A NEW APPROACH TO THE JOINED ESTIMATION OF THE HEAT GENERATED BY A SEMICONTIUNUOUS EMULSION POLYMERIZATION Qr AND THE OVERALL HEAT EXCHANGE PARAMETER UA

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Abstract - This work is concerned with the coupled estimation of the heat generated by the reaction (Qr) and the overall heat transfer parameter (UA) during the terpolymerization of styrene, butyl acrylate and methyl methacrylate from temperature measurements and the reactor heat balance. By making specific assumptions about the dynamics of the evolution of UA and Q_R, we propose a cascade of observers to successively estimate these two parameters without the need for additional measurements of on-line samples. One further aspect of our approach is that only the energy balance around the reactor was employed. It means that the flow rate of the cooling jacket fluid was not required.
Key words: emulsion polymerization, on-line calorimetry, state estimation.

INTRODUCTION

Polymer quality and properties are basically determined during production. On-line monitoring and control systems are very important in polymerization processes to ensure that the final product has the required specifications. However, the absence of inexpensive, reliable on-line sensors that provide direct physical measurement of quantities such as the polymer conversion, makes the operation of polymerization reactors hard to be accomplished in an automatized sense. These quantities can not be obtained from the open-loop mathematical model of

the process because polymerization processes are difficult to model in detail. For this reason, a significant amount of effort has been devoted to the development of algorithms that provide accurate estimates from the available open-loop models.

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

measurements and energy balance equations around the reactor.

Even though on-line calorimetry has been successfully employed in monitoring and controlling polymerization reactors, it has one major drawback: the value of the lumped parameter UA (heat exchange coefficient) has to be up-dated 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. However, for large scale reactors, this approach is not appropriate once samples must be withdrawn (sampling should always be avoided in industrial applications). Different methods, including temperature oscillation calorimetry (Carloff et al., 1994) have been proposed to overcome this problem. State observers, when properly designed and used, can provide a less demanding means of dealing with the aforementioned shortcoming.

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 together with the available on-line measurements of the state variables and the inputs. The main issue concerning the 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 sensitivity to measurement noise and response time. 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.

REVIEW

A lot of research efforts have 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.

Schimidt and Reichert (1988) used both the heat balance on the reactor and on the jacket to independently estimate the heat generated by the reaction and the heat transfer coefficient. The major drawback to this approach is that it requires the evaluation of the derivatives of the reactor and the jacket temperatures which amplifies the noise present in the measurements.

Carloff et al. (1994) showed that the multiplication of the reactor heat balance by periodic functions and integration yields the overall heat transfer. Sinusoidal temperature oscillations were induced by an electrical heater placed either in the reactor or in the jacket in order to decouple the chemical heat production from the variable heat transfer coefficient during the reaction.

Another way to independently estimate the heat transfer coefficient and the heat generated by the reaction is by combining the temperature measurements with some off-line measurements. In addition to the usual calorimetric data, Févotte et al (1996) used infrequently-available gravimetric measurements to track variations of key parameters, such as the overall heat transfer coefficient. The authors showed that accurate estimations of conversion can be obtained through the design of an adaptive state-observer, even if unpredictable conversion-dependent and/or batch-to-batch variations of the system are encountered. This approach is not suitable for large scale reactors as sampling is required.

Mosebach and Reichert (1997) 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. Even though adiabatic reaction calorimetry is a very simple method for acquisition of kinetic and caloric data, adiabatic conditions cannot usually be extended to large scale reactors since there is no control of the reactor temperature.

A new strategy for the on-line determination of the overall and individual conversions together with a key parameter related to the number of radicals in the particles (μ) during the free radical emulsion copolymerization of methyl methacrylate/vinyl acetate is presented in Févotte et al. (1998). 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 the evolution of the polymerization reaction.

McKenna et al. (1999) presented a non-linear observer combined with mechanistic models and on-line hardware and software (e.g. calorimetry) to monitor and control both co- and terpolymerizations. The pluridisciplinary sense of the approach represented the trend in the analysis of state observer as part of control strategies (Guinot et al., 2000).

Santos et al. (2001) proposed the joined use of cascade calorimetry and conductivity, along with

empirical models to provide a means of estimating the changes in the surface area of the latex particles. This information is then used to predict nucleation dynamics and latex stability.

STATE OBSERVERS

In this section we describe the background concerning the design of high-gain observers.

Basic Concepts for the High-Gain Observer

This observer is based on a linear model obtained from a coordinate change, which transforms the original non-linear system into a linear system while maintaining the non-linear relation between the output and the input (Soroush and Valluri, 1996). The concepts regarding the coordinate change come from the differential geometry, which is a branch of non-linear systems theory (Henson and Seborg, 1997, Kravaris and Kantor, 1990). In our work, only the following class of non-linear system is considered:

$$\dot{x} = f(x(t)) + g(x(t))u$$
$$y(t) = h(x(t))$$
(1)

where $x \in R^n$ is the vector of state variables; $y \in R$ and $u \in R$ are measurable output and input, respectively; f and g are analytic vector functions; and h is an analytic scalar function.

The proposed coordinate change is

$$z = \Phi(x, U) = \begin{bmatrix} h(x) \\ L_f h(x) \\ \vdots \\ L_f^{r-1} h(x) \\ L_f^r h(x) + L_g L_f^{r-1} h(x)u \\ \psi_{r+1}(x, U) \\ \vdots \\ \psi_{r+1}(x, U) \end{bmatrix}$$
(2)

where r, the relative order of the system (1), is the smallest integer for which $L_g L_f^{r-1} h(x) \neq 0$; $L_f h$ is the Lie derivative of the function h(x) and is defined by:

$$L_f h(x) = \sum_{i=1}^{n} \frac{\partial h(x)}{\partial x_i} f_i(x)$$
(3)

and the other terms are defined as follows:

$$U(t) = [u^{(0)}(t) \; u^{(1)}(t) \; ... \; u^{(n-r-1)}(t)]^T =$$

$$= \left[u(t) \quad \frac{du(t)}{dt} \quad \cdots \quad \frac{d^{n-r-1}u(t)}{dt^{n-r-1}} \right]^T$$
(4)

$$\psi_L \left[x, U, u^{(L-r)} \right] = L_{f+gu} \psi_{L-1} \left[x, U \right] +$$

$$+ \sum_{K=0}^{m(L)} u^{(K+1)} \frac{d\psi_{L-1}\left[x, U\right]}{du^{(K)}}$$
(5)

$$L = r+1, \; ..., \; n-1$$

$$m(L) = \min(\; L-3, \; r-1)$$

$$\psi_r(x, U) = L_f^r(x) + L_g L_f^{r-1} h(x)u$$
(6)

Substitution of equation 2 into equation 1 leads to the following linear representation:

$$\dot{z} = \tilde{A}z + \tilde{b}\psi_{L=n}\left[x, U\right]$$
$$y = \tilde{c}z$$
(7)

which is known as Brunowsky canonical form, where

$$\tilde{A} = \begin{bmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & 1 \\ 0 & 0 & 0 & \cdots & 0 \end{bmatrix} \in \mathbf{R}^{nxn}$$
(8)

$$\tilde{b} = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \in \mathbf{R}^{nxn}$$
(9)

$$\tilde{c} = \begin{bmatrix} 1 & 0 & \cdots & 0 \end{bmatrix} \in \mathbf{R}^{1 \, x \, n}$$
(10)

The dynamic system given by equation 7 is then employed in the observer design. Using the inverse transformation $\Phi^{-1}(z, U)$, the observer can be represented in terms of the original state variables as follows:

$$\dot{\hat{x}} = f(\hat{x}(t)) + g(\hat{x}(t))u +$$

$$+ \left[\frac{\partial \Phi(\hat{x}(t))}{\partial \hat{x}}\right]^{-1} S_\theta^{-1} C^T \left(y(t) - C\hat{x}(t)\right) \quad (11)$$

where S_θ is the unique symmetric positive-definite matrix solution of the following Lyapunov equation:

$$\theta S_\theta + \tilde{A}^T S_\theta + S_\theta \tilde{A} = \tilde{c}^T \tilde{c} \quad (12)$$

with $\theta > 0$.

CALORIMETRY

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

$$Qr = \sum Rp_i(-\Delta H_i) \quad (13)$$

where Rp_i is the rate of polymerization of the ith monomer in the mixture and $(-\Delta H_i)$ is its heat of reaction. The rate of polymerization is evaluated through a mass balance around the reactor and its cooling jacket. The energy balance around a semi-batch reactor is given as follows:

$$(mCp)r\frac{dTr}{dt} = Qr + Qfeed + Qj - Qloss \quad (14)$$

where $(mCp)_r \dfrac{dT_r}{dt}$ is the heat accumulation term of the reactor energy balance equation, Q_{Feed} is the sensible heat flow of the feed, Q_J is the heat exchanged through the cooling jacket and Q_{loss} is the overall heat losses to the surroundings term (it includes the heat evacuated through the condenser). From equation 14 it is evident that we can not evaluate Q_r directly from the accumulation terms when there are other energy contributions in the energy balance. In order to estimate the value of Q_r from equation 2 one need to be able to estimate or model Q_{feed}, Q_J and Q_{loss}.

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

$$Q_J = UA(T_J - T_r) \quad (15)$$

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

The sensible heat of the feed, Q_{Feed}, is determined as:

$$Q_{feed} = F_{feed} \cdot Cp_{feed} \cdot (T_{feed} - T_r) \quad (16)$$

where F_i is the feed flow rate, Cp_i is the inflow heat capacity and T_{feed} is the inflow temperature. This is considered to be a known quantity in the rest of this work.

Q_{loss} is a general term which includes all types of heat exchanges with the surroundings and the condenser. The importance of heat losses increases with the temperature difference between the reactor and the surroundings. The heat loss due to the condenser can be significant once the calorimeter is normally jacketed, but is usually constant at least during the semibatch 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 the batch period, the reactor temperature varies a lot, which can cause large variations in Q_{loss}.

The energy balance around the cooling jacket provides further information to evaluate Q_r. However, measurements of the cooling fluid flow rate through the jacket are assumed to be unknown, so we do not have enough information to close the energy balance around the cooling jacket. The jacket temperature, Tj, is assumed to be measured (average of inlet:outlet values) and we rely on equation 14 to design the observers.

OBSERVABILITY

The dynamic system from which we seek to construct the high-gain state observer for Qr and UA is given as follows:

$$\begin{cases} \dfrac{dTr}{dt} = \dfrac{Qr}{(mCp)r} - \dfrac{UA}{(mCp)r}(Tr - Tj) + \\[2mm] + \dfrac{\sum_i F_i Cp_i}{(mCp)r}(T_{feed} - Tr) - \dfrac{Q_{loss}}{(mCp)r} \\[2mm] \dfrac{dQr}{dt} = \varepsilon_1(t), \quad \dfrac{dUA}{dt} = \varepsilon_2(t), \quad y = Tr \end{cases} \quad (17)$$

The system given by equation 17 assumes that the dynamics of Qr and UA are described by simple random walk models (Gelb, 1974).

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 $t_0 \le t \le t_1$. As a matter of fact, two initial states, $x_1(t_0)$ and $x_2(t_0) \in \nu$ (an open space in the $\mathbf{R}^n$), such that, $x_1(t_0) \ne x_2(t_0)$, 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 17 we select a pair of initial states $x_1(t_0)=[Tr_1 \ Qr_1 \ UA_1]^T$ and $x_2(t_0)=[Tr_2 \ Qr_2 \ UA_2]^T$ such that, $Tr_1 = Tr_2 = Tr$ and $Qr_1 - UA_1(Tr - Tj) = Qr_2 - UA_2(Tr - Tj)$. In view of the selection of initial states just mentioned, we can conclude that the system 7 is observable if the difference $(Tr - Tj)$ varies as a function of time. Otherwise both initial states will follow the same trajectory and then it will not be possible to distinguish Qr and UA from measurements of reactor temperature.

THE OPEN-LOOP MODEL SIMULATINOS

The simulations of the calorimetry open-loop model given by equation 14 has been carried out in the MATLAB. The measurements of the reactor temperature Tr were simulated as follows:

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

$$\frac{dM_i}{dt} = F_i - Rp_i \qquad (18)$$

where, Mi is the amount of monomer "i" that did not react, F_i is the feed flowrate of monomer "i" and Rp_i is the overall rate of polymerization of a polymer chain. In our approach, the overall rates of polymerization are given by:

$$Rp_i = \left(\sum_i kp_{ji}P_i \right)[M_i]_p \frac{\overline{n}Np}{Na} \qquad (19)$$

where, $[M_i]_p$ is the concentration of monomer "i" in the particles at time t, $\overline{n}$ is the average number of radicals per particles (held constant and equal to 0.5 in our simulations), Np is the total number of particles per litre of emulsion (which is equal to 1.5×10^{21} within the initial 20 minutes and 3.0×10^{21} from 20 minutes on), kp_{ij} is the propagation rate coefficient 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. (1998b) propose a more comprehensive discussion about the evaluation of Rp_i given by equation 18 for a terpolymerization.

1) The rates of polymerization were then used in equation 13 to determine Qr.
2) Equation 14 was integrated along with the value of Qr to determine the "simulated on-line measurements" of reactor temperature.

Tables 1 and 2 contain the receipts used in the simulations:

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

Reaction Content	Mass (g)
MMA	880.25
STY	1761.03
BuA	2113.02
Initiator (SDS)	30.0
Water	55209.11
Total	59993.41

Table 2: Pre-emulsion Contents

Content	Mass (g)
MMA	5620
STY	11240
BuA	12990
Initiator (SDS)	60
Water	27860
Total	57770

The reactants present in the reactor at time t=0 react for 20 minutes. The pre-emulsion is then continuously fed in until the end of 280 minutes. The term Qloss is supposed to be proportional to the difference between the reactor and the environment temperature. The profile of UA imposed in the simulations is shown in Figure 1.

Figure 1 shows that UA is constant during the initial and the final batch and it decreases linearly during the semicontinuous stage as a result of the increase in the viscosity of the latex.

The overall conversion of the terpolymerization is shown in Figure 2.

The decrease in the conversion during the semicontinuous stage reflects the levels of the inflow rates employed in the simulations. It indicates that monomer accumulates in the reactor.

Figure 3 shows the evolution of Qr as a function of time.

A large amount of heat is released in the beginning due to the amount of monomer present in the reactor in the first stage of the process. A smooth decrease in Qr can be observed from about t=30 minutes untill the end of the semicontinuous operation.

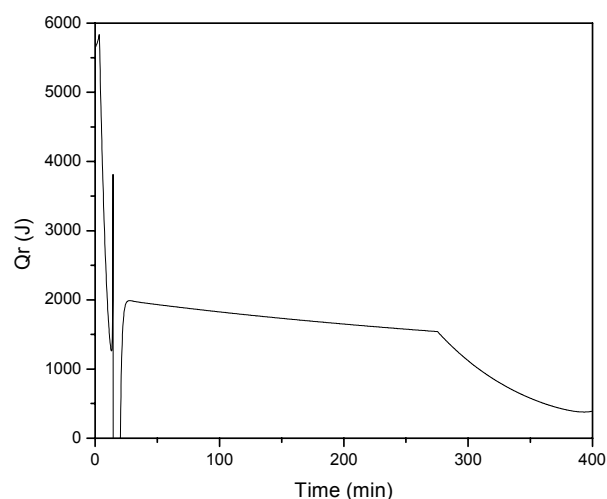The reactor and cooling jacket dynamic behavior are shown in Figure 4.

Figure 1: UA Dynamic Behavior
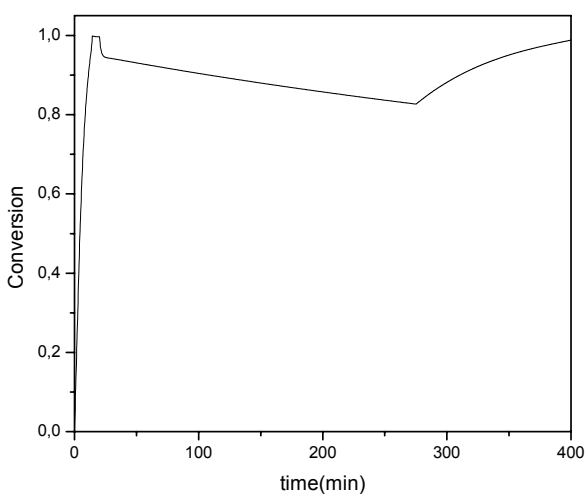
Figure 3: Qr Dynamic Behavior

Figure 2: Overall Monomer Conversion

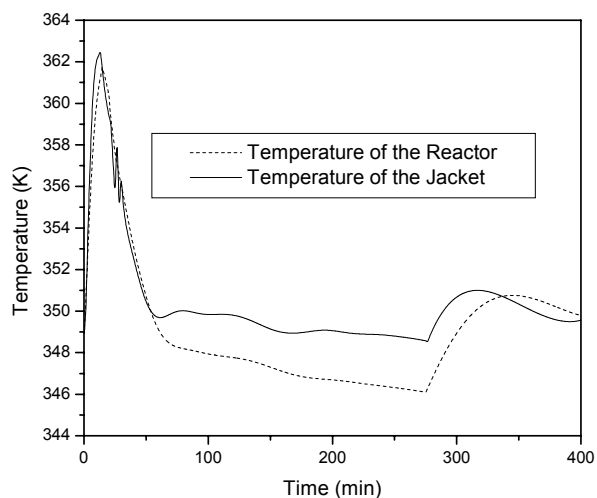**Figure 4:** Dynamic Behavior of Tr and Tj

Figure 4 shows that the dynamic behavior of Tr and Tj are very similar. It means that the difference (Tr – Tj) is close to a constant during the reaction. In view of what was described in the previous section, it is clear that we shall have difficulties if we try to estimate Qr and UA from equation 17. In order to overcome this shortcoming we propose the approach described in the following section.

CASCADE CALORIMETRY

If we know the value of UA then Qr can be readily estimated, independently of what happens to the difference (Tr – Tj). The same holds if we know the value of Qr and are to estimate UA. So, under the assumption of slow dynamics, we suppose that one of the variables remains constant within the interval between two consecutive temperature measurements and the other one is estimated (a typical digital acquisition unit can measure temperature every 10 seconds). Thus, one variable becomes the input of the observer of the other variable, and so on. The estimations of Qr and UA are carried out as follows:

$$\hat{Q}_r(0) \rightarrow \hat{U}A(1) \rightarrow \hat{Q}_r(2) \rightarrow \hat{U}A(3) \rightarrow$$

$$\rightarrow \cdots \rightarrow \hat{Q}_r(k-1) \rightarrow \hat{U}A(k) \rightarrow \cdots$$

where "^" stands for the estimated variable.

The selection of the initial values for both observers is very important. The estimations of Qr and UA take place independently and bad estimations of Qr leads to bad estimations of UA and so on, especially in the beginning of the reaction. We actually know that $\hat{Q}r(0) = 0$. The estimation of $\hat{U}A(0)$ along with Qloss(0) is described in the following paragraphs.

Estimation of $\hat{U}A(0)$ and Qloss(0) During Reactor Heat-Up

Othman (2000) developed a Kalman-like observer to estimate the initial values of estimated UA and Qloss from temperature measurements during reactor heat-up. The dynamic model employed is given by the following equation:

$$\begin{cases} \dfrac{dTr}{dt} = -\dfrac{UA}{(mCp)r}(Tr - Tj) + \\[2mm] + \dfrac{\sum_i F_i Cp_i}{(mCp)r}(T_{feed} - Tr) - \dfrac{Q_{loss}}{(mCp)r} \\[2mm] \dfrac{dQloss}{dt} = 0, \quad \dfrac{dUA}{dt} = 0, \quad y = Tr \end{cases} \quad (20)$$

The system given above can be rewritten as follows:

$$\begin{bmatrix} \dot{Tr} \\ \dot{U}A \\ \dot{Q}loss \end{bmatrix} = \begin{bmatrix} 0 & (Tj-Tr)/mCp & -1/mCp \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} Tr \\ UA \\ Qloss \end{bmatrix} \quad (21)$$

This system has the form:

$$\begin{cases} \dot{x}(t) = A(u,y)x(t) \\ y(t) = Cx(t) \end{cases} \quad (22)$$

where, x=[Tr UA Qloss]^T, C=[1 0 0],

$$A = \begin{bmatrix} 0 & f_1 & f_2 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad f_1 = \frac{(Tr - Tj)}{mCp} \quad \text{and}$$

$$f_2 = -\frac{1}{mCp}$$

A Kalman-like observer can be used to estimate the different states. The Kalman-like observer takes the following form:

$$\begin{cases} \dot{\hat{x}}(t) = A(u,y)\hat{x}(t) - S_\theta^{-1} C^T (C\hat{x}(t) - y) \\ \dot{S}_\theta = -\theta S_\theta - A^T S_\theta - S_\theta A + C^T C \end{cases} \quad (23)$$

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_θ in the corrective term, we denote R= S_θ^{-1}, therefore, R is also a symmetric matrix. The relation between $\dot{S}_\theta$ and $\dot{R}$ is given by:

$$\dot{S}_\theta = -R^{-1}\dot{R}\,R^{-1} \quad (24)$$

Substitution of equation 24 in equation 23 gives:

$$\begin{cases} \dot{\hat{x}}(t) = A(u,y)\hat{x}(t) - RC^T (C\hat{x}(t) - y) \\ \dot{R} = R\theta + RA^T + AR - RC^T CR \end{cases} \quad (25)$$

Since R is symmetric, there are 6 equations to integrate along with the states equation. Given,

$$R = \begin{bmatrix} a & d & e \\ d & b & f \\ e & f & c \end{bmatrix} \qquad (26)$$

the second equation in system 25 gives rise to the following six differential equation:

$$\begin{cases} \dot{a} = \theta a + 2df_1 + 2ef_2 - a^2 \\ \dot{b} = \theta b - d^2 \\ \dot{c} = \theta c - e^2 \\ \dot{d} = \theta d + bf_1 + ff_2 - ad \\ \dot{e} = \theta e + ff_1 + cf_2 - ae \\ \dot{f} = \theta f - e \end{cases} \qquad (27)$$

The matrix R is generally initialized at the identity matrix. The final observer of UA and Qloss:

$$\begin{cases} \dot{\hat{T}}_r = \left(\dfrac{T_j - T_r}{mCp} \right) \hat{U}A - \dfrac{1}{mCp} \hat{Q}loss - a(\hat{T}_r - T_r) \\ \\ \dot{\hat{U}}A = -d(\hat{T}_r - T_r), \qquad \dot{\hat{Q}}loss = -e(\hat{T}_r - T_r) \end{cases} \qquad (28)$$

In order to decouple the variables UA and Qloss, the jacket is heated by steps. The steps of jacket temperature and the reactor temperature is shown in Figure 5.

Figure 5 shows that the difference (Tr–Tj) varies strongly with time except at the end of each step. As a result, a temporary loss of observability is expected as it is actually seen in Figures 6 and 7.
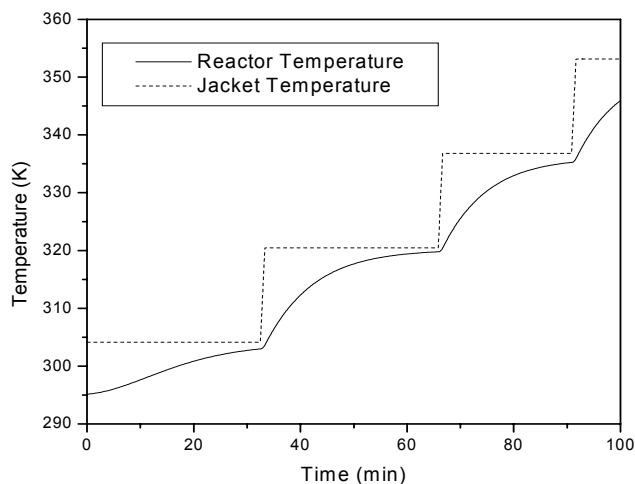

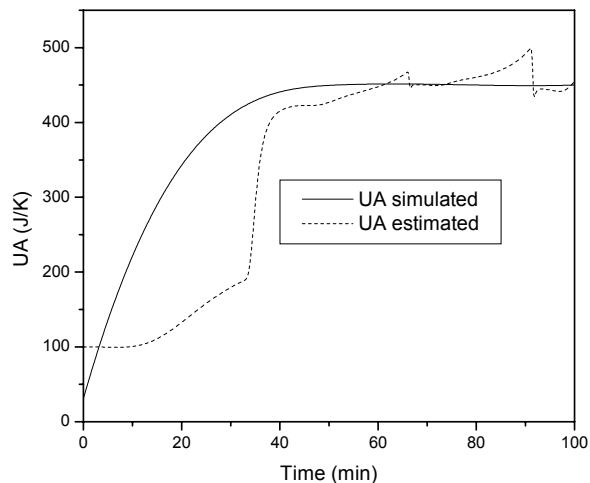**Figure 5:** Temperature Steps on the Jacket and Reactor Temperature

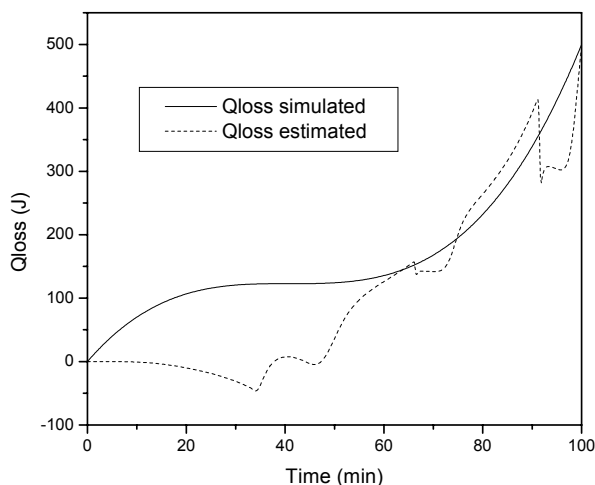**Figure 6:** Simulated and Estimated UA Dynamic Behavior

Figure 7: Simulated and Estimated Qloss Dynamic Behavior

Despite the fact that the estimations take a while before converging to the simulated value, it can be seen from Figures 6 and 7 that UA and Qloss are accurately determined at the end of the reactor heat-up. These are the initial values of the cascade calorimetry along with $\hat{Q}r(0) = 0$.

The impact of the term Qloss on the estimations was investigated in this work. The model employed by the cascade calorimetry assumed Qloss(t)=Qloss(0) throughout the reaction, while the model used to simulate reactor dynamics assumed a variable Qloss term.

The design of the cascade calorimetry is described in the next section.

A CASCADE OF HIGH-GAIN OBSERVERS

From equation 11 we propose the following high-gain observers to estimate Qr and UA, respectively:

$$
\begin{cases}
\dfrac{dTr}{dt} = \dfrac{1}{(mCp)r}\hat{Q}r + \dfrac{1}{(mCp)r}[-U\hat{A}(\hat{T}r - Tj) + \\
\quad + \sum_i F_i Cp_i (T_{feed} - Tr) - Q_{loss}] - 2\theta_{Qr}(\hat{T}r - Tr) \\
\dfrac{d\hat{Q}r}{dt} = -\theta_{Qr}^2 (mCp)r(\hat{T}r - Tr)
\end{cases}
\tag{29}
$$

$$
\begin{cases}
\dfrac{dTr}{dt} = -U\hat{A}\dfrac{(\hat{T}r - Tj)}{(mCp)r} + \dfrac{1}{(mCp)r}[\hat{Q}r + \\
\quad + \sum_i F_i Cp_i (T_{feed} - Tr) - Q_{loss}] - 2\theta_{UA}(\hat{T}r - Tr) \\
\dfrac{dU\hat{A}}{dt} = [2\theta_{UA}\dfrac{U\hat{A}}{\hat{T}r - Tj} + \theta_{UA}^2 \dfrac{(mCp)r}{\hat{T}r - Tj}](\hat{T}r - Tr)
\end{cases}
\tag{30}
$$

These high-gain observers are connected in series in order to share the estimations. At a given instant, one variable is estimated and the other one is held constant as previously described.

The observer of UA as given by equation 30 has singularity problems at the vicinities of $\hat{T}r \cong Tj$. From figure 4 it can be seen that the difference ($\hat{T}r - Tj$) is of a few units until t$\cong$50 minutes. So we may expect difficulties in the estimation of UA within this interval.

RESULTS AND DISCUSSIONS

The performance of the cascade calorimetry was investigated by simulations carried out in the MATLAB. In order to tuning the observers the tuning parameters were selected by trior and error. In the simulations that follows the tuning parameter of Qr, θ_{Qr}, is equal to 0.05. It was found that a variable tuning parameter of UA, θ_{UA}, would be appropriate to overcome the observalility singularity during the 50 initial minutes of reaction. So, during 50 minutes θ_{UA} is kept constant and equal to $1x10^{-5}$. This is an effort to maintain $\hat{U}A$ as close as possible to its initial value. From t=50 to 70 minutes, θ_{UA} is increased linearly to $6.5x10^{-2}$ and then kept constant untill t=280 minutes. From t=280 to 300 minutes θ_{UA} is decreased linearly to $1x10^{-3}$ and is kept constant untill t=400 minutes. The results are presented in Figures 8 and 9.

Figure 8 shows that the estimations are in good agreement with the simulated values. It is clear that the assumption of slow dynamics does not seem to be appropriate to describe the behavior of Qr during the batch stage. However, the strong variations in Qr coincide with constant UA and the cascade calorimetry performs almost uniquely the estimations of Qr for the initial 50 minutes.

The estimations of UA converge within a few minutes as θ_{UA} takes values of the order of 10^{-2}. The results show that the right tuning allows the cascade calorimetry to provide accurate estimations even in the presence of incertainties in the term Qloss.

Another dynamic behavior of UA considered in this work is presented in Figure 10.

The hyperbolic profile of UA is conveniently tracked by the cascade calorimetry. The performance of the cascade calorimetry with respect to Qr is shown in Figure 11.

One major disadvantage of the ordinary open-loop calorimetry which is based on the off-line calibration of the parameter UA is the sensitivity to external disturbances. Emulsion polymerizations are essentially subjected to two typical disturbances: re-nucleation and flocculation.

Re-nucleation is generally characterized by a sudden raise in the heat generated by the reaction due to an increase in the total number of particles. This phenomenon indicates that the surface area of the latex particles covered by emulsifier is above a critical value.
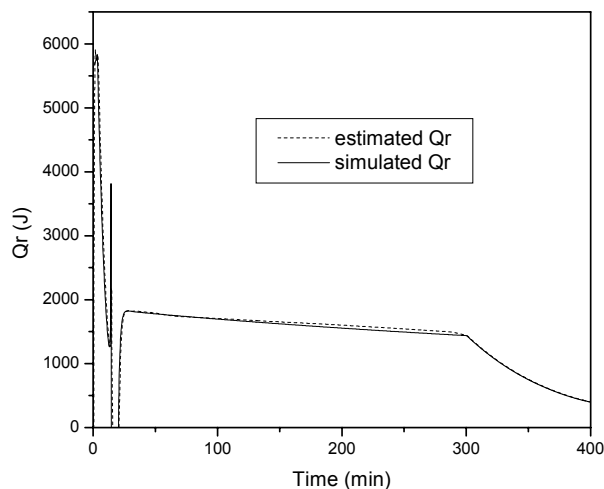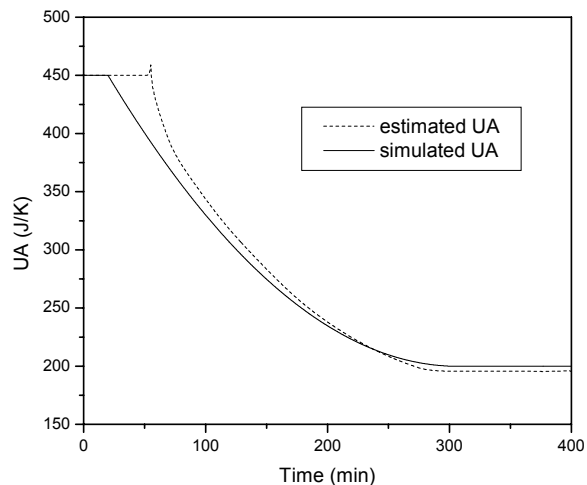
Figure 8: Estimated and Simulated Qr

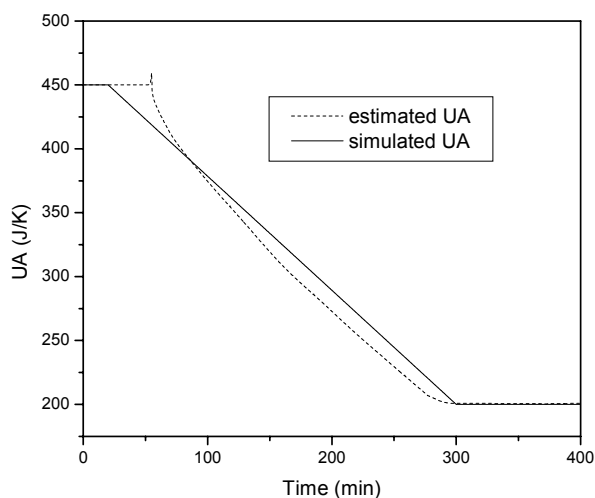**Figure 10:** Estimated and Simulated UA:
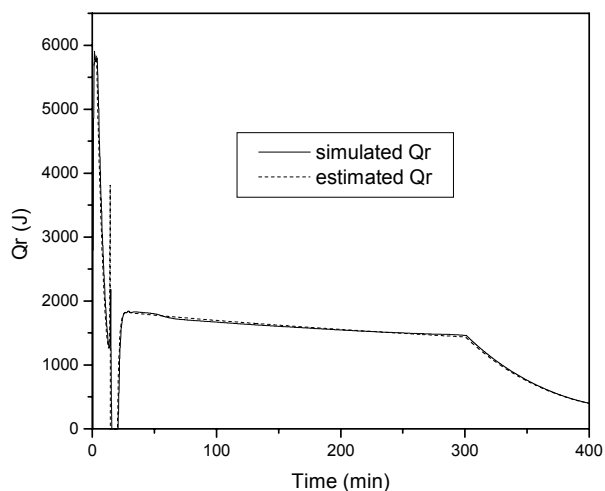Hyperbolic Profile

Figure 9: Estimated and Simulated UA

Figure 11: Estimated and Simulated Qr:
Hyperbolic Profile of UA

In order to simulate the re-nucleation we proposed a 25% increase in the value of Np at t=200 minutes. The results are shown in Figures 12 and 13.

Figure 12 and 13 show that the sudden increase in the estimated value of Qr is followed by a peak in the estimated value of UA. This is a natural response of the cascade calorimetry as both observers are expected to keep the residues as small as possible. After the occurrence of the peak, the estimated value of UA tends to follow the simulated value of UA. It is evident from the results shown in Figure 13 that the observer of Qr was able to overcome the

inaccuracies verified in the estimated value of UA after the end of the semicontinuous stage.

Flocculation is characterized by a sudden decrease in the heat generated by the reaction due to a decrease in the total number of particles. This phenomenon indicates that the surface area of the latex particles covered by emulsifier is below a critical value.

In order to simulate the effect of flocculation on the polymerization we proposed a 25% decrease in the value of Np at t=200 minutes. The results are shown in Figures 14 and 15.
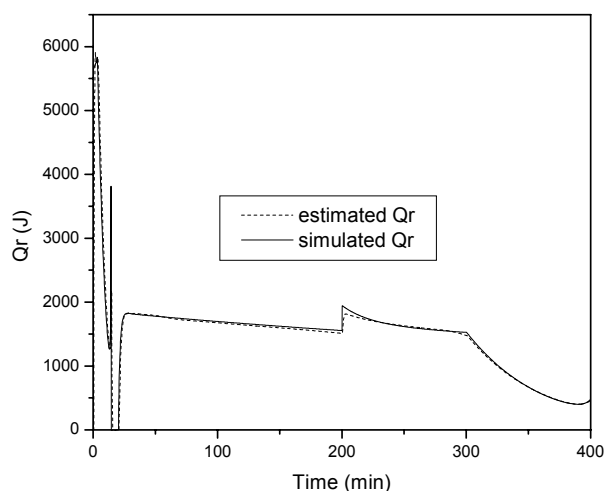
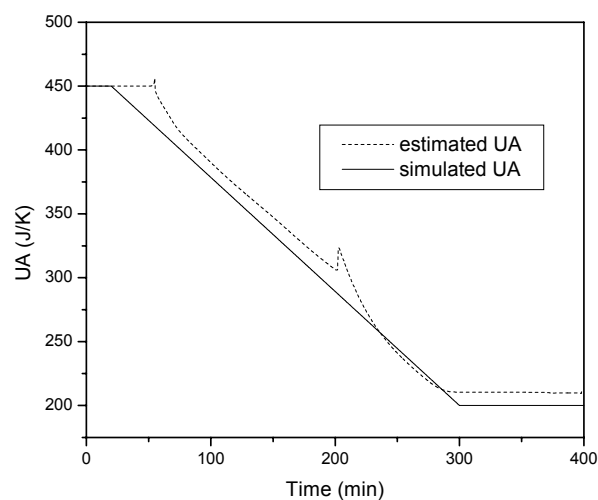**Figure 12**: Estimated and Simulated Qr under the Occurrence of Re-nucleation

Figure 13: Estimated and Simulated UA under the Occurrence of Re-nucleation
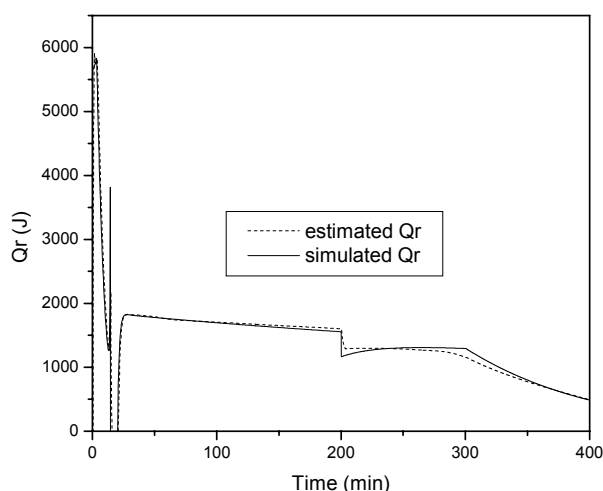

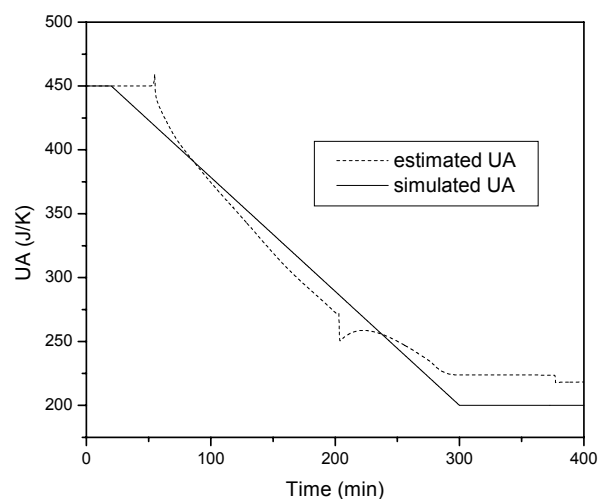**Figure 14:** Estimated and Simulated Qr under the Occurrence of Flocculation

Figure 15: Estimated and Simulated UA under the Occurrence of Flocculation

The cascade calorimetry provided accurate estimations in the occurence of flocculation. The major effect of the flocculation over the estimations is verified in the estimated value of UA, especially after end of the semicontinuous stage.

The parameter UA is indeed less sensitive to the measurements of reactor temperature than Qr. It means that the correction term is more effective in the estimations of Qr. This explains the results obtained after the occurrence of both disturbances.

CONCLUSIONS

On-line calorimetry is a powerful means of inferring information about the advancement of polimerizations. It is not complicated to implement once it relies only on heat balance equations and measurements of temperature and it provides reliable estimations of the heat generated by the reaction (Qr) as a change. However, it requires the continous update of the heat exchange coefficient which is a function of the viscosity of the reaction medium.

The coupled estimation of Qr and UA was described in this work. A cascade of non-linear state observers was used to carry out the estimations. The results obtained by simulation show that this approach can provide good estimations of Qr and UA. One major advantage of cascade calorimetry is its ability to accurately estimate the variables in the presence of external disturbances. It was shown that the observers tracked the occurance of re-nucleation and flocculation in the system.

The cascade calorimetry may be regarded as a non-optimal calibration procedure. Instead of dealing with the optimization of a set of calibration parameters, the cascade calorimetry relies on tuning parameter profiles and a correction term in a closed loop sense.

NOMENCLATURE

Cp_i heat capacity of substance "i", J/kg/K

$(-\Delta H_i)$ heat of reaction of substance "i", J/mol

F_i inflow rate of monomer "i", mol/s

$kpij$ reaction rate constant of radical "i" and monomer "j", L/mol/s

m_i mass of substance "i" in the reactor

M_i is the residual monomer "i" in the reactor

$[M_i]_p$ concentration of monomer "i" in the particles, mol/L

$\bar{n}$ average number of radicals per particle

Na Avogrado's number

Np total number of polymer particles

P_i probability that an active chain in the particle is of type "i"

$Qfeed$ sensible heat of the feed, J/s

Qj heat exchanged through the cooling jacket, J/s

$Qloss$ heat loss from the reactor to the surroundings, J/s

Qr heat generated by the polymerization, J/s

Rp_i rate of polymerization of the ith monomer in the mixture, mol/s/L

S_θ the unique solution of the algebric Lyapunov equation

$Tamb$ ambient temperature, K

$Tfeed$ temperature of the feed, K

Tj jacket temperature, K

Tr reactor temperature, K

UA overall heat transfer coefficient, J/K/s

x state vector

$\hat{x}$ estimated state vector

y measured output

Greek Letters

θ_{UA} tuning parameter of $\hat{U}A$

θ_{Qr} tuning parameter of $\hat{Q}r$

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