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An adaptive inferential measurement strategy for on-line monitoring of conversion in polymerization processes [1]

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Abstract

Much research effort has been devoted to the development of sensors capable of providing reliable on-line information about reaction advancement in polymerization processes. In particular, calorimetric techniques which have been widely investigated in the past, still present real difficulties in multipurpose applications. This article describes a new strategy for the accurate determination of conversion during batch polymerizations. In addition to the usual calorimetric data, infrequently-available gravimetric measurements are used to track variations of key parameters, such as the overall heat transfer coefficient. It is shown that accurate estimation 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. Batch and semi-batch experiments were performed in a 7-litre bench-scale well-mixed reactor to evaluate the technique. The method has been successfully applied both to solution polymerization system, i.e. vinyl acetate/butyl acrylate in ethyl acetate, and to emulsion copolymerization operations, i.e. styrene/butyl acrylate in water.

Keywords: Conversion; Emulsion polymerization; On-line Measurements; Reaction calorimetry; Software sensors

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Nomenclature

A	heat transfer area/m^2
k_1	overall polymerization kinetic constant/s^{-1}
Mw_i	molecular weight of monomer i/kg mol^{-1}
n_o	total number of moles of monomer in the reactor/mol
N_i	number of moles of unreacted monomer i in the reactor/mol
P_w	energy introduced by the electric immersion heater/W
$P_{1\text{-}4}$	varying parameters involved in the energy balance
Q_{acc}	accumulation power due to temperature changes in the reaction medium/W
Q_{feed}	heatflow power introduced by the feed/W
Q_j	heat power exchanged through the reactor wall (jacket)/W
Q_{loss}	overall heat losses to the surroundings/W
Q_{max}	total heat generated by the polymerization/J
Q_{polym}	instantaneous heat generation rate of polymerization/W
T_j	average temperature of the heat transfer fluid in the jacket/°C
T_r	reactor temperature/°C
U	overall heat transfer coefficient/W $m^{-2}K^{-1}$
X	overall monomer conversion
$X_g(t_g(i))$	gravimetric measurement of conversion obtained from the ith sample withdrawn at time $t_g(i)$

Greek letters

ΔH_p	molar heat of polymerization/J mol^{-1}
ΔT_j	difference in temperature between the reactor contents and the external jacket/°C
ΔT_o	temperature dependent offset/°C
ε	RLS prediction error/W
ψ	RLS observation vector
θ	RLS parameter vector
λ_1, λ_2	forgetting factors

1. Introduction

For the purposes of temperature and product quality control, safety, and overall economic operation, it is necessary to monitor polymerization conversion. Obviously, these goals are difficult, if not impossible, to achieve without efficient and reliable on-line measurement techniques. In the last twenty years, very accurate off-line techniques for the characterization of polymer quality have been developed. For example, molecular weight distributions (MWD) can be determined by gel-permeation chromatography (GPC), and NMR techniques are used to calculate the composition distribution of copolymers. However, the development and use of on-line sensors, which are required for any feedback control of polymerization processes, have remained rather static. For this reason, there are still relatively few on-line sensors available, especially for emulsion polymerization systems, where the presence of more than one phase leads to serious complications. Currently, most major difficulties in on-line sensor technology arise from the complex nature of these chemical systems, and sensor development requires a pluridisciplinary effort.

Few reliable and flexible approaches for the measurement of monomer conversion appear to be available in the open literature [1]. Thus, the design of new tools for such measurements remains an active field of research. The main possible techniques are briefly reviewed below.

Densimetric measurements of conversion are based upon the difference between the densities of the monomers and the polymer [2]. Successful applications of this technique have been reported in the case of solution polymerization [3–5]. However, many difficulties arise in the case of emulsion polymerizations. The use of an external sampling loop is likely to lead to the plugging of the circuit, and significant disturbances are often encountered due to monomer droplets in the mixture and possible thermal instabilities [6].

The measurement of ultrasound propagation velocity is a promising approach for conversion monitoring [7] as sound velocity in homogeneous media is a function of the state of the polymerization. This method could be faster and more sensitive than densimetry. Moreover, the probe can be directly plugged into the reactor without the need for a sampling system. However, the technique requires careful calibration and operating procedures, which, to the best of our knowledge, still have to be assessed.

State estimation and filtering techniques such as Extended Kalman Filters (EKF) may be envisaged to reconstruct key-state variables which cannot be measured, e.g individual and overall conversion, MWD, copolymer composition, etc. [8–11]. Such "software-sensing" strategies require mathematical models relating the main kinetic and thermodynamic aspects of emulsion polymerizations.

In such a context, on-line calorimetry based measurement of the heat release by the polymerization has probably been the most widely investigated method. Refs [12]–[15] are significant examples in the field of polymer manufacturing. Nevertheless, in the context of multi-purpose use, very few applications of calorimetry as a tool for monitoring the reaction progress and evolution of macromolecular properties during copolymerizations have been reported in the literature. Recently, some authors (see for example, Refs. [11] and [13]) have pointed out difficulties inherent in the evaluation of some of the unsteady-state terms in the energy balance. Problems associated with this approach also include the propagation of errors due to noise in the calorimetric measurements, i.e. temperature and flow-rate, and possible unpredictable variations of parameters involved in the energy balance of the reactor. In particular, the heat transfer coefficient through the reactor wall is subject to significant time variations due to conversion-dependent increase in the viscosity of the reaction medium. For flexible and robust calorimetric measurements of conversion, these variations should obviously be estimated. Even though it is relatively easy to correct calorimetric estimates off-line in order to account for batch-to-batch variations or constantly changing parameter values, it is more difficult to correct these same terms on-line without any corroborating measurements. Also, the presence of more than one monomer complicates the measurements procedure, since independent conversions must be defined for each monomer and since the overall conversion must be defined and estimated with respect to the units used (in terms of mass, moles and energy). In fact, the number of on-line sensors required to completely determine the conversion of each species is equal to the number of monomers [16].

The present article describes a combined methodology involving scarce measurements, parameter estimation techniques and on-line calorimetry, for the joint estimation of conversion and of the overall heat transfer coefficient variations during batch emulsion homopolymerizations and copolymerizations at azeotropic composition. A general dynamic state-space formulation of the energy balance of the polymerization reactor is proposed, where the state variables are the reactor temperature, the instantaneous heat of polymerization $Q_{\text{polym}}(t)$, and the overall monomer conversion. A simple Luenberger state-observer, derived from the state-space model, is successfully applied to the estimation of conversion during batch and semi-batch solution polymerizations, and during the batch emulsion copolymerizations of butyl acrylate and styrene.

The estimation of $Q_{\text{polym}}(t)$ is obtained by using a recursive least squares (RLS) identification algorithm in order to deal with both the noise in the calorimetric measurements and with uncertainties in the polymerization kinetics. Moreover, in order to account for both time and batch-to-batch variations in the overall heat transfer coefficient, the estimation strategy is made adaptive through the use of infrequent, but reliable, off-line gravimetric measurements of conversion. The consideration of such additional measurements allows improvements in the conversion estimates to be made, even in the case of a significant decrease in the heat transfer capacity related to the conversion-dependent viscosity of the polymerization medium.

2. Experimental setup

Fig. 1 shows a schematic representation of the microcomputer-controlled bench-scale polymerization reactor. The polymerization calorimeter (1), which is assumed to be perfectly mixed, is a 7-litre jacketted glass reactor. A helical coil has been installed in the reactor jacket (2) to improve the heat transfer capacity. The stainless steel reactor lid (3) is also jacketted to limit heat losses. A Mixell TT-axial flow profiled propeller (4) is employed at low speed (200 rpm). The temperature in the reactor is controlled by manipulating the setpoint temperature of a 2-kW heating bath (5) containing water. Cold water circulating in coils is used for cooling the bath. A centrifugal pump is employed for circulating hog fluid in the reactor jacket. The condenser (6) can be used to cool water or monomer vapours, and to maintain atmospheric pressure in the reactor. The gear pump (9) circulates a part of the reaction medium (flow rate, 40 ml min^{-1}) through a continuous Yokogawa (model DM8) densimeter. In the case of semi-batch processes, monomers are mixed in the desired ratio, stored in a tank and then fed to the reactor using a solenoid valve (7). The mass of inlet monomers is controlled through the measurements of a Mettler electronic balance (8). A regulated power supply (13) which controls a user-specified electric input power into the immersion heater (12) is used to calibrate the parameters included in the energy

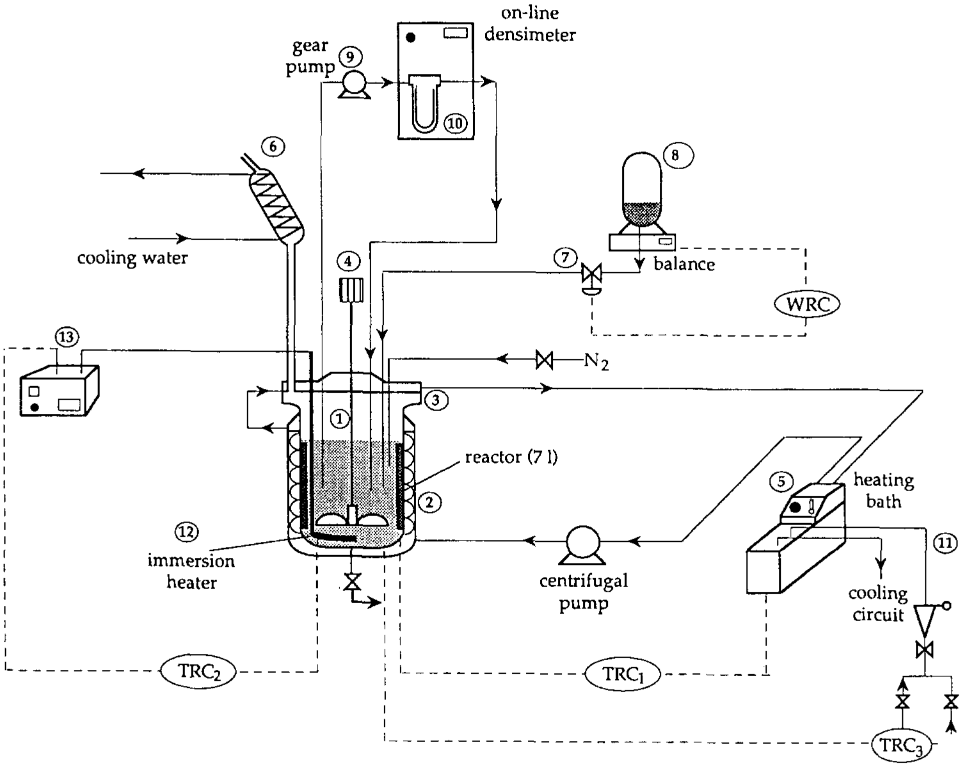

Fig. 1. Scheme of the bench-scale polymerization calorimeter.

balance. Automatic control policy introduced beforehand by the user is conducted by means of a personal computer.

As discussed below, off-line gravimetric data can be used on-line to make corrections in the energy balance parameter values estimated *a priori*. As shown in Figs. 2 and 3, rapid estimates of conversion from such gravimetric data are obtained using an infrared balance manufactured by Mettler. The accuracy of the measured conversion is approximately ± 1%. In order to reduce the duration of the off-line gravimetric measurements, optimal operating conditions have been assessed. It was found that with an oven temperature of 130°C, a gravimetric data point can be obtained every 8–10 min, depending on the solid content and the mass of sample. As soon as it is known, the gravimetric measurement of conversion is used for the on-line optimization of time-varying and conversion-dependent parameters involved in the energy balance. The optimization procedure takes about 15 min. The obtained parameters, which will be explained in more detail below, are then used every sampling period ($T = 20$ s) for the estimation of both the differential heat of polymerization and the overall monomer conversion.

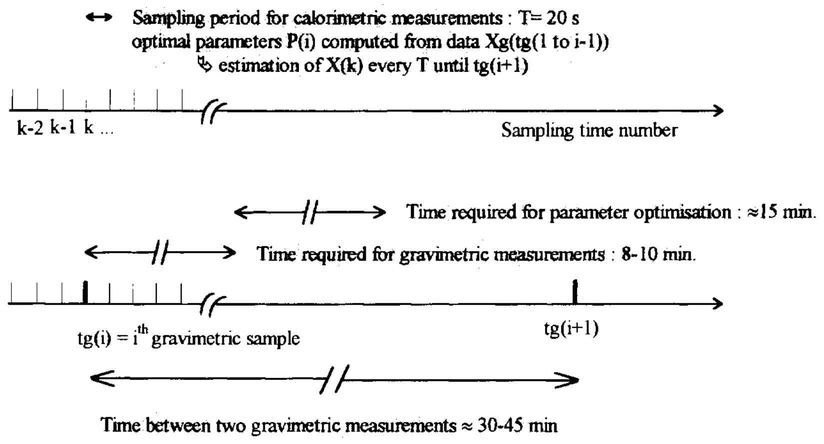

Fig. 2. Time diagram of the combined measurement strategy.

3. Adaptive identification of conversion

3.1. Estimation of the differential heat of polymerization

The entire algorithm for the estimation of conversion is represented in the block-diagram in Fig. 3. The procedure for the estimation of the differential heat of polymerization and, thus of the overall conversion $X(t)$, corresponds to block ① in Fig. 3. Taking into account the differential heat of polymerization, an enthalpy balance around the stirred tank reactor leads to the following equation

$$\begin{aligned} Q_{\mathrm{acc}}(t) &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i=\mathrm{r,m,w}} (m_i C_{p_i}(T_i(t) - T_{\mathrm{ref}})\right) \\ &= Q_j(t) - Q_{\mathrm{loss}}(t) - Q_{\mathrm{polym}}(t) + Q_{\mathrm{feed}}(t) + P_{\mathrm{w}} \qquad (1) \end{aligned}$$

For the sake of simplicity, the heat generated by dissipation of the mechanical energy of the stirring system is neglected in Eq. (1). However, as shown below, corrective heat terms may be introduced to account for remaining uncertainties in the energy balance. Q_{acc} represents the sensible heat associated with variation in temperature of the latex and the reactor. Index r refers to the reaction medium, index m to metal inserts and index w to the reactor wall. P_{w} is the energy introduced by the resistance heating coil. Heat losses by natural convection around the reactor wall and by natural evaporative mass transfer in the condenser are taken into account through the term $Q_{\mathrm{loss}}(t)$. $Q_{\mathrm{polym}}(t)$ corresponds to the differential heat of polymerization ($Q_{\mathrm{polym}} < 0$), and $Q_{\mathrm{feed}}(t)$ represents the sensible heat of the reactor feed. $Q_j(t)$ is the energy exchanged through the jacket wall. Assuming quasi-steady-state transfer, this instantaneous power may be

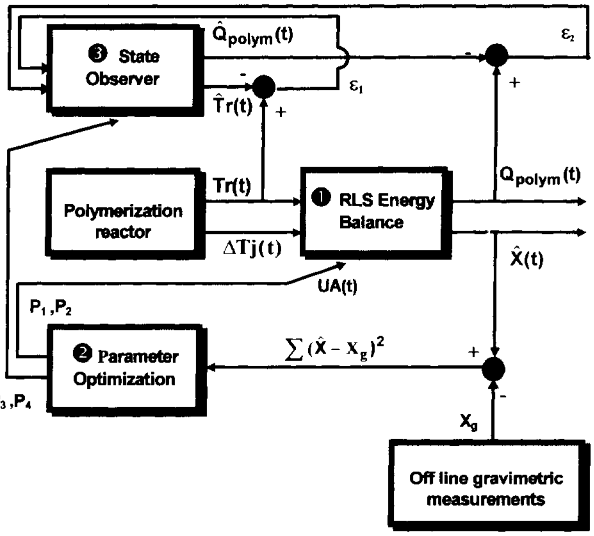

Fig. 3. Block diagram of the algorithm for the adaptive inferential estimation of conversion during polymerization processes.

assessed as follows, where ΔT_0 accounts for possible drifts in the measurements of temperature

$$Q_j(t) = U(t)A(t)(\Delta T_j(t) - \Delta T_0) \tag{2}$$

with $\Delta T_j(t) = T_j(t) - T_r(t)$; ΔT_0 is a temperature-dependent offset parameter, and $A(t)$ is the heat transfer surface or wetted area.

In a batch process, $A(t)$ is approximately constant. $U(t)$ is the overall heat transfer coefficient between the reactor contents and the external jacket, and T_j is the average temperature of the heat transfer fluid in the jacket.

As the heat losses and the correction factor ΔT_0 are temperature-dependent, calibration relationships $Q_{loss}(T_r)$ and $\Delta T_0(T_r)$ should be introduced. These relationships can be estimated through steady-state experiments, as described in Ref. [17]. For a given set of constant known inputs P_w, including $P_w = 0$, the parameters of the following equations are sought

$$\begin{aligned} \Delta T_0(T_r) &= \Delta T_{0,m} + a(T_r - T_{ref1}) \\ Q_{loss} &= b(T_r - T_{ref2}) \end{aligned} \tag{3}$$

T_{ref1}, T_{ref2} and $\Delta T_{0,m}$ are set to 60°C, 25°C and -0.04°C, respectively. The other two parameters, i.e. a and b, were estimated by using the MATLAB® optimization Toolbox

$$\Delta T_{0,m} = -0.04°\mathrm{C}; \quad a = 0.00813; \quad b = 0.086\ \mathrm{W\ K^{-1}}$$

It therefore turns out that, due to the jacketted reactor top cover, the overall heat losses do not exceed 3 W when the reactor heel is water at 60°C.

As defined in the energy balance in Eq. (1), $Q_{\mathrm{polym}}(t)$ is obtained from the heat balance terms. When $Q_{\mathrm{polym}}(t)$ is computed in the mathematical context of state-space models, different authors (see for example, Ref. [13]) propose the following equation, which is the simplest model, and which assumes that the differential heat of polymerization behaves as a constant state-variable

$$\dot{Q}_{\mathrm{polym}}(t) = 0 \tag{4}$$

Even though this assumption appears to be an obvious contradiction, it is generally expected that any state-observer should be in a position to track eventual time variations of $Q_{\mathrm{polym}}(t)$. As a trade-off between such a rough approximation and detailed, complex knowledge-based models, it might be efficient to relate $Q_{\mathrm{polym}}(t)$ as the heat of a fictitious first-order exothermic reaction, in the case of homopolymerization

$$Q_{\mathrm{p}_1}(t) = k_1(t) n_0 \Delta H_{\mathrm{p}} [1 - X(t)] \tag{5}$$

where n_0 is the total number of moles of monomer in the reactor, X is the overall monomer conversion, ΔH_{p} is the total heat of polymerization and $k_1(t)$ is an overall equivalent time-varying kinetic constant. In the case of batch copolymerization at azeotropic composition, no compositional drift is observed and the previous equation remains valid. For batch copolymerization, $Q_{\mathrm{polym}}(t)$ could still be related as a fictitious equivalent first-order exothermic reaction and the equivalent time-varying kinetic constant $k_1(t)$ includes the molar fraction: $f_1(t) = N_1(t)/(N_1(t) + N_2(t))$, where $N_1(t)$ represents the number of remaining moles of monomer 1, and $N_2(t)$ the number of moles of monomer 2.

For the identification procedure, $Q_{\mathrm{polym}}(t)$ can be viewed as a "measured" output. Moreover, Eq. (5) may provide a suitable model for the prediction of the differential heat of polymerization $\hat{Q}_{\mathrm{polym}}(t)$. Therefore, by using a standard recursive least squares (RLS) algorithm, one can minimize a so-called prediction error $\varepsilon(t)$ as follows

$$\hat{Q}_{\mathrm{polym}}(t+1) = \theta^T(t)\psi(t) \tag{6a}$$

with

$$\theta(t) = k_1(t); \psi(t) = n_0 \Delta H_{\mathrm{p}}(1 - X(t)) \tag{6b}$$

$$\varepsilon(t+1) = \frac{Q_{\mathrm{polym}}(t+1) - \hat{\theta}^T(t)\psi(t)}{\dfrac{\lambda_1(t)}{\lambda_2(t)} + \psi^T(t)F(t)\psi(t)} \tag{6c}$$

$$F(t+1) = \frac{1}{\lambda_1(t)}\left[F(t) - \frac{F(t)\psi(t)\psi^T(t)F(t)}{\dfrac{\lambda_1(t)}{\lambda_2(t)} + \psi^T(t)F(t)\psi(t)}\right] \tag{6d}$$

$$\hat{\theta}(t+1) = \hat{\theta}(t) + F(t)\psi(t)\varepsilon(t+1) \tag{6e}$$

Note that $\wedge$ refers to a predicted variable, and λ_1 and λ_2 are forgetting factors. For further details about this identification technique, the reader is referred to Ref. [18]

By doing this one can obtain both an "optimal" estimate of $Q_{\mathrm{polym}}(t)$, in a least squares sense, and an overall equivalent time-varying kinetic constant $k_1(t)$, which could be useful for the design of any further model-based control law. The sampling period for the RLS algorithm is $T = 20$ s (see Fig. 2). Also, for polymerization systems, the monomer conversion is given by the following Eq. (7) which can easily be solved on-line by using a simple integration rule

$$\hat{x}(t) = \frac{\int_0^t \hat{Q}_{\mathrm{polym}}(t)\,\mathrm{d}t}{Q_{\mathrm{max}}} \tag{7}$$

Q_{max} is a linear combination of the quantity of each monomer polymerized multiplied by the heat of reaction of each substance (ΔH_{pi})

$$Q_{\mathrm{max}} = \sum_i x_i N_i^{\mathrm{tot}}(-\Delta H_{\mathrm{pi}}) \tag{8}$$

N_i^{tot} is the total number of moles of monomer i fed to the reactor up to time t and x_i the conversion of monomer i at the end of the reaction.

In the case of copolymerization, the overall conversion should not be confused with that of a homopolymerization. As previously mentioned, the overall conversion in multi-component systems must be defined with respect to the units used. This variable can be defined in terms of mass, moles or energy (Eq. (7)) [16]

$$X_{\mathrm{ov}} = \frac{\sum_i N_i^{\mathrm{tot}} - \sum_i N_i}{\sum_i N_i^{\mathrm{tot}}} \qquad \text{(molar)}$$

$$X_{\mathrm{ov}}^{\mathrm{mass}} = \frac{\sum_i Mw_i N_i^{\mathrm{tot}} - \sum_i Mw_i N_i}{\sum_i Mw_i N_i^{\mathrm{tot}}} \qquad \text{(mass)}$$

where Mw_i is the molecular weight of monomer i.

At azeotropic composition, $X_{\mathrm{ov}} = X_{\mathrm{ov}}^{\mathrm{mass}}$ with respect to the uniform composition of the copolymer. Moreover, in the particular case of styrene/butyl acrylate copolymerization, molar and mass overall conversions were calculated for different compositions. The difference between these two variables is lower than 1.5%

3.2. *Use of off-line gravimetric data for parameter estimation*

During a polymerization operation, the overall heat transfer coefficient and heat losses also depend on the reactor contents. The viscosity evolves constantly over the course of the reaction. Therefore, a constrained relationship giving $U(t)$ as a function of the overall conversion $X(t)$ has been selected to provide a good compromise between complexity and accuracy of the energy balance adjustment for both solution and emulsion polymerization systems

$$U(X(t)) = U_{\text{init}} + P_1 X(t-1) + P_2 X^2(t-1) \tag{9}$$

assuming the constraint

$$U(x(t)) \leq U_{\text{init}} \tag{10}$$

$X(t-1)$ is the estimated overall monomer conversion at the sampling time number $t-1$. P_1 and P_2 are parameters to be optimized.

In order to improve the formulation of energy balances during polymerization operations, one can use both state observation technique and separate estimation of $UA(t)$ profiles. As corroborating measurements, off-line gravimetric data may be used to correct parameter values of the energy balance, which are referred to as *a priori* below. The basic schematic of such an optimization procedure is shown in Fig. 3. Between two gravimetric data, the available profile $UA(X(t))$ is used to calculate on-line an *a priori* estimate of the differential heat of polymerization $\hat{Q}_{\text{polym}}(t)$. Once new off-line gravimetric information becomes available, i.e. every 30–45 min, an improved *a posteriori* trajectory is computed for $UA(t)$, $\hat{Q}_{\text{polym}}(t)$ and $X(t)$.

Besides uncertainties in the time variations of the product UA, undesirable measurement drifts which are difficult to avoid with most available calorimetric equipment may arise [19–21]. To cope with such unpredictable variations, one can simply introduce a corrective heat term in the thermal balance Eq. (1). This has been successfully done as follows

$$Q_{\text{corrective}}(t) = P_3 + P_4 X(t-1) \tag{11}$$

As before with Eq. (9), P_3 and P_4 are parameters to be optimized.

Before time $t_g(n)$ i.e. before the nth gravimetric data become available, Eqs. (1), (9) and (10) are solved by using the optimal estimated parameters P_1–P_4 obtained from the previous data say data

$$X_g(t_g(1)) \text{ to } X_g(t_g(n-1)) \tag{12}$$

where $X_g(t_g(i))$ is measured gravimetrically off-line from the ith sample withdrawn at time $t_g(i)$ (see Fig. 2).

Optimal $U\hat{A}$ profiles may be computed between two consecutive off-line gravimetric measurements. Therefore, by using MATLAB® Optimization Toolbox [22], the following parameter vector is searched

$$\begin{bmatrix} P_1(t) \\ P_2(t) \\ P_3(t) \\ P_4(t) \end{bmatrix} = \text{Arg}\left[\text{Min}\left(\sum_{k=1}^{n_g}\right)[X_g(t_g(k)) - \hat{X}(t_g(k))]^2)\right] \tag{13}$$

where n_g is the number of gravimetric data available at time t.

The use of the four parameters P_1–P_4, which are the outputs of block ②, is represented in Fig. 3. Parameters P_1 and P_2 are used in the computation of UA profiles, which are inputs of block ①. Parameters P_3 and P_4 are used as corrective parameters in the state observer represented by block ③ in Fig. 3. This part of the algorithm is explained below.

3.3. A state-space representation of the batch polymerization process

In order to obtain a differential formulation of Eq. (5), a rather straightforward assumption is to describe $Q_{\mathrm{polym}}(t)$ as the output of a first-order continuous dynamic model using the following Eq. (14), where the time constant τ_{p} can be used as a tuning parameter for the whole state-estimation process

$$\tau_{\mathrm{p}} \frac{\mathrm{d}Q_{\mathrm{polym}}}{\mathrm{d}t}(t) + Q_{\mathrm{polym}}(t) = Q_{\mathrm{p}_1}(t) \tag{14}$$

By doing so, one can obtain the following third-order state-space representation from Eqs. (1), (2), (5), (7), (8) and (11)

$$\begin{bmatrix} \dot{T}_{\mathrm{r}}(t) \\ \dot{Q}_{\mathrm{polym}}(t) \\ \dot{X}(t) \end{bmatrix} = \begin{bmatrix} -\dfrac{UA(t)}{\sum\limits_i m_i C_{p_i}} & \dfrac{1}{\sum\limits_i m_i C_{p_i}} & -\dfrac{P_4}{\sum\limits_i m_i C_{p_i}} \\ 0 & -\dfrac{1}{\tau_{\mathrm{p}}} & -\dfrac{k_1(t) n_0 \Delta H_{\mathrm{p}}}{\tau_{\mathrm{p}}} \\ 0 & -\dfrac{1}{n_0 \Delta H_{\mathrm{p}}} & 0 \end{bmatrix} \begin{bmatrix} T_{\mathrm{r}}(t) \\ Q_{\mathrm{polym}}(t) \\ X(t) \end{bmatrix}$$

$$+ \begin{bmatrix} \dfrac{UA(t)(T_{\mathrm{j}}(t) - T_{\mathrm{r}}(t) - \Delta T_0) - P_3}{\sum\limits_i m_i C_{p_i}} \\ \dfrac{k_1(t) n_0 \Delta H_{\mathrm{p}}}{\tau_{\mathrm{p}}} \\ 0 \end{bmatrix} \tag{15}$$

Now, the state variables in this representation can be estimated using state observation techniques. In practice, it is worth noting that "filtering" $X(t)$ appears to be a useless exercise since the optimal solution of Eq. (13) applied to Eq. (7) provides a very smooth and accurate conversion profile. Consequently, a partial state-observer is used for the reconstruction and filtering of the output vector $[T_{\mathrm{r}}(t), Q_{\mathrm{polym}}(t)]$. For this purpose, a basic Luenberger estimator was found to be as efficient as any Kalman Filter. For recursive computation, the continuous representation (15) has been discretized by using the method of the exponential matrix, assuming a zero-order hold on the inputs. Thus, the following discrete-time equation, Eq. (16), is obtained, where an underbar denotes a vector and the exponent T, a transposed vector

$$\underline{x}(t+1) = A_{\mathrm{D}}\underline{x}(t) + B_{\mathrm{D}}\underline{u}(t) \tag{16}$$

with $\underline{x}^{\mathrm{T}}(t) = [T_{\mathrm{r}}(t)\, Q_{\mathrm{polym}}(t)]$ and $\underline{u}^{\mathrm{T}}(t) = [1 \quad 1]$

The structure of the Luenberger partial state estimator, referred to as block ③ in Fig. 3, is

$$\hat{\underline{x}}(t+1) = A_{\mathrm{D}}\hat{\underline{x}}(t) + B_{\mathrm{D}}\underline{u}(t) + K_1(\underline{y}(t) - C\hat{\underline{x}}(t)) \tag{17}$$

with $K_1 = \begin{bmatrix} K_{11} K_{12} \\ K_{21} K_{22} \end{bmatrix}$; $\underline{y}(t) = \begin{bmatrix} T_{\mathrm{r}}(t) & \text{(measured)} \\ Q_{\mathrm{polym}}(t) & \text{(from RLS)} \end{bmatrix}$ and $C = \begin{bmatrix} 1\,0 \\ 0\,1 \end{bmatrix}$.

4. Experimental results

4.1. Solution polymerization experiments

The solution homopolymerization of butyl acrylate (BuA), and the copolymerization of butyl acrylate and vinyl acetate (VAc) were carried out in ethyl acetate (EAc) solvent, using benzoyl peroxide (BPO) as the sole free radical initiator. The monomers and solvent were obtained from Janssen Chimica (France) and used without further purification. The feed policies of the two different types of experiments are given in Table 1. Run 1 was a batch reaction and Run 2 a semi-batch reaction with addition of

Table 1
Feed policies for the solution and emulsion polymerization experiments

Run number	Reactor heel/g	Addition policy
1	749 gBuA 3000 g EAc 5.0 g BPO	Batch reaction in solution No additional feeds
2	373 g VAc 77 g BuA 3000 g EAc 5.15 g BPO	300 g BuA added continuously over 3 h period. Reaction in solution
3	598.24 g Sty 3000 g Water 4.29 g KPS 4.31 g SDS	Batch reaction. No additional feeds
4	514.82 g Sty 234.85 g BuA 3000 g Water 4.33 g KPS 4.31 g SDS	Batch reaction. No additional feeds

the most reactive monomer, i.e. butyl acrylate. Samples were occasionally withdrawn from the reactor, the times and quantities of which were noted for use in calculating conversions and closing the mass balance equations. The reaction took place in the stirred reactor, and water was circulated through the jacket to maintain the reactor and its contents at 70°C. Measurements (reactor temperature, jacket temperature and eventually densities) were taken every 10 s and stored on a personal computer.

As stated above, the time variations of the overall heat transfer coefficient $U(t)$ were estimated through the use of gravimetric measurements and calorimetric estimates. These estimations were found to be consistent with the initial and final values of $U(t)$, which can be accurately determined by heat flow calorimetry before and after each experiment, by manipulating the internal electrical resistance.

The measured and predicted reactor temperature $T_r(t)$ in the case of a batch solution polymerization of BuA (run 1) are shown in Fig. 4a. The RLS estimates of the differential heat of polymerization (dashed line) are given in Fig. 4b. The corresponding Luenberger-predicted trajectory is also given in the same figure (full bold line). Both results agree quite well, and the high exothermicity of the polymerization is clearly shown by these curves which are similar to the impulse response of a first-order system.

Fig. 5a shows the behaviour of the prediction error $\varepsilon(t)$ related to the estimation of $Q_{\text{polym}}(t)$. This variable shows the transient behaviour of the RLS identification used for the prediction of the differential heat of polymerization. After about 15 min, the prediction error $\varepsilon(t)$ (see Eq. (6c)) remains unbiased and close to zero. Fig. 5b displays the estimate of the equivalent time-varying kinetic constant $k_1(t)$ for run 1. The results clearly show that it is not quite realistic to assume a "true" first-order kinetic model for

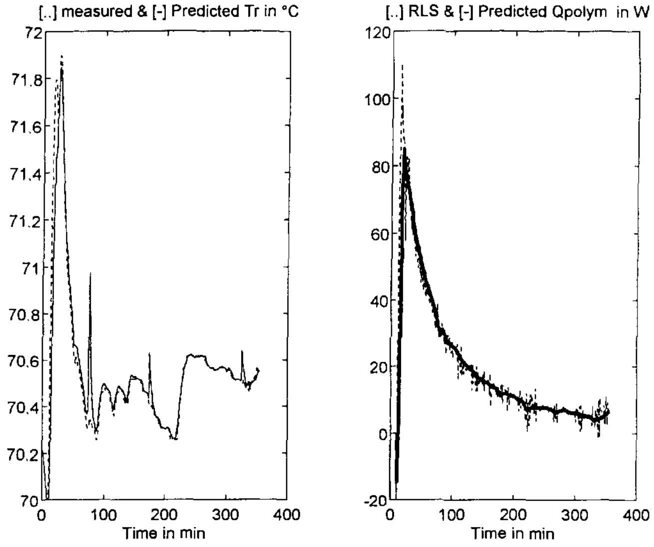

Fig. 4. a. Measured and Luenberger-predicted reaction temperatures. b. RLS and state estimate of the instantaneous power $Q_{\text{polym}}(t)$.

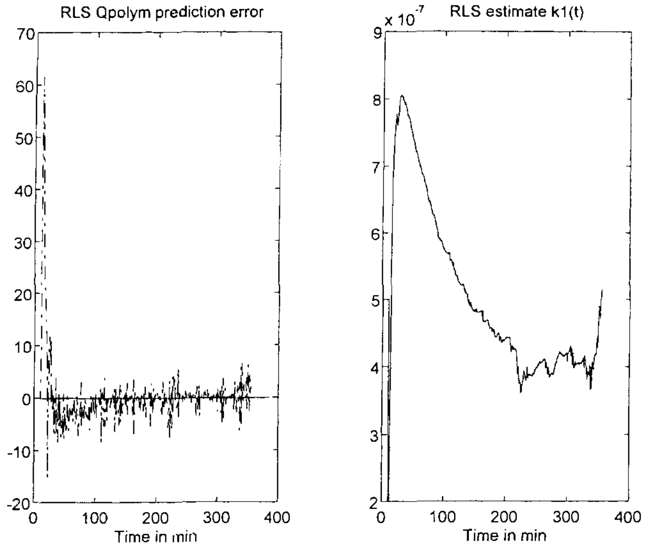

Fig. 5. a. Time variations of RLS prediction error. Run 1. b. Estimation of the "equivalent" kinetic parameter $k_l(t)$. Run 1.

the polymerization reaction. Despite only very slight temperature oscillations, the values of $k_1(t)$ evolve between about 8×10^{-7} and 4×10^{-7}. This is to be expected because $k_1(t)$ contains both the time-varying concentration of initiator as well as a termination rate constant which, at the end of the reaction, can decrease as a function of conversion, i.e. the well-known "gel effect", in certain cases. In fact, the traditional equation of the rate of polymerization is more complex. However, the approximate model of Eq. (5) seems to be efficient in relating the differential heat of polymerization and solving the energy balance of the homopolymerization.

Fig. 6a displays the estimated course of the overall heat transfer number UA for run 1. It appears that due to conversion-dependent changes in the physical properties of the polymerizing solution, no significant variations in the reactor-side heat transfer coefficient occur before 150 min, i.e. before a conversion of about 70%. Afterwards, a steep decrease in this coefficient is noted due to a sharp increase in the viscosity. A significant step may be observed in the same figure, and is due to a large sample withdrawn at that time.

The final optimal profile of the conversion during run 1 is given in Fig. 6b. As the computation is based upon the entire set of gravimetric data, this trajectory represents the best fit that can be obtained at the end of the batch homopolymerization operation. Such smooth and consistent results are really encouraging.

Similar "software measurements" were obtained in the case of the semi-batch solution copolymerization referred to as run 2 in Table 1. The estimated differential heat of polymerization $Q_{\text{polym}}(t)$ and the corresponding conversion trajectory are

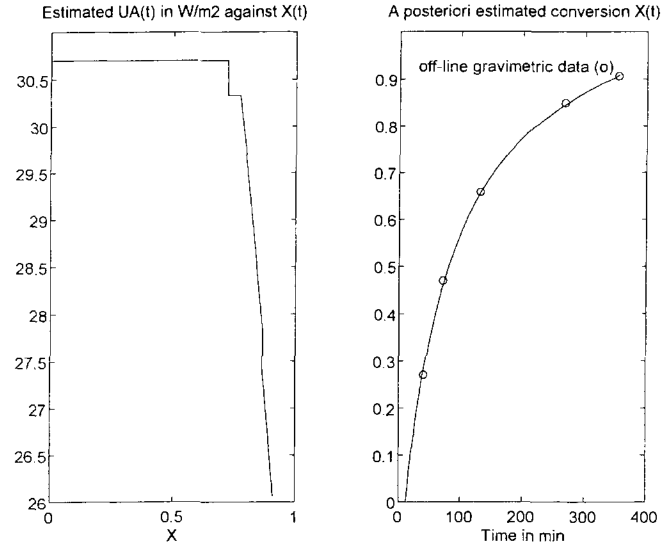

Fig. 6. a. Optimal *UA* profile. Run 1. b. Optimal *a posteriori* reconstruction of the course of $X(t)$. Run 1.

shown in Figs. 7a and 7b, respectively. The variations in the feed rate were designed to generate a constant instantaneous power during the feeding period, 180 min, followed by a decrease in the reaction rate as the polymerization finishes.

4.2. Emulsion polymerization experiments

It was initially envisaged that the continuous densimeter shown in Fig. 1 would be used in conjunction with calorimetric measurement for the monitoring of the overall and individual monomer conversion. Several identical batch homopolymerizations of styrene (Sty), and batch emulsion copolymerizations of styrene and butyl acrylate (BuA) were carried out at 60°C using potassium persulphate (KPS) as initiator and sodium dodecyl sulphate (SDS) as emulsifier. However, despite care in the assembly and operation of the external sampling loop, plugging of the pump and of the tubes took place very frequently. In addition to particle flocculation, these problems considerably impair the reliability of the density measurements. Therefore, only an adaptive calorimetric soft-sensing approach appeared to remain attractive in the field of emulsion polymerizations.

The two protocols for runs 3 and 4 are given in Table 1. Samples were withdrawn from the reactor for gravimetric, PSD (particle size distribution), MWD (molecular weight distribution), T_g (glass transition temperature) and GC (gas chromatography) measurements.

The estimated differential heat profile $Q_{\text{polym}}(t)$ for run 4 and the corresponding final overall conversion profile are displayed in Fig. 8a and 8b. This curve represents the best

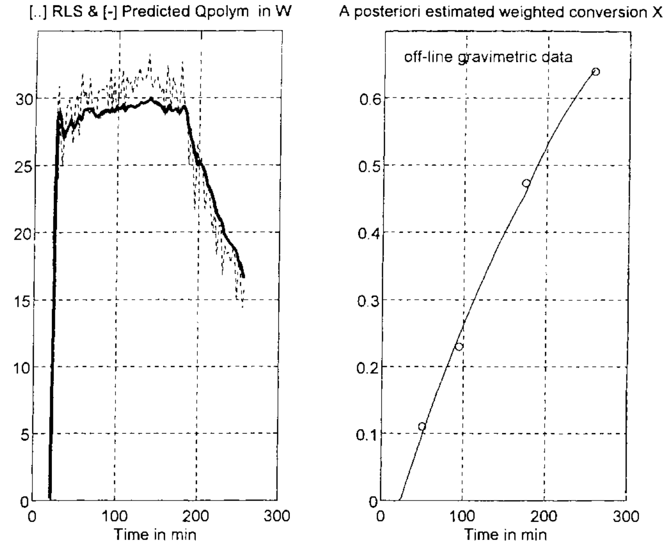

Fig. 7. a. On-line RLS estimation of $Q_{\mathrm{polym}}(t)$. Run 2. b. Estimate of $X(t)$ for semi-batch 2.

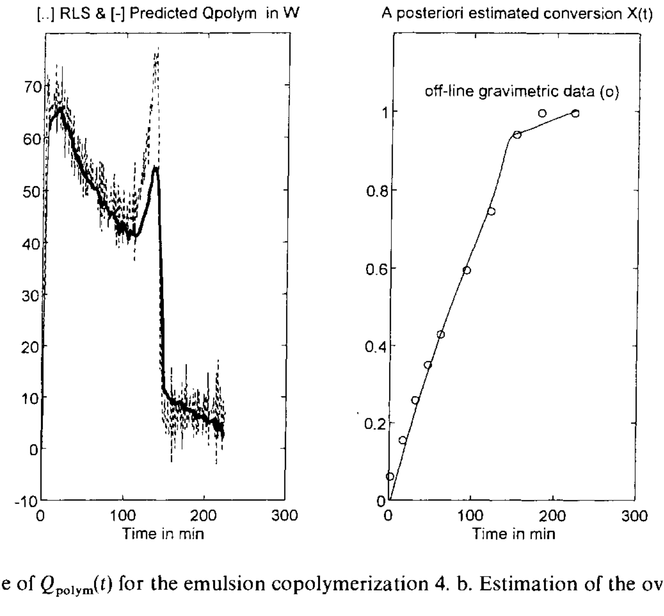

Fig. 8a. Estimate of $Q_{\mathrm{polym}}(t)$ for the emulsion copolymerization 4. b. Estimation of the overall conversion. Run 4.

fit, and is obtained at the end of the batch copolymerization. Examination of the particular experimental estimated values $Q_{\mathrm{polym}}(t)$, and of the reactor temperature reveals some acceleration of the polymerization rate at the end of the reaction. This is due to some significant gel-effect. Consequently, a slight drift of the overall estimated conversion is observed. Nevertheless, as one can see in Fig. 8b, the accuracy of the estimated conversion, even in the "worst-case" scenario appears to be better than $\pm 2.5\%$.

The evolution of the overall heat transfer coefficient was also estimated during these operations. The behaviour of this process parameter was found to be similar to that shown in Fig. 6a, but, in contrast to the case of solution polymerization, the increase in viscosity with emulsion systems remained moderate. In fact, it is likely that reductions in the internal heat transfer coefficient arise essentially from polymer deposits on the reactor wall.

The overall estimation policy was also applied to a batch emulsion homopolymerization of styrene (Run 3). Fig. 9 displays the trajectory which was computed at the end of the reaction. Despite slight differences between the measured and estimated conversions, these results are satisfactory.

Actually, a major question was to evaluate the behaviour of the adaptive estimator between two infrequent gravimetric samples, when the model parameters, UA especially, are strong functions of time. To a certain extent, this is addressed in Fig. 10a, where both the *a posteriori* optimal estimate, denoted $\hat{X}_2(t)$ obtained from gravimetric data Nos. 1–5, and the *a priori* estimate $\hat{X}_1(t)$ obtained from gravimetric data Nos. 1–4 during run 1 are displayed. As shown in Fig. 10b, the *a posteriori* prediction error

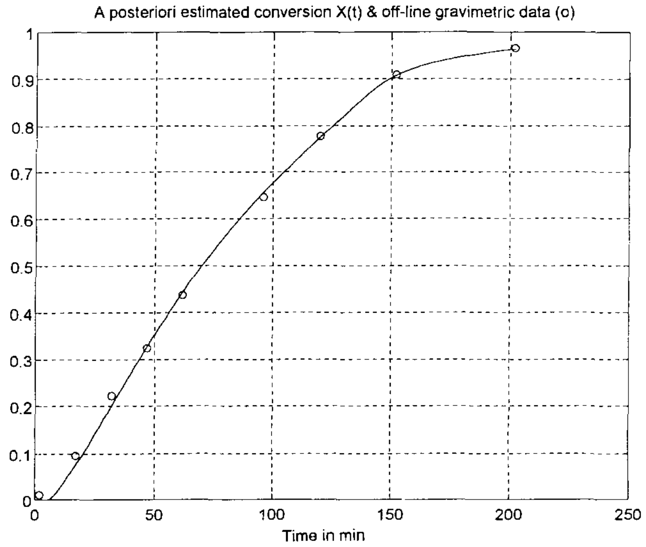

Fig. 9. Optimal *a posteriori* trajectory of the conversion. Run 3.

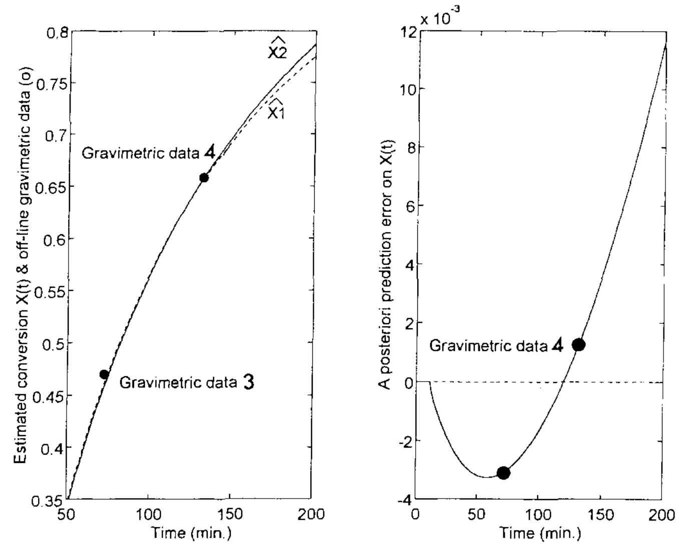

Fig. 10. a. Comparison between *a priori* and *a posteriori* estimates $\hat{X}_1(t)$, $\hat{X}_2(t)$. Run 1. b. *A posteriori* prediction error $(\hat{X}_2 - \hat{X}_1)$. Run 1.

$(\hat{X}_2 - \hat{X}_1)$ remains acceptable, despite its exponential behaviour. More than 70 min after the fourth measurement $X_g(t_g(4))$, the uncertainty on the conversion is only about 1.2%. This error is found to be more important in emulsion experiments (up to 3% in the worst case operations) than in solution polymerizations, for which the relative uncertainty always remained below 1.5%. However, it is important to notice that off-line samples were only withdrawn at half-hour intervals, even in the case of difficult emulsion polymerizations. Although only 4 different operations have been described in this article, similar results were obtained with about 20 experiments.

5. Conclusion

This work was motivated by the design of a calorimetric sensor that could be used as a means of monitoring batch solution or emulsion polymerization processes. To improve the performances of usual calorimetric approaches in the general case of multi-purpose use, it is of great importance to account for possible variations of the parameters involved in the energy balance, as well as in the polymerization kinetics. A model for the on-line energy balance of a 7-litre bench-scale reactor has thus been developed with particular attention being paid to the joint assessment of heat transfer through the jacket and monomer conversion. For the sake of the "observability" of the evolution of the reaction, additional measurements have been envisaged. Rapid, but not necessarily frequent, off-line gravimetric data were proposed as corroborating measurements that can be used on-line to perform an inferential estimation of unpredictable variations in key parameters of the system. Therefore, a combined strategy between scarce measurements, parameter estimation techniques and on-line calorimetry has been presented. A general dynamic state-space formulation of the energy balance of the polymerization reactor was proposed, and a Luenberger state-observer derived from the model was applied to the estimation of conversion during batch and semi-batch polymerizations. In order to deal with the noise in the calorimetric measurements and with uncertainties in the polymerization kinetics, the estimation of the instantaneous heat release due to polymerization was obtained by using a recursive least-squares identification algorithm. Moreover, in order to account for both time and batch-to-batch variations in the overall heat transfer coefficient, the estimation strategy was improved through the use of infrequent off-line gravimetric measurements of conversion.

The proposed combined hardware/software strategy was evaluated using our 7-litre bench-scale reactor in the case of solution and emulsion polymerizations. Encouraging experimental results, in terms of accuracy, flexibility and robustness of the estimates, have been obtained. Despite constantly changing parameter values, which were essentially associated with variations in the conversion-dependent viscosity of the reactor contents, the reconstructed course of monomer conversion was found to fit the experimental data. Moreover, it should be noted that through the adaptive knowledge of reaction-dependent parameters, the reported model-based approach is likely to lead to improved insight into several aspect of the polymerization process.

However, in order to extend the calorimetric sensor to batch multi-component polymerization processes, additional information is required to completely determine the conversion of each monomer. This problem might be solved by using density measurements and/or state estimators based upon appropriate kinetic models.

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