# Barocalorimetric Estimation of Emulsion Copolymerization Reactors

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***Abstract.*** **This work is a theoretical-experimental study on the barocalorimetric estimation of semibatch copolymerization pressurized reactors. The individual conversions, residual monomer, heat transfer and heat generation rates are estimated using mass and energy balances, two simple models for the pressure and monomers partition and calorimetric and pressure measurements. The solvability of the estimation problem is studied with a nonlinear constructive geometric approach giving the conditions for the suitability of the technique in terms of physical significance: vapour pressure of monomers, reaction heats and thermal capacitances. The implementation and tuning of the estimator is straightforward and tractable by tools and notions of linear systems. The batch emulsion copolymerization of styrene-butadiene is presented as a case study with results of simulation experimentally corroborated.**

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## I. INTRODUCTION

Calorimetry is a powerful tool with applications to monitoring and control of jacketed stirred tank reactors. In this type of reactor the dynamic mass and energy balances can be used to calculate the reaction energy generated by using the measured jacket and reactor temperatures as well as theirs time derivatives. In a recent theoretical-experimental study, the calorimetric problem was formulated as the estimation of the reaction and heat transfer rates identifying the nonlinear detectability property that underlies the solvabililty of the problem and providing a methodology for the systematic construction-tuning scheme and an error analysis accounting for the unmodeled dynamics [1]. Related to copolymerization reactions, the calorimetric techniques have been employed for the estimation of individual conversions of monomers as a measure of the composition of the copolymer [2]. Other measurements, in addition to calorimetry, have been considered for this purpose e.g. densimetry [3]; chromatography and spectroscopy [4]. The pressure measurement has been used as an indicative of the reaction extent where one reactant is volatile as in styrene-butadiene copolymerization [5],[6].

In this work, it is addressed the problem of on-line estimating the heat generation rate and the individual conversions of monomers in a pressurized emulsion copolymerization reactor by means of a barocalorimetric technique. With a constructive nonlinear geometric approach [7], the solvability of the estimation problem will be studied and cast in terms of physical insight. The analysis and synthesis methodology will provide us with a systematic construction and a tuning scheme tractable with standard notions of linear control systems.

## II. ESTIMATION PROBLEM

Let us consider a typical industrial emulsion copolymer semibatch reactor where monomers are converted into polymer via an exothermic free-radical reaction. The reactor is loaded with water, surfactant, and initiator and heated to the desired temperature. Then, the polymerization is started by feeding the monomers. The rates of monomer addition and of heat exchange are coordinated in such a way that the reactor temperature tracks a prescribed trajectory and the amount of monomer is kept around a prescribed value.

The barocalorimetric model for the semibatch copolymerization reactor is built based on standard concepts of free radical copolymerizations, heat transfer, and thermodynamics applied to a jacketed stirred tank reactor [8]. The corresponding heat and mass balance are given by:

$$\frac{dT}{dt} = C^{-1}\big[Q_G - Q_E - T(R_1(c_{p1} - c_{M1}) + R_2(c_{p2} - c_{M2}))$$
$$+ w_{M1}c_{M2}(T_{M1e} - T) + w_{M2}c_{M2}(T_{M2e} - T)$$
$$+ w_w c_w(T_{We} - T)\big] \tag{1a}$$

$$\frac{dT_j}{dt} = C_j^{-1}\big[Q_E - w_j c_{pj}(T_{je} - T_j)\big] \tag{1b}$$

$$\frac{dM}{dt} = -R + w_M \tag{1c}$$

$$\frac{dM_1}{dt} = -R_1 + w_{M1} \tag{1d}$$

$$\frac{dP_1}{dt} = R_1 \tag{1e}$$

$$\frac{dM_T}{dt} = w_e \tag{1f}$$

where $T$ and $T_j$ are the emulsion and fluid jacket temperatures, $M$, $P_1$, and $M_T$ are respectively the masses of total monomer, polymer 1 and emulsion, $w_{M1}$, $w_{M2}$, and $w_M$ are respectively the monomers 1, 2, and the total monomer

inlet flow feed rate, $w_e$, and $w_W$ are the total monomer (sum of monomer 1 and 2) and the water inlet feed rate, $Q_G$ is the generated heat, $Q_E$ is the exchanged heat. $R_1$, $R_2$ and $R$ are respectively the rate of disappearance of monomer 1, 2 and total monomer. $c_{p1}$, $c_{p2}$, $c_{M1}$, $c_{M2}$ and $c_w$ are respectively the calorific capacity of polymer 1, 2, monomer 1, 2, and water. $T_{M1e}$, $T_{M2e}$ and $T_{We}$ are respectively the inlet temperature of monomer 1, 2, and water. $C$ is the emulsion heat capacity including the stirrer and the baffles, and $C_j$ is the heat capacity of jacket system made by the reactor, jacket, and insulator walls as well as by the jacket fluid. According to the preceding mass and (lumped) heat conservation model, the emulsion-jacket heat exchange rate ($Q_E$), the monomer conversion ($\eta$), and the instantaneous composition of the copolymer are given by:

$$Q_E = U(T - T_j), \qquad \eta = \frac{M_T - M - W}{M_M} \qquad (2a)$$

$$c = \frac{R_1}{R} \qquad (2b)$$

where $M_M$ is the mass of total monomer fed over the entire semibatch period, $U$ is the heat transfer coefficient, and $W$ is the water content in the reactor.

The measured input ($d$), the measured temperatures ($x_T$), barocalorimetric parameters ($p$), and the variables of interest are given by:

$$d=(w_1,w_2,T_{M1},T_{M2}), \qquad x_T=(T,T_j), \qquad (3a)$$
$$p=(c_{M1},c_{M2},c_{P1},c_{P2},c_W,C_j,\Delta_1,\Delta_2,\Pi) \qquad (3b)$$
$$\Pi=(A_i,B_i,\chi_{ip}) \qquad v=(Q_G,Q_E,U,\eta,c) \qquad (3c)$$

$\Pi$ is the subset of barometric parameters, $A_i$, and $B_i$ are the constants of Antoine's equation for monomer 1, 2 and water, and $\chi_{ip}$ are the monomer-polymer interaction parameter.

The input ($y_d$) and output ($y_T$, $y_\pi$) measurements are given by

$$y_d=d+e_d, \qquad y_T=x_T+e_T, \qquad y_\pi=\pi+e_\pi \qquad (3d)$$

where $\pi$ is the reactor's pressure and $e_d$, $e_T$ and $e_\pi$ are the measurements errors.

In terms of first-principles kinetics, thermodynamics and heat transfer model descriptions, the actual polymerization rates $R_1$, $R$, heat generation rate $Q_G$ by chemical reaction, heat transfer coefficient $U$, and pressure (based on Flory-Huggins theory) are given by:

$$Q_G=R_1\Delta_{1+}(R-R_1)\Delta_2, \quad R=f_R(T,M,P_1,M_T,W,I,N) \qquad (4a)$$
$$R_1=f_{R1}(T,M,P_1,M_T,W,I,N) \quad U=f_U(T,M,P_1,M_TW) \qquad (4b)$$
$$\pi = P_1^0\phi_{1p}\,exp(\phi_{pp}+\chi_{1p}\phi_{pp}^2)$$
$$+ P_2^0\phi_{2p}\,exp(\phi_{pp}+\chi_{2p}\phi_{pp}^2)+P_w^0 \qquad (4c)$$

where $P_1^0$, $P_2^0$ and $P_w^0$ are respectively the vapour pressure of monomer 1, 2, and water. $\phi_{1p}$, $\phi_{2p}$ and $\phi_{pp}$ are respectively weight fraction of monomer 1, 2, and copolymer in the particle, and can be obtained of a partition mass balance coupled with the swelling factor expression, and the volume

additivity equation. The nonlinear function pair ($f_R$, $f_U$) depends on two states which are not included in the calorimetric model: the initiator concentration, $I$, and the number of latex particles per unit volume of aqueous phase , $N$. The idea of the barocalorimetric estimation method is to employ the model (1), (2), and (4c), in order to infer the conversion and the copolymer composition without requiring the (usually uncertain) kinetics and heat transfer models

Thus, our estimation problem consists in designing a dynamic data processor

$$\frac{d\hat{x}}{dt} = f_e[\hat{x}, y_d(t), y_T(t), y_\pi(t), \hat{p}], \hat{x}(0) = \hat{x}_0 \qquad (5a)$$
$$\hat{v} = (\hat{x}, \hat{p}), \qquad 0 \le t \le t_f \qquad (5b)$$

which built on the basis of the mass and lumped heat balances with their approximated parameters ($\hat{p}$), and driven by the input ($y_d$) and output ($y_T$, $y_\pi$) measurements, it yields an on-line estimate ($\hat{v}$) of the variables of interest. Methodologically speaking, we are interested in: (i) the identification of the detectability property which underlies the robust functioning of any barocalorimetric estimator, (ii) the derivation of an estimator with a systematic construction-tuning procedure coupled with a robust convergence criterion, and (iii) the testing of the estimation approach with experimental data.

## III. BAROCALORIMETRIC ESTIMATOR

In this section it is presented the nonlinear geometric approach [7], to our semibatch emulsion copolymerization problem, including robust solvability conditions, estimator construction and gain tuning.

### A. Estimability property

According to the nonlinear estimability or detectability definitions [7], based on the notions on nonlinear instantaneous and asymptotic observabilitiy [9], the barocalorimetric reactor motion:

$$x(t)=\tau_R[t,t_0,x_0,d(),p], \; x=(M,R,T,Q_G,T_j,Q_E,M_T,M_1,P_1)^T \quad (6)$$

is detectable if at each time $t$ the state $x$ is uniquely determined by the initial state, the input-output realization $d(t)$-$y(t)$, and its time derivatives; and the robust fulfillment of this detectability property signifies that the reactor motion $x(t)$ can be reconstructed by means of a dynamic nonlinear estimator. Physically speaking, such reactor motion detectability property amounts to the solvability of the following differential barocalorimetric estimation problem [7]: given the heat and mass balances (1) in conjunction with the data

$$D=\{x_{m0}, p, d, y_a(t)\}, \qquad x_{m0}=(M_{T0},M_{10},P_{10}) \qquad (7a)$$
$$y_a = (\pi, \frac{d\pi}{dt}, T, \frac{dT}{dt}, T_j, \frac{dT_j}{dt}) \qquad (7b)$$

reconstruct the reactor motion (6), and the trajectory $v(t)$, (3c).

Next the above stated differential barocalorimetry problem is addressed. In geometric terms we have the observability index:

$[k_1(\pi),k_2(T),k_3(T_j)] = (2,2,2)$         $k=6$

The functionality of these measurements and their temporal derivatives are:

$$y_1 = f(M,T,M_1), \qquad y_2 = T, \qquad y_3 = T_j \qquad (8a)$$

$$\frac{dy_1}{dt} = f(M,R,T,Q_G,Q_E,M_T,M_1), \qquad (8b)$$

$$\frac{dy_2}{dt} = f(Q_G,Q_E,M_T), \qquad \frac{dy_3}{dt} = f(T_j,Q_E) \qquad (8c)$$

The observability index proposed let us construct the map:

$$\phi_I(x) = \left[\pi,g_\pi,x_3,g_T,x_5,g_{Tj}\right] \qquad (9)$$

$\phi_I$ is a nonlinear map and $g_i$ denotes the temporal derivative of the measurements.

The non-observable part of the plant is formed by the rest of the states:

$$\phi_{II}(x) = [x_7,x_8,x_9,x_{10}]^T \qquad (10)$$

The observablility map is then:

$$\phi(x,u) = \left[\ \pi,g_\pi,x_3,g_T,x_5,g_{Tj}\right.$$
$$\left. ,x_5,g_{Tj},x_7,x_8,x_9,x_{10}\ \right]^T \qquad (11)$$

The Jacobian determinant of the observability map is:

$$det(\phi_x) = \frac{\partial \pi}{\partial M}\frac{\partial g_\pi}{\partial R}\frac{\partial g_T}{\partial Q_G}\frac{\partial g_{Tj}}{\partial Q_E} \qquad (12a)$$

with $\dfrac{\partial g_T}{\partial Q_G} = C^{-1}$,         $\dfrac{\partial g_{Tj}}{\partial Q_E} = C_j^{-1}$    (12b)

$$\frac{\partial \pi}{\partial M} = -\frac{(P_1^0\alpha - P_2^0\beta)M_1}{M^2} \qquad (12c)$$

$$\frac{\partial g_\pi}{\partial R} = \frac{(P_1^0\alpha - P_2^0\beta)M_1}{M^2}$$
$$+ g_{\pi 21}g_{\pi 22}\frac{(P_1^0\alpha - P_2^0\beta)}{M}\frac{\Delta H_2/PM_2}{\Delta H_1/PM_1 - \Delta H_2/PM_2} \qquad (12d)$$

$$g_{\pi 21} = -\frac{1}{MCT_K^2} \qquad (12e)$$

$$g_{\pi 22} = M_1\alpha P_1^0 B_1 + (M - M_1)\beta P_2^0 B_2 \qquad (12f)$$

where $\alpha = \dfrac{\delta}{1+\delta}exp(\phi_{pp} + \chi_{1p}\phi_{pp}^2)$,    (12g)

$$\beta = \frac{\delta}{1+\delta}exp(\phi_{pp} + \chi_{2p}\phi_{pp}^2) \qquad (12h)$$

$\delta$ is the swelling factor. The non-singularity of $\phi_x$ is determined by the non-vanishing value of $det(\phi_x)$ and this condition is generally met in a standard copolymerization pressurized reactor where a monomer presents a low vapour pressure, that is:

$$C^{-1} > 0, C_j^{-1} > 0,\ -(P_1^0\alpha - P_2^0\beta) > 0 \qquad (13)$$

Then $\phi(x) = \left[\phi_I + \phi_{II}\right]^T$ is Rx invertible (Robustly x invertible) and the states of the plant can be reconstructed with the measurements considered.

### B. Estimator construction

In this section we construct a non-linear geometric barocalorimetric estimator based in the output measuring to generate robustly convergent plant states estimates and to infer the variables of interest.

The state estimator we propose is of the type predictor-corrector and has the form:

$$\frac{d\chi}{dt} = f[\chi,u(t),\rho] + G(\chi,s_o)[y(t) - h(\chi,\rho)], \qquad (14a)$$

$$\varsigma = g(\chi,\rho) \qquad (14b)$$

where    $G(\chi,s_o) = \Theta_I(\chi,u)K_o(s_o)$    (14c)

$$[\Theta_I,\Theta_{II}] = \phi_x^{-1} \qquad (14d)$$

$\chi$ is the states estimates vector (it contains the estimates of $R$, $R_I,Q_G$ y $Q_E$), $\varsigma$ is the robustly convergent estimate of the variables of interest, $\rho$ is the approximate parameters set and $s_0$ is a global tuning parameter . The gains matrix $K_o$ is a measure of the rate of convergence. In terms of the characteristic frequency, $\omega$, and damping factor, $\xi$, of each output, these gains are given:

Pressure:

$$s_o k_{11}^o = 2\xi_P\omega_P \qquad s_o^2 k_{21}^o = \omega_P^2 \qquad (15a)$$

Reactor temperature:

$$s_o k_{12}^o = 2\xi_T\omega_T \qquad s_o^2 k_{22}^o = \omega_T^2 \qquad (15b)$$

Jacket temperature:

$$s_o k_{13}^o = 2\xi_{Tj}\omega_{Tj} \qquad s_o^2 k_{23}^o = \omega_{Tj}^2 \qquad (15c)$$

Once determined the characteristic frequency and damping factor for each output, the parameter $s_o$ let us change the global convergence velocity of the estimator.

### C. Estimator implementation and tuning

The estimator consists of nine non-linear ordinary differential equations and its implementation requires the barocalorimetric parameters ($\hat{p}$), listed in (3), nine initial conditions and one tuning parameter ($s_o$). The estimator proposed was tested in simulation mode with a first-principles model of the styrene-butadiene copolymerization. This system fulfills the conditions for observability as it has a very low vapour pressure monomer (butadiene). The estimator performs quite well as the tuning parameter is varied from 1 to 10. The best results were obtained with a value of 10, showing the validity of the heuristic rule that the estimator must be at least ten times faster than the plant.

### IV. EXPERIMENTAL TESTING

### A. Experimental setting and test motion

A batch copolymerization run was designed and executed in a glass/metal laboratory reactor. Differently from some of the recent calorimetric estimation studies which employ

commercial laboratory calorimetric reactors, here the experimental setting is made of standard laboratory reaction, heating-cooling, and data acquisition equipment. The experimental setting, which is depicted in Fig. 1, consists of 4-liter jacketed reactor equipped with variable speed agitator, thermal insulator, a pump to circulate the heat transfer medium, two heat exchangers for heating and cooling, a high-pressure dosing pump to feed the monomers or initiator, five temperature sensors and one pressure transducer. These measurements were gathered and processed in a personal computer equipped with commercial data acquisition system (Field Point) and supervisory software (LABVIEW).

The copolymerization run was batch-wise with continuous feeding of initiator. For comparison and validation purposes, latex samples were withdrawn from the reactor every one or two hours, inhibited with hidroquinone to stop further polymerization, and analyzed by gravimetry and nuclear magnetic resonance (NMR) to determine the conversion and the copolymer composition.

Fig. 2 shows the time evolution of reactor and jacket temperatures. It can be observed the reaction thermal effect by noting the accentuated reduction of jacket temperatures as the polymerization starts and then a slow recovery until they reach the initial values. The pressure measuring, in the next graphic, has a light increase at the beginning of the reaction and then a continuous decrease until the end. The slight pressure increment at first, in spite of butadiene consumption, is explained by the dominant increase of the pressure due to the reactor temperature rising. The later fall in pressure is due to both decrease in reactor temperature and butadiene consumption. The next two graphics in Fig. 2 show the gravimetric conversion and the copolymer composition. In the last one is noted a decreasing effect in composition as the reaction ends and the butadiene contents of the reaction medium exhausts.
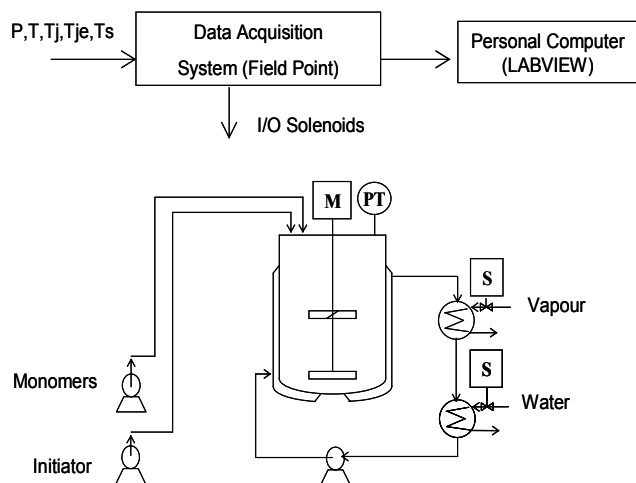
## B. Estimator performance

Using the estimator tuning parameters presented before, the interest variables estimates for the experimental copolymerization run are presented in Fig. 3. In the first graphic it can be seen that the pressure and its estimate coincide through all the reaction. The next two graphics show a reasonably well estimated conversion and individual rates. The acumulated composition obtained with the estimator captures the trend of the measured composition as shown in the last graphic.

As can be seen, the estimator produces good estimates of the interest variables. The conversion estimate is good enough for monitoring and controlling purposes, and the same can be observed on the copolymer composition estimate.

## V. CONCLUDING REMARKS

On the basis of a robust detectability approach, the feasibility of on-line estimating the heat generation rate and the individual polymerization rates has been established. This verifies some reports made in earlier reactor calorimetric estimation studies [10], and constitutes an improvement with respect to the recently developed polymerization reactor calorimetric estimators which require independent gravimetric measurements to perform the task [11].
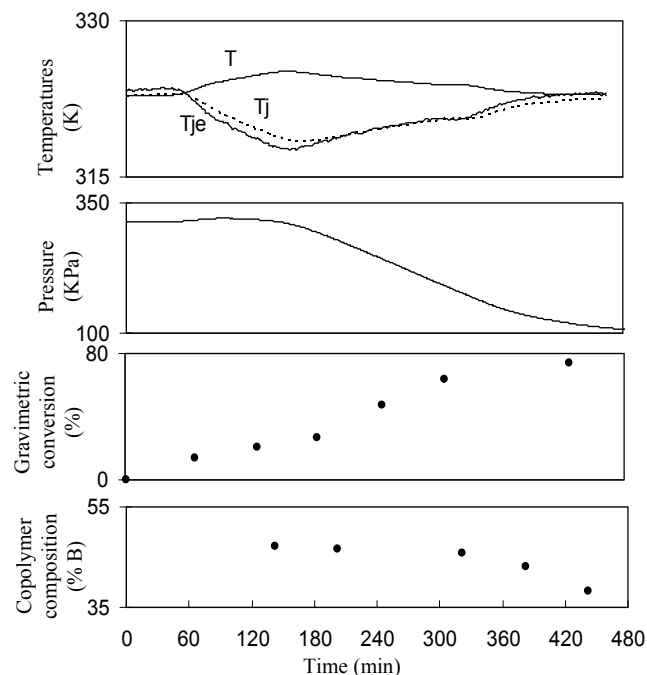
Fig. 2. On-line temperatures and pressure measurements, and off-line (•) gravimetric conversion and copolymer composition.
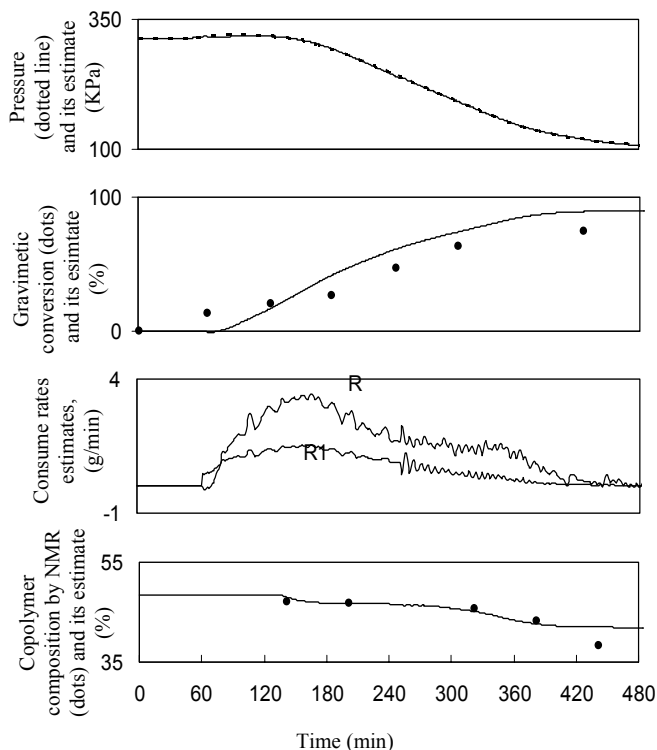
Fig. 1. The laboratory scale baro-calorimetric reactor.

Fig. 3. Barocalorimetric results for the reactor pressure, gravimetric conversion , consume rates, and copolymer composition.

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