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Inferential conversion monitoring and control in emulsion polymerisation through calorimetric measurements

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Abstract

A dynamic model has been developed describing the emulsion polymerisation of styrene within a batch/semi-batch stirred tank reactor (BSTR). This model includes the initiation, propagation and termination steps for styrene polymerisation, along with the relevant mass balance equations (including those for polymeric radicals) and energy balance equations—the latter covering heat of reaction, internal and external heat transfer effects, as well as external heat losses. The resulting set of (differential/algebraic) equations was solved for both species concentrations and temperature profiles as functions of time. Experiments were conducted in a laboratory BSTR instrumented with platinum resistance thermal transducers and gravimetric conversion measurement devices. The model predictions compared well with inferential calorimetric measurements which were validated using experimental gravimetric data. Subsequent implementation of a model-based optimal control strategy resulted in a 13% relative increase in monomer conversion, together with a 28% reduction in batch time.

Keywords: Emulsion polymerisation; Polystyrene; Calorimetry; Soft-sensor; Optimal control

1. Introduction

Emulsion polymerisation has grown to become one of the major means for the production of synthetic polymers. Currently, a large variety of polymers are produced by emulsion polymerisation including synthetic elastomers, bulk plastics, and plastic/elastomeric lattices for coatings. Due to this importance, there are substantial incentives for improved design and control of emulsion polymerisation reactors [1,2]. However, the monitoring and control of such reactors is still a major challenge due to the lack of on-line sensors capable of monitoring the complex physico-chemical behaviour within such systems.

In emulsion polymerisation, monitoring and control of monomer conversion is crucial both for proper process operation (so as to reduce downstream separations), and for obtaining products with desired properties (due to the influence of conversion on polymer molecular weight and particle size distributions). Techniques currently implemented to determine conversion (such as gravimetry, gas chromatography, and indirectly through viscosity and density measurements) have notable drawbacks. Such techniques are generally carried out off-line, resulting in a considerable measurement delay that is undesirable for any form of real-time control. Thus, this work focuses on the development of an alternative approach to conversion monitoring that is suitable for on-line implementation.

Since most polymerisation reactions are exothermic, it is possible to determine the reaction rate and monomer conversion via temperature measurements by operating the reactor in conjunction with an on-line calorimeter [2–11]. This method is certainly seen as a promising candidate for eventual industrial application. However, determining monomer conversion from temperature readings on a reactor requires a thorough understanding of the heat transfer mechanisms occurring within the system. In this study, a detailed calorimetric model is developed for inferring monomer conversion in a batch/semi-batch laboratory reactor where polystyrene latex is produced via emulsion polymerisation. The significant advance here over existing calorimetric monitoring schemes is that the present development makes use of a dynamic model of the process. As will be shown, the calorimetric based results compared well with conversion data obtained off-line by gravimetry. Consequently, the feasibility of applying calorimetry within an inferential model-based control was also investigated.

1.1. Emulsion polymerisation reactor model

For a semi-batch reactor (schematic diagram shown in Fig. 1) employing a time-dependent monomer feed rate, the

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Nomenclature

A	heat transfer area (m^2)
C_p	heat capacity of reactor contents (J/g °C)
C_{pm}	heat capacity of the monomer (J/g °C)
C_{pw}	heat capacity of water (J/g °C)
d	impeller diameter
D	inner reactor diameter (m)
ΔH_p	heat of polymerisation (J/mol)
$F_{m,in}$	monomer feed rate (mol/s)
J	objective function
m_j	mass of water in the jacket (g)
M	mass contents of the reactor (g)
MW_m	molecular weight of the monomer (g)
N	agitation speed (rev/s)
N_m	number of moles of monomer in the reactor (mol)
$N_{m,T}$	total number of moles of monomer fed to the reactor (mol)
N_p	number of moles of polymer in the reactor (mol)
P_s	power input by stirrer (W)
$Q_{j,loss}$	heat losses from jacket (W)
$Q_{r,loss}$	heat losses from reactor (W)
R_p	reaction rate (mol/m^3 s)
t	time (s)
T_{amb}	ambient temperature (°C)
T_e	reactor temperature (°C)
$T_{j,in}$	inlet jacket temperature (°C)
$T_{j,out}$	outlet jacket temperature (°C)
U	heat transfer coefficient (W/m^2 K)
V	reactor contents volume (m^3)
V_{wo}	water volume (m^3)
W_c	mass flow rate inside the jacket (g/s)
X	instantaneous conversion
X_s	conversion set-point

Greek letters

α	coefficient for heat losses (W/°C$^\beta$)
β	power coefficient
λ	weighting factor
ρ	density (kg/m^3)
τ	process time constant (s)

monomer mole balance gives:

$$\frac{dN_m}{dt} = F_{m,in} - R_p V; \quad N_m(0) = N_{m0} \tag{1}$$

where N_m is the number of moles of monomer in the reactor, $F_{m,in}$ the monomer feed flowrate and R_p the polymerisation reaction rate. Similarly, the number of moles of polymer formed can be obtained using:

$$\frac{dN_p}{dt} = R_p V; \quad N_p(0) = 0 \tag{2}$$

The volume of the reactor contents, V, can be determined from:

$$V = \frac{N_m MW_m}{\rho_m} + \frac{N_p MW_m}{\rho_p} + V_{wo} \tag{3}$$

where ρ_m and ρ_p are the monomer and polymer densities, respectively, MW_m the molecular weight of the monomer and V_{wo} the volume of water employed in the polymerisation "recipe".

The instantaneous monomer conversion, X, may be calculated as follows:

$$X = 1 - \frac{N_m}{N_{m,T}} \tag{4}$$

where $N_{m,T}$ is the total amount of monomer added during the reaction, being related to $F_{m,in}$ by:

$$\frac{dN_{m,T}}{dt} = F_{m,in}; \quad N_{m,T}(0) = N_{m0} \tag{5}$$

In batch mode, $F_{m,in}$ is equal to zero while $N_{m,T}$ is equal to the total amount of monomer (in moles) charged into the reactor.

1.2. Heat transfer analysis

The dynamic heat balances for the reactor and external jacket contents are given by the following equations:

$$\frac{d(MC_pT_e)}{dt} = F_{m,in} MW_m C_{p_m} (T_{amb} - T_e) + UA(T_{j,out} - T_e) - Q_{r,loss} + R_p V \Delta H_p + P_s; \quad T_e(0) = T_{e0} \tag{6}$$

$$m_j C_{pw} \frac{dT_{j,out}}{dt} = W_c C_{pw} (T_{j,in} - T_{j,out}) - UA(T_{j,out} - T_e) - Q_{j,loss}; \quad T_{j,out}(0) = T_{j,out0} \tag{7}$$

where M and m_j are the masses of the reactor and jacket contents, while C_p, C_{pw} and C_{pm} are the heat capacities of the reactor contents, water and monomer, respectively. It should be noted that changes in both the mass of the reactor contents and its specific heat were incorporated for the case of semi-batch operation. $Q_{r,loss}$ and $Q_{j,loss}$ are the heat losses from the reactor contents and the water in the jacket, respectively. T_{amb} is the ambient temperature while ΔH_p is the heat of reaction (−69 900 J/mol, for styrene polymerisation). W_c is the mass flowrate of water through the jacket while P_s is the power input by stirring the reactor contents, being defined as [12]:

$$P_s = K\rho N^3 d^5 \tag{8}$$

where K is a constant, N the stirrer speed, d the impeller diameter and ρ the density of the latex calculated from:

$$\rho = \frac{N_m MW_m + N_p MW_m + V_{w0}\rho_w}{(N_m MW_m)/\rho_m + (N_p MW_m)/\rho_p + V_{w0}} \tag{9}$$

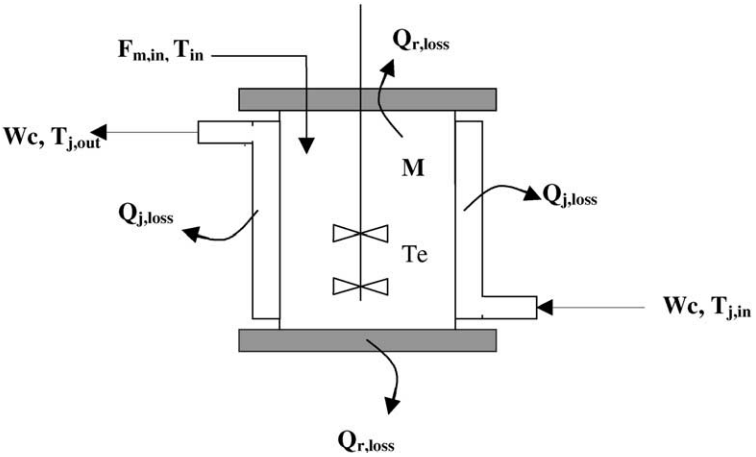

Fig. 1. Reactor variables for heat and mass balance calculations.

In order to solve for R_p, Eqs. (6) and (7) require accurate estimates for both the heat transfer coefficient and the heat losses. These may be obtained from an analysis of the reactor dynamics.

1.2.1. Eliminating the dynamics on the jacket side

Since our focus here is on the monitoring and control of gross reactor behaviour, it is reasonable to simplify the governing model equations. In particular, the dynamics of the external jacket system can be neglected by employing a relatively high water flow rate, thus ensuring a maximum inlet to outlet temperature differential of about 0.3 °C across the jacket. Under such conditions, Eq. (7) is reduced to an algebraic equation with U and $Q_{j,loss}$ as the only unknowns. By eliminating the jacket side dynamics, Eq. (6) (relating to the behaviour of the reactor contents) is the only dynamic equation requiring solution. However, this equation has three time-dependent parameters that need to be determined, as shown in the following sections.

1.2.2. Determination of U

The processes contributing to heat transfer within a polymerisation reactor are the heat of reaction, thermal losses and the heat of evaporation/condensation. Ignoring any of these factors would ensure a poor estimate of the reaction rate. However, simplifications are possible—as the heat of stirring was found to be negligible (estimated at about 0.5 W), while with the reactor contents being mostly water, the impact of viscosity changes was found to be negligible.

With these simplifications made, the heat transfer coefficient, U, was determined from data taken during the early stages of a run when the reactor contents were being heated. With all ingredients (except the small quantity of initiator) charged into the reactor, with thermal insulation on the reactor top and bottom surfaces and with no addition of feed (i.e. batch mode operation), the impact of evaporation/condensation and heat losses from the reaction medium are kept at a minimum. Under these conditions, Eq. (6) reduces to the following:

$$MC_p \frac{dT_e}{dt} = UA(T_{j,out} - T_e) \qquad (10)$$

which on rearrangement gives:

$$\frac{MC_p}{UA}\frac{dT_e}{dt} + T_e = T_{j,out} \qquad (11)$$

where $\tau = (MC_p/UA)$ is the process time constant for this first-order system.

Given M, C_p and A, then U can be obtained from an estimate of τ. At low temperature conditions (where $T_{j,out} \cong T_{amb}$) and for step changes in the jacket temperature (of the order 5–10 °C), τ can be obtained from the system's dynamic response using:

$$\tau = 1.5(t_{0.632} - t_{0.283}) \qquad (12)$$

where $t_{0.283}$ and $t_{0.632}$ are the times required by the system to reach 28.3 and 63.2% of the dynamic response to the eventual steady-state, respectively.

1.2.3. Effect of heat loss and heat of evaporation/condensation

Once U has been estimated, heat losses to the surroundings along with heat effects associated with any evaporation/condensation processes can be considered. These mechanisms are complex (being functions of both the reactor temperature, T_e, and the ambient temperature, T_{amb})—therefore, all were lumped within an empirical formula of the form:

$$Q_{r,loss} = \alpha(T_e - T_{amb})^{\beta} \qquad (13)$$

where α and β are constants. Then, during the initial heating phase (when no initiator is present and no feed is being added), values for α and β may be estimated by matching the measured thermal response of the reactor contents to that obtained from the solution of Eq. (14):

$$\alpha(T_e - T_{amb})^{\beta} = UA(T_{j,out} - T_e) - MC_p\frac{dT_e}{dt} \qquad (14)$$

A value of β greater than one was expected due to the non-linear behaviour of evaporation and condensation with respect to this temperature differential.

With U and $Q_{\mathrm{r,loss}}$ estimated as previously described, on addition of the reaction initiator, the heat being generated by the polymerisation reaction (and hence R_{p}) can be estimated from Eq. (6).

2. Experimental

Semi-batch emulsion polymerisation of styrene was carried out at 50 and 70 °C (under slight nitrogen pressure) in a 1 l laboratory glass reactor (PDC Machines, Inc.) equipped with a digital tachometer and an agitation speed controller. The reactor details are given in Table 1. This reactor is fitted with three RTD sensors (Pt-100) connected to data acquisition modules (ADAM-4000 and ADAM-4013 from Advantech Australia) for on-line temperature measurements. Sampling every second was found to be adequate, as the total experimental time is of the order 3–5 h.

The monomer was added in situ under starved feed conditions via a metering pump (Prominent gamma/4-RS). A heating circulator (Julabo HD-4) provides a constant high water flowrate through the external jacket. The water inside the circulator is cooled with cooling water circulating inside a coil in the heating circulator. An MVS controller adjusts the cooling water flowrate by manipulating a solenoid valve (on/off control). A schematic diagram of the reactor system is shown in Fig. 2.

Polymerisations were carried out with monomer, water and surfactant added to the reactor and brought up to the desired reaction temperature. Temperature readings were taken during this heating process, so as to allow estimation of both U and the heat loss parameters α and β. Thereafter, the preheated initiator solution (at the reaction temperature) was added to the reactor contents. Temperature readings were continually taken during the reaction stage. The polymerisation "recipe" used in these runs is given in Table 2.

Monomer conversion was determined off-line via gravimetric analysis of taking samples from the reactor. These samples were weighed, then placed in an oven (at 160 °C) for 15 min to determine their solid content.

Table 1
Reactor dimensions and operating parameters

Reactor height (m)	0.18
Reactor diameter (m)	0.085
Jacket height (m)	0.13
Jacket volume (ml)	350
Water flowrate through jacket (ml/s)	92
Agitation speed (rpm)	395

Table 2
Polymerisation procedure and amounts of feed

Monomer (g)	166.40
Water (g)	531.66
Initiator-persulfate $K_2S_2O_8$ (g)	1.16
Surfactant-SDS (g)	1.03
$NaHCO_3$-buffer (g)	1.00
Monomer feed:	
17.1% initial charge	
45 min pre-period	

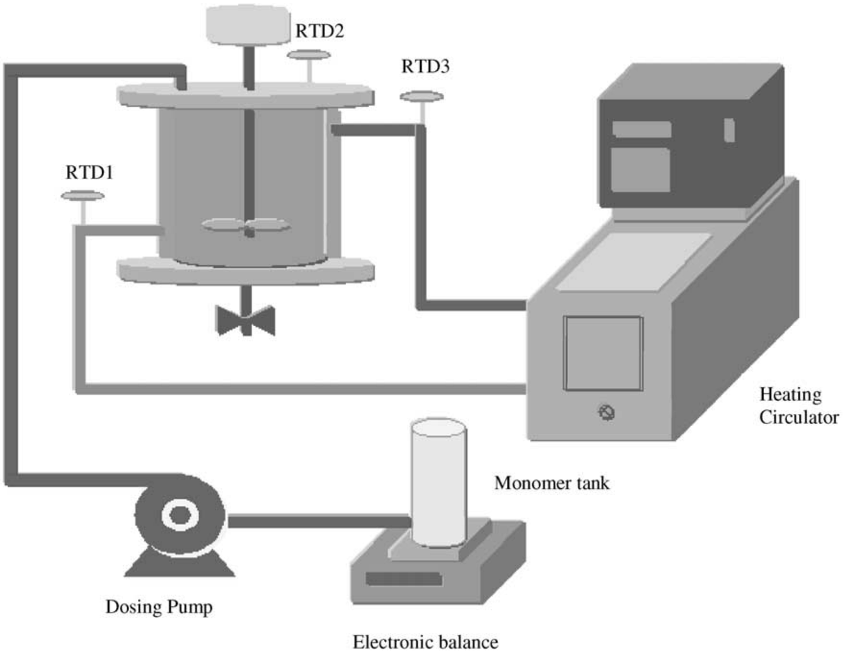

Fig. 2. Schematic diagram of the polymerisation reactor system.

2.1. Data acquisition and parameter estimation

A program (written in MS Excel-97 and Microsoft Visual Basic) performed the calorimetric calculations from the on-line temperature and monomer flowrate readings—this calorimetric model being linked via a dynamic data exchange (DDE) protocol to the control and data acquisition software.

Least-squares linear regression analysis was used during the heating cycle to determine α and β. Rearranging a discretised version of Eq. (14) (for a sampling interval of 60 s) gives:

$$\begin{aligned}\varLambda + \beta \ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}) &= \ln\left[UA(t)(T_{\mathrm{j,out}}(t) - T_{\mathrm{amb}}) - M(t)C_{\mathrm{p}}\frac{T_{\mathrm{e}}(t) - T_{\mathrm{e}}(t-1)}{\Delta t}\right]\end{aligned} \tag{15}$$

where $\varLambda = \ln\alpha$.

$\varLambda$ and β are then obtained from:

$$\varLambda = \frac{\left(\sum Y(t)\sum(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))^2\right) - \left(\sum \ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}})\sum(Y(t)\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))\right)}{n\left(\sum(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))^2\right) - \left(\sum(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))\right)^2} \tag{16}$$

$$\beta = \frac{n\left(\sum Y(t)\right)\left(\sum(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))\right)\left(\sum(Y(t)(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))\right)}{n\left(\sum(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))^2\right) - \left(\sum(\ln(T_{\mathrm{e}}(t) - T_{\mathrm{amb}}))\right)^2} \tag{17}$$

where

$$Y(t) = \ln\left[UA(t)(T_{\mathrm{j,out}}(t) - T_{\mathrm{amb}}) - M(t)C_{\mathrm{p}}\frac{T_{\mathrm{e}}(t) - T_{\mathrm{e}}(t-1)}{\Delta t}\right] \tag{18}$$

and n is the number of samples.

The low solids contents (reaching a maximum value of some 24%) and the high agitation rate (395 rpm) ensured a constant heat transfer coefficient, U, throughout the reaction phase. The heat transfer area of the cylindrical jacket was calculated as a function of time from the reactor diameter, D, and the reaction volume (which increased with monomer addition) as follows:

$$A(t) = \frac{4V(t)}{D} \tag{19}$$

2.2. Advanced control of the reactor

The control of polymerisation processes in general, and emulsion systems in particular, requires a thorough understanding of all key polymer properties and how they are influenced by conditions in the reactor. The determination of possible manipulated variables (which can be used to regulate these properties) is equally important.

Following the successful development of an on-line estimator for the extent of styrene conversion, an optimal control strategy based on the calorimetric model described above was considered next in this study. The control objective here was to maximise reactor productivity (that is, to achieve maximum monomer conversion, X, per unit time). The monomer feed rate was chosen as the only controlled variable in this exemplar system, where the “cost function” to be minimised, J, was defined as follows:

$$\min_{F_{\mathrm{m,in}}} J = \lambda(X - X_{\mathrm{s}})^2 \tag{20}$$

subject to the time and flowrate constraints,

$$t_{\min} \le t \le t_{\max} \quad \text{and} \quad F_{\mathrm{m,in(min)}} \le F_{\mathrm{m,in}} \le F_{\mathrm{m,in(max)}}$$

In this optimisation problem, monomer conversion is forced to the desired value, X_{s}, by minimising the square of the difference between the required set-point and the estimated value. Strictly speaking, the weighting factor, λ, is not needed here—but becomes important when the objective function is comprised of a number of different terms. The difference between the measured and estimated conversion values, caused by model inaccuracies, is represented in the optimal control formulation by a disturbance term, d.

3. Results and discussion

3.1. Heat transfer results

The determination of U, α and β was carried out using data from runs at reactor temperatures ranging between 50 and 80 °C, and for monomer feed rates between 0.085 and 0.7 ml/min. The effect of variations in the ambient temperature on the heat transfer analysis was taken into account. A value of 83 W/m^2 K was estimated for the heat transfer coefficient, while the heat losses parameters α and β were estimated at 10^{-7} W/°C$^{\beta}$ and 5, respectively.

The calculated heat outputs from the polymerisation reaction in the batch and semi-batch cases are compared in Fig. 3. It is clear that the batch run exhibited the larger exotherm, with an approximately 8 °C increase in reactor temperature, due to the higher monomer content in this “recipe”. This exotherm decayed away with time as the concentration of monomer decreases, reaching very low values at high monomer conversion. In the semi-batch experiments, less monomer (17.1% of the initial charge) was present initially, giving a smaller exotherm that reached no more than 2 °C a short while after the monomer feed started.

After completion of the heat transfer analysis, monomer conversion was calculated using the calorimetric model with values of U, α and β kept constant. As noted previously, this assumption is felt to be reasonable due to the low solids content resulting from this recipe and the high shear rate inside the reactor.

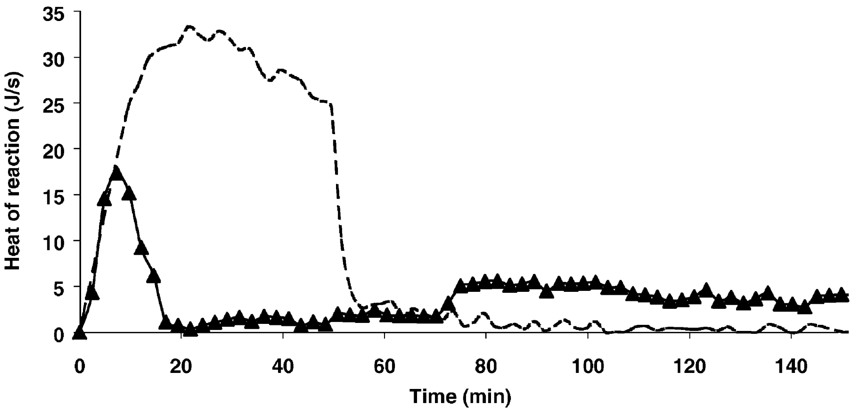

Fig. 3. Exotherm estimated by calorimetry under batch (---) and semi-batch modes (- ▲).

3.2. Model predictions

The instantaneous monomer conversion was calculated at different monomer flow rates and reactor temperatures. A high feed rate resulted in a high reaction rate. This is because the monomer concentration in the particles increases with an increase in feed rate, thus leading to an increase in the reaction rate. This behaviour is clearly shown in Fig. 4.

The accuracy of the on-line calorimetric analysis was investigated by plotting monomer conversion versus time along with the results obtained by off-line gravimetry, as shown in Fig. 5. The accuracy of the gravimetric data was ensured by the cessation of reaction once outside the reactor, due to exposure of the samples to the inhibitory action of oxygen. Good agreement was obtained between the on-line calorimetric measurements and the off-line gravimetric results. Hence, the calorimetric model can be used as a "soft-sensor" for styrene conversion, having a 3–5% prediction error which is quite acceptable for on-line monitoring and control purposes.

The effect of the monomer flow rate on the overall monomer conversion in the reactor was next analysed online by introducing a step change in the feed rate, as shown in Fig. 6. An initial decrease in conversion was followed by a sharp increase. This behaviour was due to the sudden increase in monomer flow rate leading to an accumulation of monomer inside the reactor. However, the resultant decrease in conversion is short-lived, as the concentration

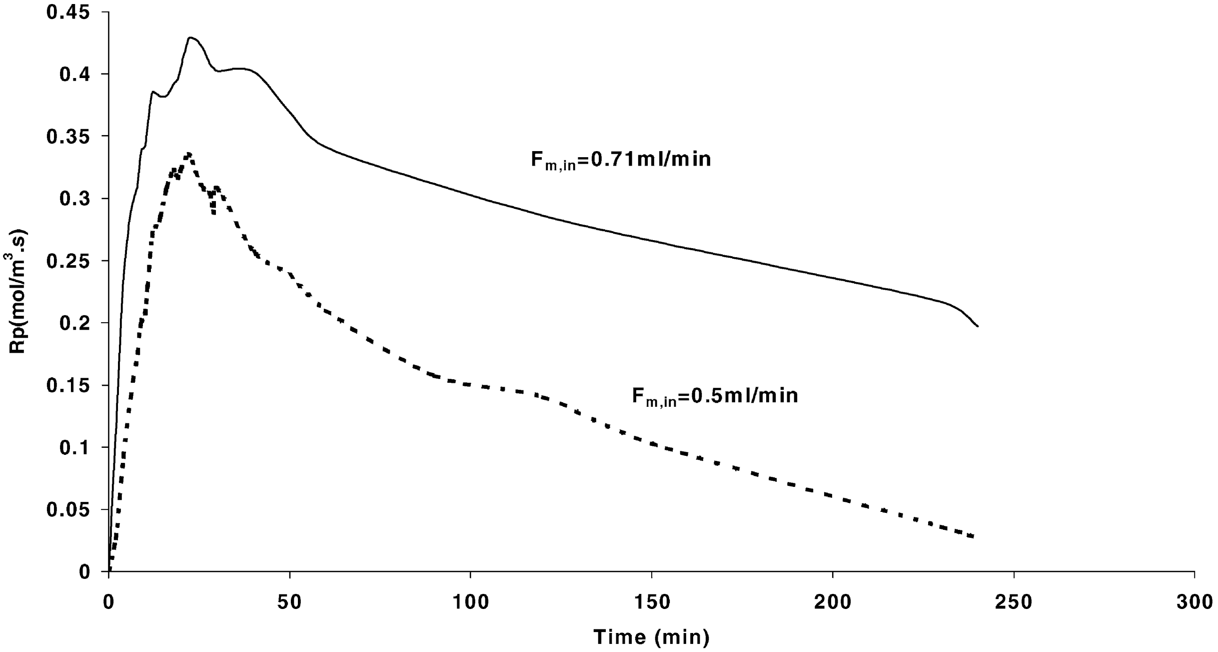

Fig. 4. Calorimetric results for the reaction rate at 70 °C (two different monomer feed rates).

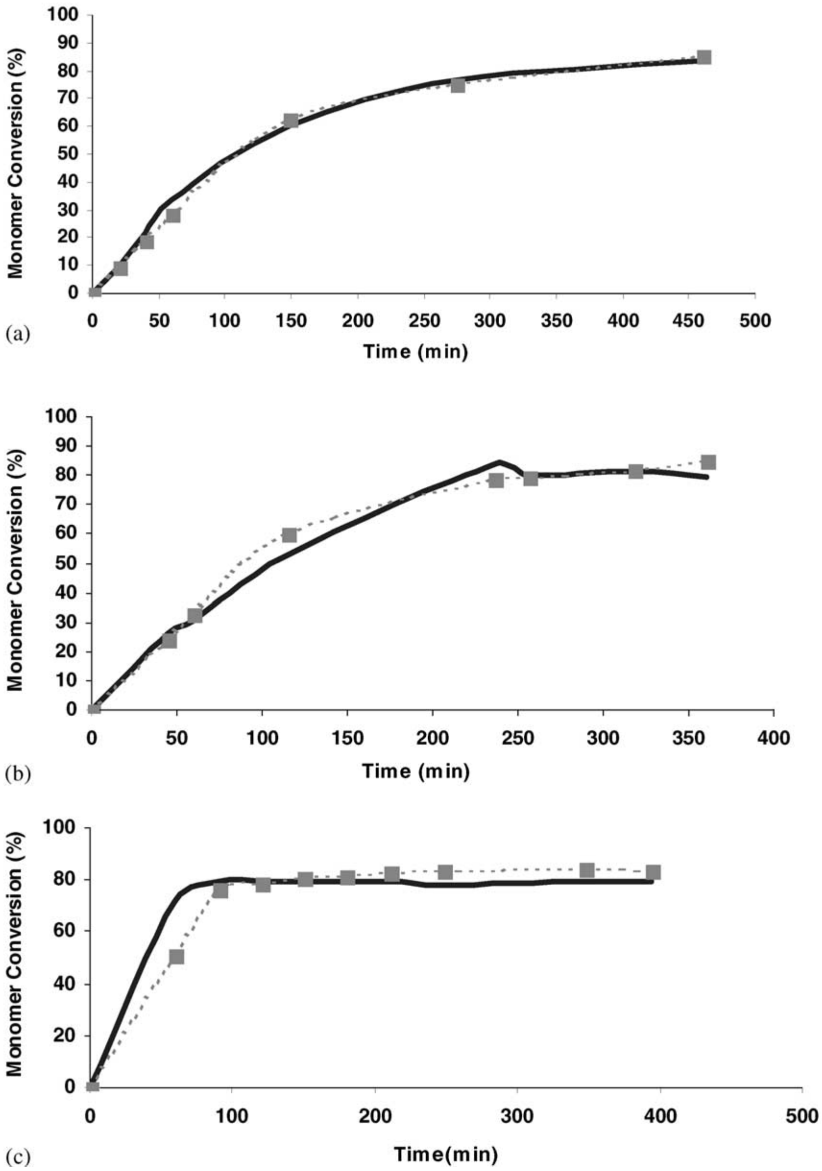

Fig. 5. Instantaneous conversion vs. time curves ((■) gravimetry, (---) calorimetry): (a) 50 °C, monomer feed rate = 0.36 ml/min; (b) 50 °C, monomer feed rate = 0.5 ml/min; (c) 70 °C, monomer feed rate = 0.44 ml/min.

inside the latex particles rapidly increases as monomer diffuses in from the aqueous phase, and the reaction rate (and monomer conversion) increases.

3.3. Optimisation results

After validation of the calorimetric model, the optimal control of the reactor was investigated. An optimal control strategy (as described previously) was computed under the following constraints.

- The total monomer added in the recipe should not exceed 1.6 mol.

$$N_{\mathrm{m,T}} \leq 1.6\,\mathrm{mol}$$

- The reaction terminates when all the monomer is fed into the reactor.

The objective here was to maximise reactor productivity (which can be done by increasing monomer conversion and decreasing reaction time). For operational purposes, the monomer feed rate was bounded as follows,

$$10^{-5}\,\mathrm{mol/s} \leq F_{\mathrm{m,in}} \leq 3.2 \times 10^{-4}\,\mathrm{mol/s}$$

as this guarantees “starved feed” operation, while taking into account known pump limitations. The initial reaction temperature was set at 70 °C with a 45 min batch pre-period. The optimal control algorithm (incorporating the calorimetric “soft-sensor” for monomer conversion) is shown in Fig. 7a. The optimal monomer feed trajectory, determined

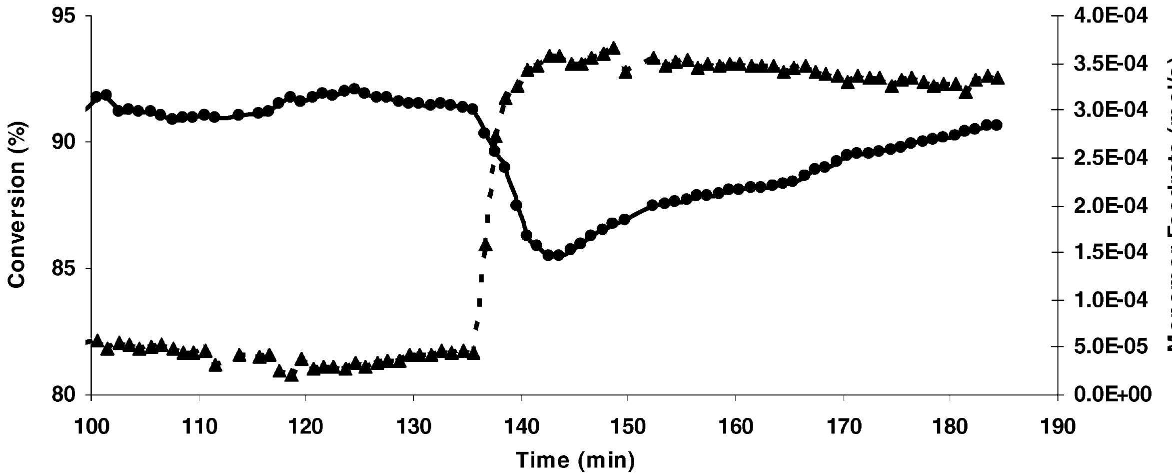

Fig. 6. Response of monomer conversion (●) to a step change in monomer feed rate (▲).

from computations described earlier, gave a maximum conversion of 93.5% which was achieved in 4.82 h as shown in Fig. 7b. This result was a significant reactor productivity improvement, compared with previous (recipe based) experimental results. For example, relative to the results shown in Fig. 5c, the optimal policy showed a 13% increase in conversion with a 28% relative reduction in the run time.

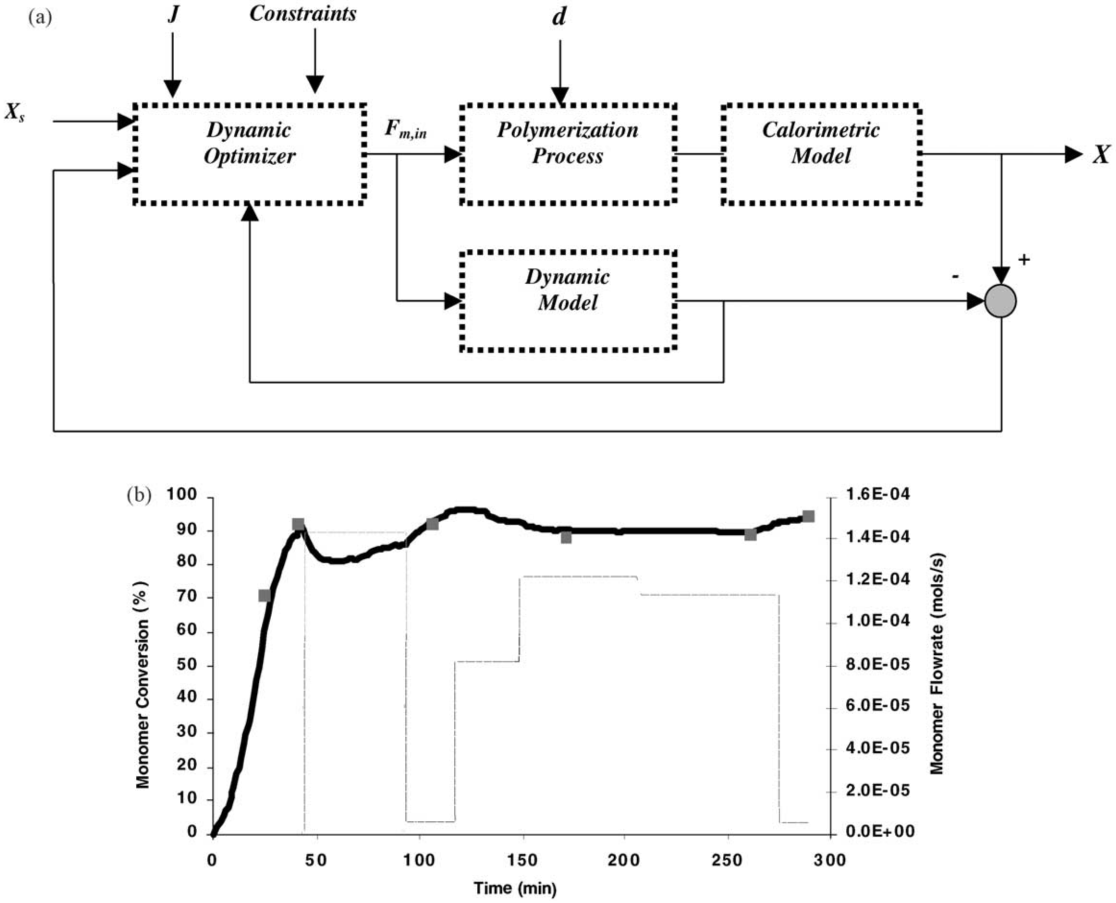

Fig. 7. (a) Schematic diagram of model-based control algorithm using calorimetric model as a soft-sensor. (b) Responses to optimal control strategy for monomer conversion ((■) by gravimetry, (—) by calorimetry) and the trajectory of the manipulated variable ((----) monomer flowrate).

4. Conclusions

An approach to estimating monomer conversion in emulsion polymerisation systems using reaction calorimetry as a “soft-sensor” was investigated. The method was validated for the semi-batch polymerisation of styrene carried out in a laboratory scale reactor, with the on-line calorimetry measurements being in good agreement with off-line gravimetric results. Using this estimator, it was shown that the monomer feed rate has a major impact on the progress of this reaction. Exploiting this fact, a model-based control strategy using the calorimetric model was developed whereby the monomer feed rate was used to control monomer conversion. The implemented optimal control strategy showed a significant increase in reactor productivity (relative to an established styrene polymerisation “recipe”). On-line reaction calorimetry would, thus, seem to be a powerful tool for inferential measurements, as well as having a pivotal place in the model-based control of polymerisation reactors.

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