*Macromol. Symp.* **2004**, *206,* 15—28

# Temperature Oscillation Calorimetry by Means of a Kalman-like Observer: The Joint Estimation of $Q_r$ and UA in a Stirred Tank Polymerization Reactor

*Fábio Bentes Freire, Reinaldo Giudici**

Departamento de Engenharia Química, Escola Politécnica, Universidade de São Paulo
Laboratório de Simulação e Controle de Processos, (LSCP/DEQ/EP/USP)
Caixa Postal 61548, CEP 05424–970, São Paulo, SP, Brasil
(Fax 55-11-3813-2380, e-mail : rgiudici@usp.br)

**Summary:** The present work is concerned with the joint estimation of the rate of heat produced by the emulsion terpolymerization of styrene, butyl acrylate and methyl methacrylate ($Q_r$), and the overall heat transfer coefficient (UA) from temperature measurements and reactor heat balance. By making specific assumptions on the dynamics of the parameters UA and $Q_r$, we designed a Kalman-like observer to carry out the estimation of these two time-varying parameters, without the need for neither additional measurements nor on-line samples. Temperature oscillations are induced in the cooling jacket in order to ensure the observability of the system. One further aspect of our approach is that it only requires the reactor energy balance to perform the estimation.

**Keywords:** emulsion polymerization; Kalman Filters; nonlinear systems;
on-line calorimetry; process monitoring

## Introduction

The quality of a polymer is in a large extent determined during its synthesis. For this reason, polymerization processes must rely on efficient on-line monitoring and control systems in order to ensure that the final product has the desired quality specifications. It is well known, however, that reliable on-line sensors that directly measure important physical properties are not always available for a number of applications in polymerization reactors. These quantities cannot be accurately determined from open-loop mathematical models either because polymerization processes are difficult to model in detail. A lot of attention has been given to the development of new algorithms that provide improved estimations from simplified open-loop models and available on-line measurements.

Another important aspect of polymerization processes is that they are generally exothermic. The amount of heat generated, once quantified, can be used to infer valuable information about the advancement of the reaction (global conversion, particle size variation,…). The main objective of on-line calorimetry is to continuously estimate the rate of heat generated by the reaction from temperature measurements and energy balance equations.

DOI: 10.1002/masy.200450202

Even though on-line calorimetry has been successfully employed for monitoring and controlling polymerization reactors, it still has one major drawback: the value of the parameter UA (overall heat exchange coefficient) has to be updated throughout the reaction. This parameter can vary significantly due to conversion-dependent increase of the viscosity of the reaction medium, fouling, etc. For laboratory scale reactors, updating UA can be done by introducing infrequent global conversion measurements obtained from gravimetry [1] However, for large scale industrial reactors, this approach is not appropriate since samples must be withdrawn from time to time. It has been shown that state observers can deal with the joined estimation of $Q_r$ and UA in a simple manner [2]. State observers can be thought of as multivariable compensators, which operate sequentially on the data as they become available. Their design is based on a dynamic model of the process and on the available on-line measurements of the state variables and the inputs. The main issue concerning on-line state estimation is to properly weight the contributions from the process model and the measurement residues. Tuning an observer is always a compromise between the sensitivity to measurement noise and the estimations dynamics. The latest efforts in the development of new observer designs are aimed at the use of non-linear systems concepts to specify a coordinate change that allows simple observing techniques to be employed.

The main purpose of the present work is the application of a Kalman-like observer on the joined estimation of the rate of heat generation, $Q_r$, and the overall heat exchange coefficient, UA, from reactor temperature measurements. In order to ensure the observability of the system, periodic oscillations are induced in the temperature of the jacket. This approach requires no information from the electrical heater and it is exclusively based on the reactor energy balance.

## Review

A lot of research effort has been focused on the development of on-line calorimetry strategies as a means of monitoring the evolution of polymerization. The outlines of some of the works concerning the design of calorimeters and their applications are presented in this section.

A high priority application of calorimetry is temperature control to ensure safe reactor operation, especially for reactions that can suddenly change mechanism causing a runaway reaction. The cost of an accident can be significant for an industrial reactor and therefore monitoring and control systems of reactor temperature is essential from an economic, humanistic, and environmental points of view. A contribution to the safe operation of exothermic polymerization is found in Schmidt and Reichert[3].

Carloff et al.[4] showed that the multiplication of the reactor heat balance by periodic functions and integration yields the overall heat transfer rate, provided that neither $Q_r$ nor UA varies strongly within one oscillation cycle. In order to mathematically decouple the rate of heat generated from the time-varying heat transfer coefficient, sinusoidal temperature oscillations were induced by an electrical heater placed either in the reactor or in the jacket.

Another way to independently estimate the heat transfer coefficient and the rate of heat generated by the reaction is accomplished by combining temperature measurements with some off-line measurements. In addition to the usual calorimetric data, Févotte et al.[5] used infrequently available gravimetric measurements to track the variations of key parameters, such as the overall heat transfer coefficient. The authors showed that accurate estimations of conversion could be obtained from an adaptive state-observer, even in the presence of both unpredictable conversion-dependent and batch-to-batch variations. This approach is not suitable for large-scale reactors, as sampling is required.

Mosebach and Reichert [6] dealt with the determination of kinetic and thermodynamic data of free-radical polymerization by adiabatic reaction calorimetry. The overall rate constants were determined from the measured temperature-time courses of the polymerizations. Although adiabatic reaction calorimetry is a very simple method for acquisition of kinetic and caloric data, adiabatic conditions cannot usually be extended to largè-scale reactors since there is no control of the reactor temperature.

A new strategy for the determination of the overall and individual conversions along with a key parameter related to the number of radicals in the particles ($\mu$) during free radical emulsion copolymerization of methyl methacrylate/vinyl acetate is presented by Févotte et al.[5]. The scheme was based on measurements of conversion obtained by on-line calorimetry. It was shown that with only a rough model of the process, it was possible to obtain reliable estimates of evolution of the polymerization reaction.

Guinot et al.[7] showed that the absence of inexpensive, reliable on-line sensors that directly measure important physical properties is one of the main difficulties in developing on-line monitoring and control systems for polymerization reactors. The authors have demonstrated that even off-line measurements of molecular weight and particle size distributions are hard to be obtained.

Santos et al.[8] proposed the joined use of cascade calorimetry and conductivity, along with empirical models, to predict the changes in the surface area of the latex particles. This information was then used to predict nucleation dynamics and latex stability.

## Calorimetry

The heat released by the polymerization reaction is quantified by the following equation:

$$Q_r = \Sigma Rp_i(-\Delta H_i) \qquad (1)$$

where $Rp_i$ is the rate of polymerization of the $i^{th}$ monomer in the mixture and $(-\Delta H_i)$ is its heat of reaction. The rate of polymerization is evaluated by a mass balance equation on the reactor and its cooling jacket. The energy balance around a batch reactor is given as follows:

$$(mCp)_r \frac{dT_r}{dt} = Q_r + Q_J - Q_{loss} \quad (2)$$

where $(mCp)_r \frac{dT_r}{dt}$ is the heat accumulation term of the reactor energy balance equation, $Q_J$ is the heat exchanged through the cooling jacket and $Q_{loss}$ is the overall heat loss to the surroundings (it includes the heat removed in the condenser). From equation 2 it is evident that we cannot evaluate $Q_r$ directly from the accumulation term because there exist other energy contributions in the energy balance. In order to estimate the value of $Q_r$ from equation 2 it is necessary to measure, estimate or model $Q_J$ and $Q_{loss}$.

The heat exchanged through the cooling jacket, $Q_J$, is defined by the following equation:

$$Q_J = UA(T_J - T_r) \quad (3)$$

where $T_J$ is the average temperature inside the jacket and $T_r$ is the temperature of the mixture inside the reactor.

$Q_{loss}$ is a general term, which includes all types of heat exchanged with the surroundings and the condenser. The higher the temperature difference between the reactor and the surroundings the more significant is the term $Q_{loss}$, as one should expect. The whole reactor is normally jacketed, with the exception of the condenser. For this reason the condenser is the main source of heat loss, even though the total heat loss may be usually held constant at least during the batch growth stages. Attention should be given to this term when the heat balance is applied to large-scale reactors (the heat capacity of the reactor components increases with volume). One should also note that during batch operation, the reactor temperature may vary significantly, which can cause large variations in $Q_{loss}$.

The inclusion of the jacket energy balance would provide further information to evaluate $Q_r$. However, to use the jacket heat balance one would need information on the flow rate of the cooling fluid and the inlet and outlet jacket temperatures. Although these measurements are simple to be made, they are not always available [2]. In addition, the higher the cooling fluid flow rate, the lower will be the difference between the inlet and the outlet jacket temperatures, therefore measurements with high accuracy would be required for using the jacket heat balance. For these reasons, our approach was based on the reactor energy balance.

## Kalman-like Observer

In this section we describe the factors related to the design of Kalman-like observers.

Basic Concepts – The Kalman-like observer first appeared in technological literature by the end of the eighties[9],[10]. Consider the reactor energy balance stated as follows:

$$\begin{cases} \dfrac{dT_r}{dt} = -\dfrac{UA}{(mCp)_r}(T_r - T_J) + \dfrac{Q_{tot}}{(mCp)_r} \\ \dfrac{dQ_{tot}}{dt} = \varepsilon_1 \\ \dfrac{dUA}{dt} = \varepsilon_2 \\ y = T_r \end{cases} \tag{4}$$

where, $Q_{tot} = Q_r - Q_{loss}$ and $\varepsilon_1$ and $\varepsilon_2$ are infinitesimal numbers. The system given by equation 4 describes approximately the dynamic behavior of the reactor temperature $T_r$ and the parameters $Q_r$ and UA. The unknown dynamics of $Q_r$ and UA are modeled as a random-walk process. A random-walk process derives its name from the example of a man who takes fixed-length steps in arbitrary directions.

Under the assumption that both $\varepsilon_1$ and $\varepsilon_2$ are much smaller than the other amounts involved in equation 4, we may rewrite it as follows.

$$\begin{bmatrix} \dot{T}_r \\ \dot{UA} \\ \dot{Q}_{tot} \end{bmatrix} = \begin{bmatrix} 0 & (T_J - T_r)/(mCp)_r & 1/(mCp)_r \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} T_r \\ UA \\ Q_{tot} \end{bmatrix} \tag{5}$$

This system has the form:

$$\begin{cases} \dot{x}(t) = A(u,y)x(t) \\ y(t) = Cx(t) \end{cases} \tag{6}$$

where, $x=[T_r\ UA\ Q_{tot}]^T$, $C=[1\ 0\ 0]$, $A = \begin{bmatrix} 0 & f_1 & f_2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$, $f_1 = \dfrac{(T_J - T_r)}{(mCp)_r}$ and $f_2 = \dfrac{1}{(mCp)_r}$

This means that the system given by the equation 5 is represented in canonical form and a Kalman-like observer can then be directly used (without any coordinate change) to estimate the system states. The Kalman-like observer takes the following form:

$$\begin{cases} \dot{\hat{x}}(t) = A(u,y)\hat{x}(t) - S_\theta^{-1}C^T(C\hat{x}(t) - y) \\ \dot{S}_\theta = -\theta S_\theta - A^T S_\theta - S_\theta A + C^T C \end{cases} \tag{7}$$

where $\theta$ is the observer tuning parameter.

The second differential equation is the Ricatti equation that must be solved simultaneously with the estimated state differential equations. In order to avoid the inversion of $S_\theta$ in the corrective term, we denote R= $S_\theta^{-1}$, therefore, R is also a symmetric matrix. The relation between $\dot{S}_\theta$ and $\dot{R}$ is given by:

$$\dot{S}_\theta = -R^{-1}\dot{R}\,R^{-1} \tag{8}$$

Substitution of equation 8 in equation 7 gives:

$$\begin{cases} \dot{\hat{x}}(t) = A(u,y)\hat{x}(t) - RC^T(C\hat{x}(t) - y) \\ \dot{R} = R\theta + RA^T + AR - RC^TCR \end{cases} \tag{9}$$

Since R is symmetric, there are six equations to integrate along with the states equation. Given,

$$R = \begin{bmatrix} a & d & e \\ d & b & f \\ e & f & c \end{bmatrix} \tag{10}$$

the second equation in the system described by equation 9 results in the following six differential equation:

$$\begin{cases} \dot{a} = \theta a + 2df_1 + 2ef_2 - a^2 \\ \dot{b} = \theta b - d^2 \\ \dot{c} = \theta c - e^2 \\ \dot{d} = \theta d + bf_1 + ff_2 - ad \\ \dot{e} = \theta e + ff_1 + cf_2 - ae \\ \dot{f} = \theta f - e \end{cases} \tag{11}$$

The matrix R is generally initialized as an identity matrix. The final observer of UA and Qtot is then given as follows:

$$\begin{cases} \dot{\hat{T}}_r = \left(\frac{T_J - T_r}{mCp}\right)\hat{UA} - \frac{1}{mCp}\hat{Q}_{tot} - a(\hat{T}_r - T_r) \\ \dot{\hat{UA}} = -d(\hat{T}_r - T_r) \\ \dot{\hat{Q}}_{tot} = -e(\hat{T}_r - T_r) \end{cases} \tag{12}$$

where the hat symbol (^) stands for the estimated variable. The system observability is investigated in the next section.

## Observability

A dynamic system is said to be observable if there exists a time $t_1$ such that any initial state $x(t_0)$ can be distinguished from any other state $x_0$ using the input $u(t)$ and the output $y(t)$ over the time interval $t_0 \leq t \leq t_1$. As a matter of fact, two initial states, $x_1(t_0)$ and $x_2(t_0) \in V$ (an open space in the $\mathbf{R}^n$), such that, $x_1(t_0) \neq x_2(t_0)$, are said to be indistinguishable if we verify the equality $y(t,x_1,u)=y(t,x_2,u)$ and if both outputs $y(t,x_1,u)$ and $y(t,x_2,u)$ follows the same trajectory in the state space.
From the system given by equation 4 we select a pair of initial states $x_1(t_0)=[T_{r1}\ Q_{r1}\ UA_1]^T$ and $x_2(t_0)=[T_{r2}\ Q_{r2}\ UA_2]^T$ such that, $T_{r1} = T_{r2} = T_r$ and $Q_{r1} - UA_1(T_r - T_J) = Q_{r2} - UA_2(T_r - T_J)$. In view of the choice of initial states just mentioned, we can conclude that the system 4 is observable if the difference $(T_r - T_J)$ varies as a function of time. Otherwise $y(t,x_1,u)$ will be equal to $y(t,x_2,u)$ and both initial states will follow the same trajectory leading the system to be indistinguishable with respect to the variables $Q_r$ and UA.

## The Estimations carried out by the Kalman-like observer

The evaluation of the observer performance has been carried out through the simulation of reactor dynamics with MATLAB. The case study presented refers to an emulsion terpolymerization of methyl methacrylate (MMA), styrene (Sty) and butyl acrylate (BuA). The variables $Q_r$ and UA were estimated by equation 12 along with the values of reactor temperature $T_r$. In order to determine the values of $T_r$ we followed the steps below:

- From the reactor mass balance we obtained the overall rates of polymerization, $Rp_i$:

$$\frac{dM_i}{dt} = -Rp_i \tag{13}$$

where, Mi is the amount of monomer “i” and $Rp_i$ is the overall rate of polymerization. In our approach, the overall rates of polymerization are given by:

$$Rp_i = \left(\sum_i kp_{ij} P_i\right) [M_i]_p \frac{\bar{n} N_p}{Na} \tag{14}$$

where, $[M_i]_p$ is the concentration of monomer “i” in the particles at time t, $\bar{n}$ is the average number of radicals per particle (held constant and equal to 0.5 in our simulations), $N_p$ is the total number of particles per liter of emulsion, $kp_{ij}$ is the propagation rate constant of growing chain of type “i” with monomer of type “j” and $P_i$ is the probability that an active chain in the particle will be of type “i”.

Févotte et al. [11] propose a more comprehensive discussion on the evaluation of $Rp_i$ given by equation 14 for a terpolymerization.

- The rates of polymerization were then used in equation 1 to determine $Q_r$.

Let the jacket energy balance be given by the following equation:

$$\frac{dT_J}{dt} = \frac{1}{(mCp)_J}\left[UA(T_r - T_J) + \dot{m}Cp_{cooling}(T_{Jinlet} - T_J) + Q_w\right] \tag{15}$$

where, $Q_w$ is the rate of heat provided by the electrical heating, $\dot{m}$ is the flow rate of the cooling fluid, $Cp_{cooling}$ is the heat capacity of the cooling fluid and $T_{Jinlet}$ is the inlet temperature of the cooling fluid. The rate of heat provided by the electrical heating is given as follows:

$$Q_w = Q_o(1+\sin(w.t)) \tag{16}$$

where $Q_o$ is the amplitude of the signal, $w=2\pi/\tau$ and $\tau$ is the frequency of the signal. The periodic oscillation induced in the jacket temperature is an effort to ensure the observability of the system, that is, to ensure the inequality $\frac{d(T_r - T_J)}{dt} \neq 0$.

- Equation 2 and 15 were integrated along with the value of $Q_r$ to give the "simulated on-line measurements" of reactor temperature $T_r$.

- The values of Tr were then fed into the observer every 10 seconds.

Table 1 presents the recipe used in the simulations. The total number of particles Np was supposed to be constant and equal to $4.5\times10^{20}$ throughout the polymerization. The tuning parameter $\theta$ was set at $4.5\times10^{-2}$. Table 2 contains the values of the most important parameters involved in the simulations.

Table 1 – Initial Amounts in the Reactor (t=0)

| Reaction Content | Mass (g) |
|---|---|
| MMA | 280.00 |
| Sty | 575.00 |
| BuA | 715.00 |
| Initiator | 30.00 |
| Water | 1050.00 |
| Total | 2650.00 |

Table 2 – Most Important Parameters Involved in the Simulations [12]

| Parameter | Value | Units |
|---|---|---|
| $kp_{BuA,BuA}$ | 33700 | $L.mol^{-1}s^{-1}$ |
| $kp_{BuA,MMA}$ | 84250 | $L.mol^{-1}s^{-1}$ |
| $kp_{BuA,Sty}$ | 112333 | $L.mol^{-1}s^{-1}$ |
| $kp_{MMA,BuA}$ | 392 | $L.mol^{-1}s^{-1}$ |
| $kp_{MMA,MMA}$ | 843 | $L.mol^{-1}s^{-1}$ |
| $kp_{MMA,Sty}$ | 1686 | $L.mol^{-1}s^{-1}$ |
| $kp_{Sty,BuA}$ | 424 | $L.mol^{-1}s^{-1}$ |
| $kp_{Sty,MMA}$ | 675 | $L.mol^{-1}s^{-1}$ |
| $kp_{Sty,Sty}$ | 297 | $L.mol^{-1}s^{-1}$ |
| $Cp_{BuA}$ | 1923 | $J.kg^{-1}K^{-1}$ |
| $Cp_{MMA}$ | 1720 | $J.kg^{-1}K^{-1}$ |
| $Cp_{Sty}$ | 1714 | $J.kg^{-1}K^{-1}$ |
| $Cp_{water}$ | 4180 | $J.kg^{-1}K^{-1}$ |
| $(-\Delta H_{BuA})$ | 78000 | $J.mol^{-1}$ |
| $(-\Delta H_{MMA})$ | 55500 | $J.mol^{-1}$ |
| $(-\Delta H_{Sty})$ | 71060 | $J.mol^{-1}$ |

From the reactor mass balance, we determine the overall conversion shown in figure 1:

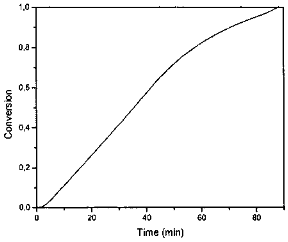

Figure 1 – Monomer Overall Conversion

In order to simulate the dynamic behavior of the polymerization reactor a profile of UA was imposed. This profile is showed in figure 2:

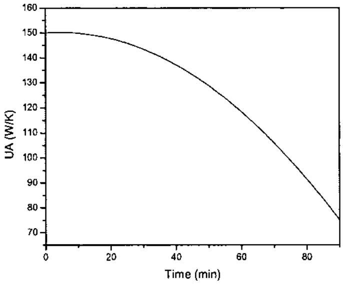

Figure 2 – Dynamic Behavior of the Parameter UA

Figure 2 shows that the initial value of UA decreases non-linearly during the reaction. It reaches 50% of its original value in the end of the reaction. The dynamic behavior of the reactor and jacket temperature are showed in figure 3:

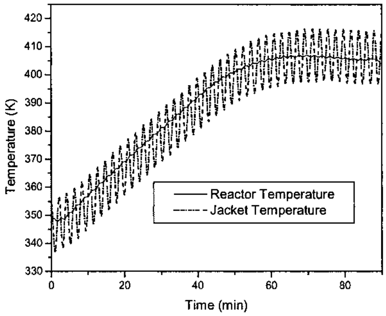

Figure 3 – Dynamic Behavior of the Reactor and Jacket Temperature: Oscillation Amplitude = 10 K and Period = 3 minutes

As can be seen in figure 3, the differential inequality $\frac{d(T_r - T_J)}{dt} \neq 0$ is verified throughout the polymerization. The estimated values of UA and $Q_r$ are showed in figures 4 and 5, respectively. Figure 4 shows a 500% deviation in the initial value of the observer. From the results obtained it is clear that the observer operates independently of the specification of the initial values. The estimated values of UA converge to the actual ones after about 5 minutes.

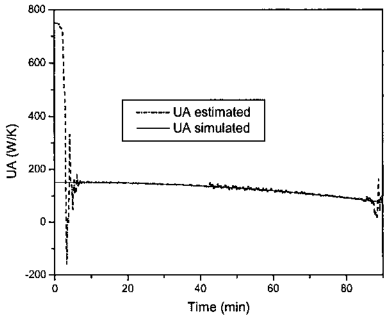

Figure 4 – Estimated Values of UA: $T_J$ Oscillation Amplitude = 10 K and Period = 3 minutes

The estimations of $Q_r$ take less than 5 minutes to converge. It can be seen in figure 5 that the estimated and simulated values of $Q_r$ are in a good agreement after convergence is attained. We note as well that the strong variation of $Q_r$ in the last minutes of reaction leads to damped oscillations in the estimated values of UA. This is partially due to the system output ($T_r$) being less sensitive to UA than it is to $Q_r$.

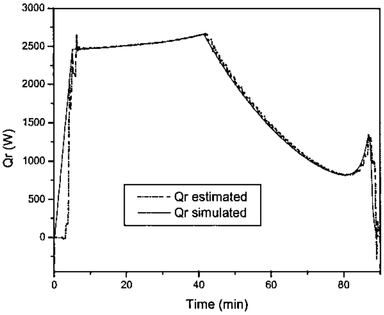

Figure 5 – Estimated Values of $Q_r$: $T_J$ Oscillation Amplitude = 10K and Period = 3 minutes

The oscillations of about 10 K in the jacket temperature are not easy to be implemented in large scale-reactors. In figure 6 we proposed periodic oscillations of 1.5K in $T_J$ and we cut by half the period of one cycle. The results of the estimations are presented in figures 7 and 8.

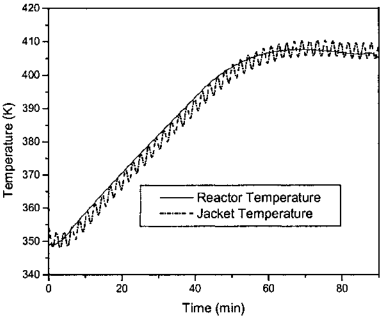

Figure 6 – Dynamic Behavior of the Reactor and Jacket Temperature: Oscillation Amplitude = 1.5K and Period = 1.5 minutes

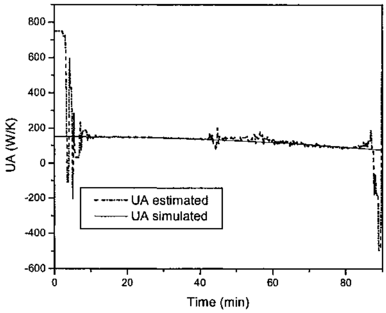

Figure 7 – Estimated Values of UA: $T_J$ Oscillation Amplitude = 1.5K and Period = 1.5 minutes.

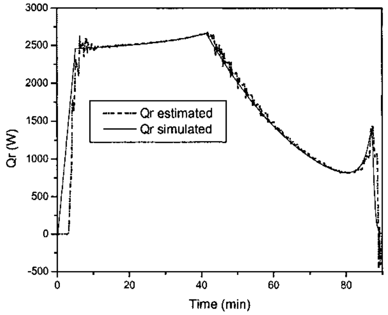

Figure 8 – Estimated Values of $Q_r$: $T_J$ Oscillation Amplitude = 1.5K and Period = 1.5 minutes

The estimations of UA and $Q_r$ are still in good agreement with its respective simulated values. However, it is clear from figure 7 that the deviations of the estimated value of UA around the expected value are stronger when compared to those of the previous results presented in this section. The same holds for the estimated values of $Q_r$. In fact, the estimation of $Q_r$ and UA is highly coupled, which means that bad estimations of $Q_r$ lead to bad estimations of UA and vice-versa.

A very important issue concerning the electrical heating is the amount of energy required to ensure the observability condition of the system. In order to reduce the cost of energy supply we proposed the interrupted period cycles shown in figure 9: The results of the estimations are presented in figures 10 and 11.

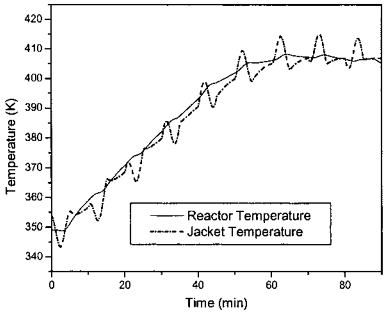

Figure 9 – Dynamic Behavior of the Reactor and the Jacket Temperature: Interrupted Oscillations

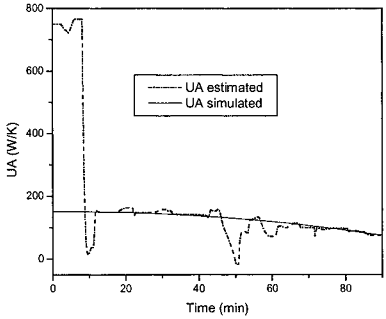

Figure 10 – Estimated Values of UA: Interrupted Oscillations

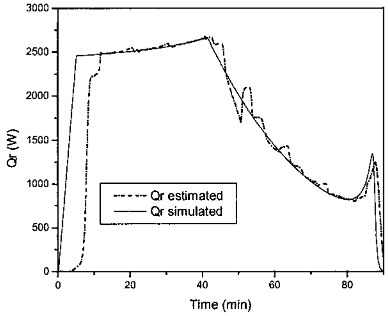

Figure 11 – Estimated Values of $Q_r$: Interrupted Oscillations

Figures 10 and 11 show that the estimated values of the variables converge to the expected ones after 10 minutes whereas in the previous simulations convergence was attained after 5 minutes. This difference could be reduced by the choice of a new set of tuning parameters.

One aspect that is evident in figures 10 and 11 is the loss of accuracy in the estimations everytime the observability condition is weaken by the dynamic behavior of $T_r$ and $T_J$. It is remarkable from figure 9 that in the vicinity of 40 and 50 minutes the condition $\frac{d(T_r - T_J)}{dt} \neq 0$ is not completely satisfied. Furthermore, the difference between $T_r$ and $T_J$ approaches zero during short intervals of time. This prevents the observer from carrying out the estimation of the variable UA within these intervals.

## Conclusions

On-line calorimetry is a simple means of inferring useful information about the advancement of polymerizations. The method is based on energy balance equations and temperature measurements. One major drawback of on-line calorimetry is the tracking of changes in the overall heat-transfer coefficient UA. The joint estimation of $Q_r$ and UA was described in the present work and illustrated for the case study of an emulsion terpolymerization process. A Kalman-like observer was used to carry out the estimations. Temperature oscillations were induced in the jacket in order to ensure the observability of the system. The results obtained show that the approach used gives accurate estimations of $Q_r$ and UA. One important aspect of the use of state observers concerns their independence from the initial values of the estimated variables. It means that no previous procedure is required to determine the value of UA in the beginning of the reaction. Another aspect of the present approach is that no information about the electrical heating is required. The dynamic behavior of the observer is determined by the choice of tuning parameters and estimations are possible everytime the observability condition $\frac{d(T_r - T_J)}{dt} \neq 0$ is verified.

The authors thank FAPESP, CNPq and CAPES for the financial support.

[1] G. Févotte, I. Barudio, J. Guillot, *Thermochimica Acta*, **1996**, 289, 223.
[2] S. Benamor, D. Colombié, T. McKenna, *Ind. Eng. Chem. Res.*, **2002**, 41, 4233
[3] C. U. Schmidt, K. H. Reichert, *Chem. Eng. Sci.* , **1988**, 43, 8, 2133.
[4] R. Carloff, A. Prob, K. Reichert , *Chem. Eng. Technol.* , **1994**, 17, 406.
[5] G. Févotte, T. F. McKenna, S. Othman, H. Hammouri, *Chem. Engng. Sci.*, **1998**, 53, 4, 773.
[6] M. Mosebach, K. Reichert, *Journal of Applied Polymer Science*, **1997**, 66, 673.
[7] P. Guinot, N. Othman, G. Févotte, T. F. McKenna, Polymer Reaction Engineering, **2000**, 8, 2, 115.
[8] A. Santos, F. B. Freire, S. Ben Amor, J. C. Pinto, R. Giudici, T. McKenna, *"DECHEMA Monographs"*, **2001**, 137, 609.
[9] G. Bornard, N. Couenne, F. Celle, *"Proceedings of the 29 International Conference on Nonlinear System Theory"*, Springer Verlag, **1988**, 122.
[10] H. Hammouri, J. de Leon, *"29th IEEE CDC"*, Honolulu, Hawaii, **1990**.
[11] G. Févotte, T. F. McKenna, S. Othman, A. Santos, *Comp. Chem. Eng. Suppl.* , **1998**, 22, 443.
[12] Othman, N. "Stratégies Avancées de Contrôle de Composition Lors de Polymérisations Semi-Continues en Emulsion", Lyon, France, Université Claude Bernard, Ph.D. Thesis, 2000.