor pressure dependency on its temperature and mass contents is determined by the associated phase-equilibrium thermodynamics. Without restricting the approach, let us consider a set of assumptions that apply to our case example (styrene–butadiene): (1) the particle phase behaves like a Flory–Huggins' solution¹⁴ [eq. (5a)], (2) the monomers are immiscible in water,¹⁹ (3) the free monomer-to-polymer content quotient [eq. (5b)] in the particle phase is described by a constant swelling factor¹⁵ (k_s), and (4) the free-monomer 1 (or 2) drop-to-particle concentration quotient [eq. (5c)] [or eq. (5d)] is set by a constant partition coefficient¹⁵ k_1 (or k_2). These considerations are reflected in the following pressure [eq. (5a)] and equilibrium [eqs. (5b)–(5d)] equations:

$$p = (F_1^p/P)\exp[P/M_p + \nu_1(P/M_p)^2]p_1(T) + (F_2^p/P)\exp[P/M_p + \nu_2(P/M_p)^2]p_2(T) + p_w(T) \quad (5a)$$

$$k_s = F_p/P \quad (5b)$$

$$k_1 = (F_1^d/V_d)/(F_1^p/V_p) \quad (5c)$$

$$k_2 = (F_2^d/V_d)/(F_2^p/V_p) \quad (5d)$$

where p (or T) and P are the reactor pressure (or temperature) and copolymer content, respectively; M_p is the mass of particles; F_1^p (or F_2^p) is the free-monomer 1 (or 2) mass in the particles; p_1 (or p_2) and p_w are the vapor pressure dependencies on temperature of monomer 1 (or 2) and water, respectively; F_p is the free-monomer mass in the particles; F_1^d (or F_2^d) is the free-monomer 1 (or 2) mass in the drops; V_d (or V_p) is the volume of the drops (or particles), and ν_1 (or ν_2) is the monomer–polymer 1 (or 2) interaction parameter. The related mass balances are given by

$$M = P + F \quad F = F_p + F_d \\ F_1 = F_1^p + F_1^d \quad F_1^d = F_d - F_1^d \quad F_2^p = F_p - F_1^p$$

$$P_2 = P - P_1 \quad V_d = F_1^d/\rho_1^m + F_2^d/\rho_2^m \\ V_p = F_1^p/\rho_1^m + F_2^p/\rho_2^m + P_1/\rho_1^p + P_2/\rho_2^p$$

In terms of the barocalorimetric states P_1 , P , M_1 , and M , the joint solution of these equations and the system

of equilibrium equations [eqs. (5a)–(5d)] yields the pressure function:

$$\delta(M, P) \geq 0 \text{ (drop presence)}$$

$$\begin{aligned} \pi(T, P_1, P, M_1, M) &= [k_s(1 + k_s)]^{-1}(M - P)^{-1} \\ &\quad \times [(M_1 - P_1)e_1^d p_1(T) \\ &\quad + (M + P_1 - P - M_1)e_2^d p_2(T)] + p_w(T) \\ e_1^d &= \exp[(1 + k_s + \nu_1)/(1 + k_s)^2] \\ e_2^d &= \exp[(1 + k_s + \nu_2)/(1 + k_s)^2] \quad (6a) \end{aligned}$$

$$\delta(M, P) < 0 \text{ (drop absence)}$$

$$\begin{aligned} \pi(T, P_1, P, M_1, M) &= [(M_1 - P_1)/M]e_1^s(P, M)p_1(T) \\ &\quad + [(M + P_1 - P - M_1)/M]e_2^s(M, P)p_2(T) + p_w(T) \\ e_1^s(P, M) &= \exp[(P/M) + \nu_1(P/M)^2] \\ e_2^s(M, P) &= \exp[(P/M) + \nu_2(P/M)^2] \quad (6b) \end{aligned}$$

where

$$\delta(M, P) = M - (1 + k_s)P$$

$$(M_i - P_i/M)(1 + 21_i P/M) = 0; (P, M, M_i, P_i)$$

Solvability conditions

In a way that is analogous to the treatment of the previously studied calorimetric homopolymer case without pressure measurement,^{3,4,16} in what follows the same nonlinear geometric estimation approach^{7,13,17} is applied to our present barocalorimetric copolymer case. Recall the measurement eq. (4a), take its time derivative, replace $(\dot{x}_I, \dot{x}_{II})$ by (f_I, f_{II}) , and draw the following nonlinear dependency of the measurements and their derivatives on the state-input pair:

$$\psi = \phi(x_I, x_{II}, d) \quad \psi = (y_j, \dot{y}_j, y_T, \dot{y}_T, y_p, \dot{y}_p)' \quad (7)$$

where

$$\begin{aligned} \phi(x_I, x_{II}, d) &= [T_j, f_j(x_I, d), T, f_T(x_I, x_{II}, d_T), f_p(x_I, x_{II}), F_p(x_I, x_{II}, d)]' \\ F_p(x_I, x_{II}, d) &= [\partial_{P_j} f_p(x_I, x_{II})](Q_1/\Delta_1) \\ &\quad + [\partial_{T_j} f_p(x_I, x_{II})]f_T(x_I, x_{II}, d) + [\partial_{M_j} f_p(x_I, x_{II})]w_1 \\ &\quad + [\partial_{M_j} f_p(x_I, x_{II})]w + [\partial_{p_j} f_p(x_I, x_{II})] \\ &\quad \times [\Delta_2^{-1}Q + (\Delta_1^{-1} - \Delta_2^{-1})Q_1] \end{aligned}$$

and $F_p = \dot{p}$. The nonsingular observability matrix O [eq. (8), unobservable dynamics [eq. (9), and its unob-

servable motion [eq. (10)] are given by [ϕ^{-1} is the solution of eq. (7) for x_I]

$$O(x_I, x_{II}, d) = \partial_{x_I} \phi(x_I, x_{II}, d) \quad \det[O(x_I, x_{II}, d)] \\ = [\partial_{Q_1} F_p(x_I, x_{II})][\partial_{P_1} f_p(x_I, x_{II})]/[C_j f_C(P_1, P, M_1, M)] \neq 0 \quad (8)$$

$$\dot{x}_{II} = f_{II}\{\phi^{-1}[x_{II}, d, \psi(t), x_{II}, d_w(t)]\} \\ = f^*\{x_{II}, d(t), \psi(t)\} \quad x_{II}(0) = x_{II0} \quad (9)$$

$$x_{II}(t) = \tau_1[t, x_{II0}, d(\cdot), \psi(\cdot)] \quad (10)$$

From conservation and finite-capacity arguments,^{3,4} the stability of the motion $x_{II}(t)$ follows, meaning that typical density, specific heat capacity, and equilibrium parameter errors produce growing errors $\tilde{x}_{II}(t)$, which remain acceptably bounded. These observability and stability features imply the detectability of the barocalorimetric motion [i.e., the solution of eq. (4)], and this in turn means that the total (Q) and partial (Q_1) heat generation rates can be quickly reconstructed by a dynamic nonlinear estimator. Because the product $\Delta_1 C_j f_C > 0$ is strictly positive, the barocalorimetric estimation problem is solvable if the following conditions are met over time:

Presence of drops

$$e_1^d p_1(T) \neq e_2^d p_2(T) \quad (11)$$

Absence of drops

$$1 \neq [e_1^s(P, M)p_1(T)][e_2^s(M, P)p_2(T)] \quad (12a)$$

$$\neq (\Delta_1/\Delta_2) \frac{1 - (1 - \Delta_2/\Delta_1)0_2}{1 - (1 - \Delta_1/\Delta_2)0_1} \quad (12b)$$

Conditions (11) and (12a) indicate that the monomer effective vapor pressures must be different. Condition (11b) indicates that, in the presence of drops, the effective pressure and heat of reaction ratios must be different. These general-purpose solvability conditions formally explain and delimit earlier reports on the possibility of using the pressure measurement to monitor the behavior of a pressurized copolymer reactor.^{8,9}

Estimator

Provided the above-stated solvability conditions (11a), (11b), and (12) are met, the corresponding barocalorimetric estimator is given by^{7,13,17}

$$\dot{\hat{x}}_I = f_I(\hat{x}_I, \hat{x}_{II}, d) + O^{-1}(x_I, \hat{x}_{II}, d)K[y - h(\hat{x}_I, \hat{x}_{II})] \\ \hat{x}_I(0) = \hat{x}_{I0} \quad (13a)$$

$$\dot{\hat{x}}_{II} = f_{II}(\hat{x}_I, \hat{x}_{II}, d_w) \quad \hat{x}_{II}(0) = \hat{x}_{II0} \quad (13b)$$

where

$$K = \begin{bmatrix} k_j & 0 & 0 \\ 0 & k_T & 0 \\ 0 & 0 & k_p \end{bmatrix} \quad k_j = \begin{bmatrix} 2\zeta_j \omega_j \\ \omega_j^2 \end{bmatrix} \\ k_T = \begin{bmatrix} 2\zeta_T \omega_T \\ \omega_T^2 \end{bmatrix} \quad k_p = \begin{bmatrix} 2\zeta_p \omega_p \\ \omega_p^2 \end{bmatrix}$$

and ω_a (or ζ_a) is the convergence rate (or damping factor) of the a th output ($a = j, T, p$), one for each measurement. The estimator is a dynamic data processor with two components: (1) the innovated subsystem [eq. (13a)] with a balance model-based prediction term (f_I) plus a measurement-based correction [$O^{-1}K(y - h)$], and (2) the noninnovated subsystem [eq. (13b)] with a balance model-based prediction term (f_{II}). The correction term of the first subsystem [eq. (13a)] is made by the product of the gain $O^{-1}K$ with the so-called innovation ($y - h$), which injects the information contained in the measurements and not in the model. Thus, this innovation injection enables the determination of the heat generation (Q and Q_1) and exchange (H) rates, on the basis of a rather simple model [i.e., $\dot{H} \approx 0$, $\dot{Q} \approx 0$, and $\dot{Q}_1 \approx 0$ in eq. (1)], without needing the reaction rate (f_1 and f_2) and heat-transfer (f_{IT}) dependency functions.

In detailed notation, the barocalorimetric estimator is given by

$$\dot{\hat{T}}_j = C_j^{-1}[H - U_j(\hat{T}_j - T_s) + Q_j] \\ + 2\zeta_j \omega_j (y_j - \hat{T}_j) \quad \hat{T}_{j0} = y_{j0}$$

$$\dot{\hat{H}} = (2\zeta_j \omega_j U_j + \omega_j^2 C_j)(y_j - \hat{T}_j) \quad \hat{T}_0 = y_0$$

$$\dot{\hat{T}} = f_C^{-1}(P_1, P, M_1, M)\{\hat{Q} - \hat{H} + w_1 c_{m1}(T_{1e} - \hat{T}) \\ + (w - w_1)c_{m2}(T_{2e} - \hat{T})\} + 2\zeta_T \omega_T (y_T - \hat{T})$$

$$\dot{\hat{Q}} = (2\zeta_j \omega_j U_j + \omega_j^2 C_j)(y_j - \hat{T}_j) \\ + (2\zeta_T \omega_T g_T^Q + \omega_T^2 h_T^Q)(y_T - \hat{T}) + 2\zeta_p \omega_p g_p^Q (y_p - \hat{p})$$

$$\dot{\hat{P}}_1 = \hat{Q}_1/\Delta_1 + (2\zeta_T \omega_T g_T^{P1})(y_T - \hat{T}) \\ + (2\zeta_p \omega_p g_p^{P1})(y_p - \hat{p}) \quad \hat{H}_0 = \hat{Q}_0 = \hat{Q}_{10} = \hat{P}_{10} = 0$$

$$\hat{Q}_1 = (2\zeta_T \omega_T g_T^{Q1} + \omega_T^2 h_T^{Q1})(y_T - \hat{T}) + [2\zeta_p \omega_p g_p^{Q1} + \omega_p^2 h_p^{Q1}](y_p - \hat{p})$$

$$\hat{P} = \hat{Q}/\Delta_2 + (1/\Delta_1 - 1/\Delta_2)\hat{Q}_1 \quad \hat{M}_1 = w_1$$

$$\hat{M} = w \quad [\hat{P}, \hat{M}_1, \hat{M}]_0 = [0, \hat{y}_{M_{10}}, \hat{y}_{M0}]$$

where the predicted pressure (\hat{p}), the nonlinear gain terms are given by

$$\hat{p} = \pi(\hat{T}, \hat{P}_1, \hat{P}, \hat{M}_1, \hat{M})$$

$$(g_T^Q, g_p^Q, g_T^{P1}, g_p^{P1}, g_T^{Q1}, h_T^{Q1}, g_p^{Q1}, h_p^{Q1})' = g(\hat{x}_I, \hat{x}_{II}, d)$$

and the entries of g are given in the Appendix. As a result of the poorness of the observability property [eq. (8)] in the beginning of the reaction, when the polymerized content is small, the entries of g are excessively large and, consequently, a limit on those terms must be imposed. In the absence of monomer 1 load and/or addition (i.e., $\hat{M}_{10} = 0$, implying that $P_1 = 0$ and $Q_1 = 0$) and of pressure measurement (i.e., $y_p - \hat{p} = 0$), the preceding barocalorimetric estimator reduces to its previously reported calorimetric counterpart.^{3,4,16}

The robust estimator functioning is attained by setting the three adjustable parameter pairs:

$$(\zeta_j, \omega_j) \quad (\zeta_T, \omega_T) \quad (\zeta_p, \omega_p) \quad (14)$$

according to the following tuning rules¹³: (1) set the damping factors at $\zeta_a = 2^{-1/2}$ ($a = j, T, p$) and the frequencies at $\omega_a = \omega$; (2) increase ω until the measurement predictions become excessively oscillatory at ω^* , back off to $\omega \approx \omega^*/3$ to $\omega^*/4$, and, if necessary, increase ζ to approximately 1 to 1.5; and (3) if an output, say a ($=j, T$, or p), presents a comparatively more oscillatory response than that of the other ones, decrease its frequency (ω_a), and/or increase its damping factor (ζ_a), until a satisfactory response is obtained.

TABLE I
Copolymerization Recipe and Operating Conditions

Recipe	
Water, g	1657
Butadiene, g	300
Styrene, g	492
Sodium dodecyl sulfate, g	92
Initiator concentration, %	4
Operating conditions	
Reactor temperature, K	323
Pressure, kPa	329
Stirrer speed, rpm	450
Initiator flow, g/min	0.3: $t \in [0, 100]$
t , min	0.2: $t \in (100, 160]$
	0.1: $t \in (160, 460]$

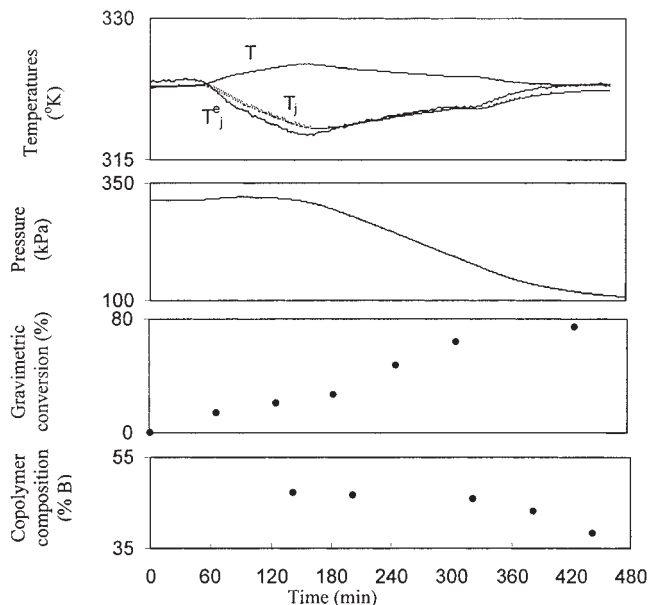


Figure 2 Reactor on (— and - - -), and off (●) line temperature, pressure, conversion, and composition.

EXPERIMENTAL TESTING

Experimental run

A styrene–butadiene batch (i.e., $w_1 = w = 0$) copolymerization run was executed in a 4-L glass–metal jacketed reactor (Fig. 1), stirred with turbine impellers, and a hydraulic shaft seal (up to 10 atm) supported on the metal cover. The heat-exchange system consisted of a jacket with recirculation loop by a high-temperature centrifugal pump, a double-pipe heat exchanger cooled by tap water, and a 3000-W immersion electric heater. Variable-speed dosing pumps were used to load the monomers and the initiator. The jacket fluid-to-surroundings heat-exchange rate (Q_j) was calculated from the recirculation water flow leaving the jacket (w_j) and the jacket inlet (T_j^e) and outlet (T_j) temperatures: $Q_j = w_j c_j (T_j - T_j^e)$, $c_j = c_w$. The reactor (T) and surrounding (T_s) temperatures were measured, and the jacket-to-surroundings heat-exchange coefficient (U_j) was determined from a standard response test with water. The reactor pressure was measured with a calibrated diaphragm pressure transducer. The measured signals were gathered and processed with data-acquisition equipment (μ MAC-1060 Analog Devices; Azonix, Houston, TX). The data display, processing, and control were performed with a supervisory control package (GENESIS process control software, ADAC, Milpitas, CA). A standard proportional and integral (PI) cascade scheme was used to control the temperature. Further details on the reactor instrumentation and control can be seen in a previous study.¹⁸

Potassium persulfate was used as initiator, and sodium dodecyl sulfate was used as surfactant. The ini-

TABLE II
Barocalorimetric Model Parameters

Parameter	Ingredient				
	Butadiene	Styrene	Polybutadiene	Polystyrene	Water
Density, ¹⁹ g/L	0.645	0.906	0.897	1.0711	1
Specific heat, ¹⁹ cal g ⁻¹ °C ⁻¹	0.41	0.33	0.52	0.27	1
Drop-particle coefficient ¹⁵	2	2			
Interaction parameter ¹⁵	1.8	0.23			
		Butadiene		Styrene	Water
Antoine's coefficient ¹⁹ A (for $P [=]$ mmHg)		16.5934		18.001	20.163
Antoine's coefficient ¹⁹ B (for $P [=]$ mmHg)		-2673.58		-4755	-5048
Swelling factor ¹⁵		0.6			
Jacket heat capacity, cal/C		9000			
Jacket heat transfer coefficient, cal min ⁻¹ °C ⁻¹		18			
Recirculating water flow, g/min		750			

tiator was added with three intervalwise constant rates. The recipe and operating conditions are listed in Table I. The pressure and temperature data that run the estimator are presented in Figure 2. In the same figure are presented a series of discrete conversion (c) and copolymer composition (c_1) off-line determinations, drawn with gravimetric and NMR techniques, respectively. Basically, the behavior features presented in Figure 2 are in agreement with previous reports on the styrene-butadiene copolymerization system.^{8,9}

Estimator implementation

The estimator parameter vector p [eq. (4)] was set with values reported in the literature (listed in Table II), that is: densities,¹⁹ specific heat capacities,¹⁹ heats of reaction,¹⁹ swelling factor,¹⁵ interaction parameters,¹⁵ and Antoine's coefficients¹⁹ for the vapor pressure dependencies on temperature.

The application of the tuning guidelines led to the following estimator settings [eq. (14)]:

$$\begin{aligned}
 (\zeta_j, \omega_j) &= (2^{-1/2}, 0.61 \text{ min}^{-1}) \quad (\zeta_{pr}, \omega_p) \\
 &= (2^{-1/2}, 0.16 \text{ min}^{-1}) \quad (\zeta_{p1}, \omega_{p1}) = (2^{-1/2}, 0.09 \text{ min}^{-1})
 \end{aligned}$$

Because of the fast mixing and recirculation dynamics, the jacket temperature and pressure measurement signals contain high-frequency components and, consequently, their gains had to be tuned slower than those of the reactor temperature measurement. The barocalorimetric estimation results are presented in Figure 3, showing: the pressure (\hat{p}), conversion (\hat{c}), and composition (\hat{c}_1), as well as the total (\hat{R}) and monomer 1 (\hat{R}_1) polymerization rate predicted evolutions. For comparison purposes, in the same figure are presented the on-line pressure measurements, as well as the off-line determinations of conversion (y_c) and

composition (y_{c_1}). As expected from the output-matching capability of the estimator, the estimated and actual pressure and temperature plots basically coincide.^{7,13} Although the composition estimates match rather well the off-line NMR experimental determinations, the conversion estimate exhibits an off-set trend, which starts negative, becomes zero at about 120 min, and remains positive thereafter. It must be pointed out that the model parameters taken from the literature were deliberately not adjusted. The conversion offset can be reduced or eliminated by calibrating one or various thermodynamic parameters, as should occasionally be done in an actual industrial setting.

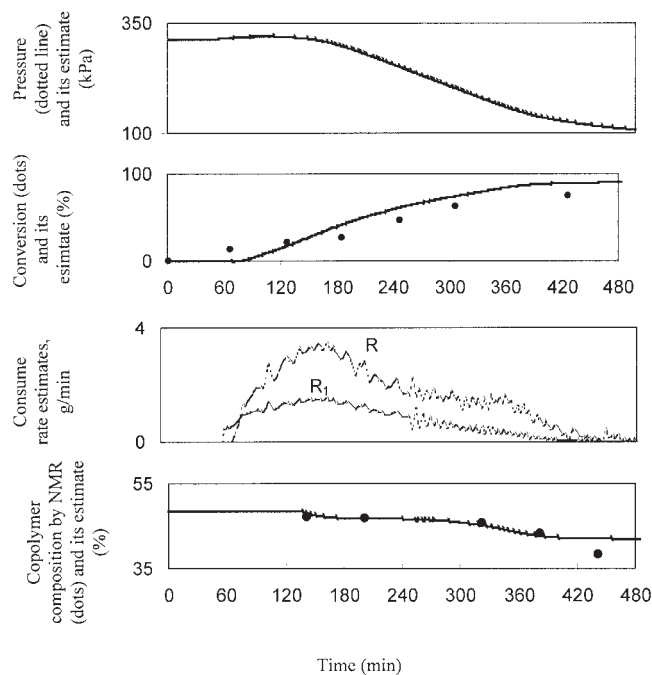


Figure 3 Barocalorimetric estimates (---), as well as on-line (—) and off-line (●) measurements.

CONCLUSIONS

On the basis of a robust detectability approach, the conditions for the feasibility of on-line estimation of the conversion and composition evolutions in a pressurized copolymer reactor with pressure, temperature, and flow measurements have been established as follows: (1) the monomer effective vapor pressures must be different; (2) in a starved regime, the effective pressure and heat of reaction rates must be different; and (3) there must be sufficient polymerized material. These general-purpose solvability conditions explain and formalize previous feasibility reports drawn from experimental studies on particular copolymerization systems.^{8,9} The estimator construction and tuning amount to straightforward systematic tasks. The technique was successfully tested with a representative laboratory styrene-butadiene system. The estimator was run with parameters taken from the literature: densities, specific heat capacities, heats of reaction, swelling factor, interaction parameters, and Antoine's coefficient sets.

APPENDIX

Estimator gain terms

In the \hat{Q} equation

$$g_T^Q = f_C \{ (\partial_{P_i} f_T) (\partial_{T_i} f_p) - \partial_{T_i} f_T \} / (\partial_{P_i} f_p) \quad h_T^Q = f_C$$

$$g_P^Q = -f_C (\partial_{P_i} f_T) / (\partial_{P_i} f_p)$$

In the \hat{P}_1 equation

$$g_T^{P1} = -(\partial_{T_i} f_p) / (\partial_{P_i} f_p) \quad g_P^{P1} = 1 / (\partial_{P_i} f_p)$$

In the \hat{Q}_1 equation

$$h_T^{Q1} = f_C (\partial_{Q_i} F_p) / [(\partial_{Q_i} F_p)] \quad h_P^{Q1} = 1 / (\partial_{Q_i} F_p)$$

$$g_P^{Q1} = [f_C (\partial_{P_i} f_T) (\partial_{Q_i} F_p) - (\partial_{P_i} F_p)] / [(\partial_{P_i} f_p) (\partial_{Q_i} F_p)]$$

$$g_T^{Q1} = [(\partial_{T_i} F_p) (\partial_{P_i} F_p) - f_C (\partial_{P_i} f_T) (\partial_{T_i} f_p) (\partial_{Q_i} F_p)] / [(\partial_{Q_i} F_p) \times (\partial_{P_i} f_p) + [f_C (\partial_{T_i} f_T) (\partial_{Q_i} F_p) - (\partial_{T_i} F_p)] / [(\partial_{Q_i} F_p)]]$$

References

1. Wu, R. S. H. *Chem Eng Prog* 1985, 81, 57.
2. MacGregor, J. F. In: *On-line Reactor Energy Balances by Kalman Filtering*, Proceedings of IFAC Conference on Instrumentation and Automation in Rubber, Plastics and Polymerization Industries, Akron, OH, 1986; pp. 35-39.
3. Zaldo, F.; Hernandez, M.; Alvarez, J. In: *Joint Process and Control Design of a Semibatch Emulsion Polymer Reactor*, Proceedings of ADCHEM-IFAC Symposium, 2003; pp. 91-96.
4. Alvarez, J.; Zaldo, F.; Oaxaca, G. In: *Towards a Joint Process and Control Design for Batch Processes: Application to Semibatch Polymer Reactors*; Seferlis, P.; Georgeadis, M., Eds.; The Integration of Process Design and Control; Elsevier: Amsterdam, 2004; pp. 604-634.
5. McKenna, T. F.; Othman, S.; Fevotte, G.; Santos, A. M.; Hammouri, H. *Polym React Eng* 2000, 8, 1.
6. Saenz de Buruaga, I.; Echevarria, A.; Armitage, A. P.; De La Cal, J.; Leiza, J.; Asua, J. M. *AIChE J* 1997, 43, 1069.
7. López, T.; Alvarez, J. *J Process Control* 2004, 14, 99.
8. Meehan, E. *J Am Chem Soc* 1949, 71, 628.
9. Araujo, O.; Saldívar, E.; Ray, W. H. *J Appl Polym Sci* 2001, 79, 2360.
10. Hamielec, A. E.; MacGregor, J. F.; Penlidis, A. *Makromol Chem Macromol Symp* 1987, 10/11, 521.
11. Gelb, A. *Applied Optimal Estimation*; MIT Press: Boston, MA, 1974.
12. López-Serrano, F.; Puig, J. E.; Alvarez, J. *AIChE J* 2004, 50, 2246.
13. Alvarez, J.; López, T. *AIChE J* 1999, 45, 107.
14. Sawada, H. *Thermodynamics of Polymerization*; Marcel Dekker: New York, 1976.
15. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Interscience: New York, 1966.
16. Zaldo, F. Ph.D. Thesis, National Autonomous University of México (UNAM), Mexico, 2004 (in Spanish).
17. Alvarez, J. *J Process Control* 2000, 10, 59.
18. Infante, J. R.; Villarreal, L. A.; Cisneros, A.; Peralta, R. D.; López, R. G.; Treviño, M. E. *J Appl Polym Sci* 1996, 62, 2311.
19. Perry, R., Ed. *Chemical Engineers Handbook*; McGraw-Hill: New York, 1986.