

OPTIMIZATION OF EMULSION COPOLYMERIZATION REACTIONS. EXPERIMENTAL VALIDATION

C. SAYER[†], R. GIUDICI[‡] and P.H.H. ARAÚJO[†]

[†] *Dpto. de Eng. Química, Univ. Fed. de Santa Catarina, Florianópolis - SC, Brasil*

csayer@enq.ufsc.br; pedro@enq.ufsc.br

[‡] *Dpto. de Eng. Química, Univ. de São Paulo, São Paulo - SP, Brasil*

rgiudici@usp.br

Abstract— Time optimal monomer and reactor temperature set-point profiles were computed and implemented experimentally for the control of copolymer composition and minimization of reaction time in emulsion copolymerization systems. Iterative Dynamic Programming (IDP) was used for the off-line calculation of the optimal profiles. This approach can deal with constrained optimization of systems described by complex mathematical models, as those needed for the emulsion copolymerization. The optimization procedure was applied to vinyl acetate / butyl acrylate emulsion copolymerization under industrial-like conditions, which includes safety constraints normally found in the operation of large-scale reactors. The dynamics of the reactor heat exchange system were also taken into account in the mathematical model. The optimal trajectories obtained by the IDP procedure were implemented in a jacketed reactor with automated control of temperature and monomers feed flow rates. The real-time implementation of the optimal trajectories was successfully carried out resulting in a significant reduction in reaction time and the production of homogeneous copolymer composition.

Keywords— Semicontinuous reaction; Optimal trajectories; Emulsion polymerization, Iterative Dynamic Programming.

I. INTRODUCTION

Emulsion polymerization is used in industry to produce a great variety of polymers of multiple uses (e.g. paints, adhesives, coatings). This process produces polymer via free radical in dispersed media resulting in polymer particles of 80-400 nm dispersed in an aqueous phase. The global mechanism of polymerization in such multiphase system is extremely complex due to process interactions that occur in each phase and diffusion mechanisms of the components between these phases. Many applications of polymer latex require a homogeneous copolymer composition as it may affect final properties as the formation of a continuous film. Monomers with very different reactivity ratios may lead to an undesired copolymer composition drift. In order to reduce such drift, emulsion copolymerization is frequently carried out under starved conditions where both monomers are fed to the reactor at very low flow rates

to assure a low concentration of monomers in the reactor at any time. Another advantage of conducting an emulsion copolymerization at starved conditions is to keep the safety of operation as polymerization via free radical is usually very exothermic. Reducing the amount of monomer concentration in the reactor reduces the peak of heat generation. Although, starved conditions also leads to very large reaction time as monomers are fed at very low flow rates.

Industrial semicontinuous emulsion copolymerization, usually, does not take full advantage of the reactor heat removal capacity as the reaction conditions are often defined to control the peak of heat generation or copolymer composition (in starved conditions). Nevertheless, using a detailed mathematical model for the emulsion copolymerization system it is possible to calculate the time varying control variables in order to minimize reaction time, taking the safety aspects into account, and to control copolymer composition (Araújo and Giudici, 2003, 2004). It is worth pointing out that the success of the open-loop strategy relies on the goodness of the mathematical model and the absence (minimization) of unmodeled process disturbances (Vicente et al., 2002). Therefore, for a successful implementation of such optimal profiles the dynamics of the heat exchange system must be taken into account as the reactor temperature depends on it and may vary according to the heat exchange capacity. Any optimization strategy to be implemented in an industrial emulsion polymerization reactor has to include the dynamics of reactor temperature control as the reaction is, usually, very exothermic and the reactor heat removal capacity is limited. Nevertheless, the complexity of the system increases when the dynamics of the reactor temperature control is included. This is one of the reasons for the scarce number of works in the literature dealing with the implementation and validation of this kind of procedure in an experimental emulsion polymerization system.

The goal of the present work was the implementation and validation of optimal profiles for the controlled production of VA/BA copolymers with homogeneous composition (80/20 in weight basis) at minimum reaction time including the dynamics of reactor temperature control and taking safety aspects into account by means of an open-loop control strategy. The process variables chosen to reach the simultaneous control of copolymer composition and minimization of reaction time were the

feed flow rate trajectory of the less reactive monomer (in this case, VA) and the profile of the reactor temperature set-point. A Non-Linear Adaptive (NLA) Controller as proposed by Leiza et al. (1993) was implemented to calculate the flow rate of the more reactive monomer (BA) eliminating the problem of introducing one more target into the objective function, in this case, the copolymer composition. The set-point of the reactor temperature was chosen as manipulated variable in order to give a more feasible aspect to the experimental implementation of the optimal trajectories.

Iterative Dynamic Programming (Bojkov and Luus, 1996; Luss, 1999) was used to compute optimal feed trajectory for the less reactive monomer (in this case, VA) and for the set-point of the reactor temperature. This approach presents the advantage of being able to handle constrained optimization of systems described by complex mathematical models, as those needed for non-linear emulsion copolymerization systems. The mathematical model describing the VA/BA emulsion copolymerization was validated previously (Araújo & Giudici, 2001) with experimental data from Araujo (1997). The time optimal trajectories were validated by real-time experiments carried out in an experimental set-up composed of a 3000 ml jacketed stainless steel reactor with automated control of reactor temperature and monomers feed flow rates.

The particle size is an important property of the final latex. Nevertheless, the nucleation step of an emulsion polymerization reaction is profoundly affected by reactant concentrations and reaction temperature. Therefore, in order to assure that the final pre-specified particle size is obtained, the optimization procedure was implemented (optimal profiles) after the nucleation step when the number of particles was constant. The nucleation step corresponded to the first 30 minutes after the initial charge was added to the reactor.

II. DYNAMIC OPTIMIZATION

In this work the production of copolymers with homogeneous copolymer compositions (80/20 VA/BA in weight basis) at a minimum reaction time and maximum conversion were considered for dynamic optimization using intervals with varying lengths as described by Araújo and Giudici (2003, 2004). In order to allow the minimization of the reaction time, the amounts of the less reactive monomer fed during each optimization interval were fixed, while the lengths of these intervals could vary. The optimization goals were included in the following objective function:

$$F = p_1 \left[\frac{t_f - t_f^d}{t_f^d} \right]^2 + p_2 \left[\frac{x_f - x_f^d}{x_f^d} \right]^2 + p_3 R \quad (1)$$

where the first term of the right hand side of the objective function (Eq. 1) compares the deviation related to the desired reaction time (t_f^d), the second term accounts

for the difference at final conversion, and the third term includes other constraints related to the process temperature. As the objective of this work is to minimize the reaction time, the value assigned to the desired reaction time should be very low, a value virtually impossible to be reached at the desired reaction conditions. The first two terms of the objective function are inversely related to each other, as the reduction in reaction time would reduce final conversion. Nevertheless, the second term had more weight as minimum reaction time was related to a specific final conversion (x_f^d). Once the desired final conversion is reached the optimization drives to a more efficient reduction of the reaction time. To reduce simulation time, when the desired final conversion is reached the simulation is stopped and the objective function (F) is calculated with the new final reaction time (t_f) and the program returns to optimization procedure. The value assigned for t_f^d was equal to 30 minutes (this time corresponds to 60 minutes of reaction time) and the value assigned to x_f^d was equal to 0.98.

To keep the safety of the operation, constraints were applied at the objective function when the reactor temperature reached a pre-specified value (this value may not be the same for all intervals since at the end of the reaction higher temperatures could be attained to reduce residual monomer content). The boiling point of VA is around 72°C. To avoid high evaporation rates of VA at the beginning of the reaction, the maximum reaction temperature was set equal to 71°C for the first 4 intervals and 76°C for the last interval. The other constraint was the maximum total adiabatic temperature (total adiabatic temperature is the temperature reached by the reaction medium if all reactants present in the reactor reacted at adiabatic conditions), in this case 85°C. If one of these conditions (temperatures lower than the maximum reaction temperature or the maximum adiabatic temperature) were not satisfied, at any interval, R would assume a value equal 1, otherwise it remained equal zero. As the penalty factor, p_3 , is very high ($p_3 = 1000$) when compared to the other penalty factors ($p_1 = 1$ and $p_2 = 10$), the objective function assumes a very high value and the value is rejected as the optimal result. As conversion should reach 0.98, p_2 should be higher than p_1 to guarantee that.

To allow the control of copolymer composition along the reaction, two different feed streams were used. The first feed stream contained the less reactive monomer (in this case, VA) which partially controls the reaction rate and the second feed stream contained the more reactive monomer (BA), which controls the composition during the reaction. Both monomer feed streams contained 1% (w/w) of acrylic acid (AA) to improve polymer particle stability. The less reactive monomer is fed in the first intervals and a NLA controller is used to calculate the flow rate of the more reactive monomer throughout the reaction.

The mathematical model of a semicontinuous emulsion copolymerization reaction carried out in a jacketed reactor with controlled temperature used in the optimi-

zation procedure is presented in detail in Araújo and Giudici (2003, 2004).

III. EXPERIMENTAL

Emulsion polymerization reactions were performed with industrial-grade inhibited monomers: butyl acrylate (BA), vinyl acetate (VA), acrylic acid (AA). Distilled and deionized water and technical grade reactants, emulsifier: sodium lauryl sulfate (SLS), initiator: sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and pH buffer: sodium carbonate (Na_2CO_3), were used in the reactions. A 3000 ml jacketed stainless steel reactor (Büchi Glass) connected to a condenser to avoid monomer losses due to evaporation during the reaction was used. The startup procedure in all reactions comprised filling the reactor with the initial charge (without the initiator) and heating it up until the reaction temperature was reached. At this point the initiator was added and reaction started. The reaction proceeded for 30 minutes before monomers feed flow started. The monomers were fed in two different streams: 1) vinyl acetate and 2) butyl acrylate. In order to remove traces of dissolved oxygen, the initial charges were purged with nitrogen during a period of 60 minutes and both feed tanks and the reactor were continuously purged with nitrogen.

Reaction formulation is provided to a software and includes the reaction temperature set-point and the amount of monomer fed at each given interval of time. Reaction temperature control is achieved by a PID controller that opens/closes the valves of hot water (85°C), provided by the inductive heater (COELMA), and cold water (25°C). Both streams are mixed before entering the jacket. The set-point of the reaction temperature is sent by the computer to the controller according to the reaction formulation. Monomer feedings are carried out by dosing pumps (Prominent). Feed flow rates were controlled by a PID controller that checks every 10s the

weight of monomers that remains at the feeding vessels, constantly weighted by the balances (Marte), and determine the number of pulses of the pumps at any given time according to the reaction formulation. Figure 1 shows the experimental set-up.

Two reactions were performed, the first one at low monomers feed flow rate (Run 1) and constant reactor temperature and the second one following the optimal trajectories (Run 2). Table 1 shows the basic formulation of the reactions. Both reactions were conducted at 200 rpm.

Table 1. Formulation of the emulsion copolymerization, Run 1 (60°C , feed time = 120 min), Run 2 (optimal trajectories).

Reagents	Initial Charge (g)	Feed 1 (g)*	Feed 2 (g)*
VA	62.7	554.6	-
BA	15.7	-	140.0
AA	0.8	5.5	1.4
Water	1804.0	-	-
SLS	8.8	-	-
$\text{Na}_2\text{S}_2\text{O}_8$	4.4	-	-
Na_2CO_3	13.2	-	-

* Overall masses added at each *feed stream*.

Analytical methods used for measuring residual monomer concentrations and average particle sizes were, respectively, head-space gas chromatography (GC, HS-GC17A Shimadzu) and photon correlation spectroscopy (Coulter N4-Plus). Conversion was calculated by gravimetry. Cumulative molar composition of the copolymer was calculated from the unreacted amounts of monomer measured by gas chromatography, GC and the material balances of the monomers.

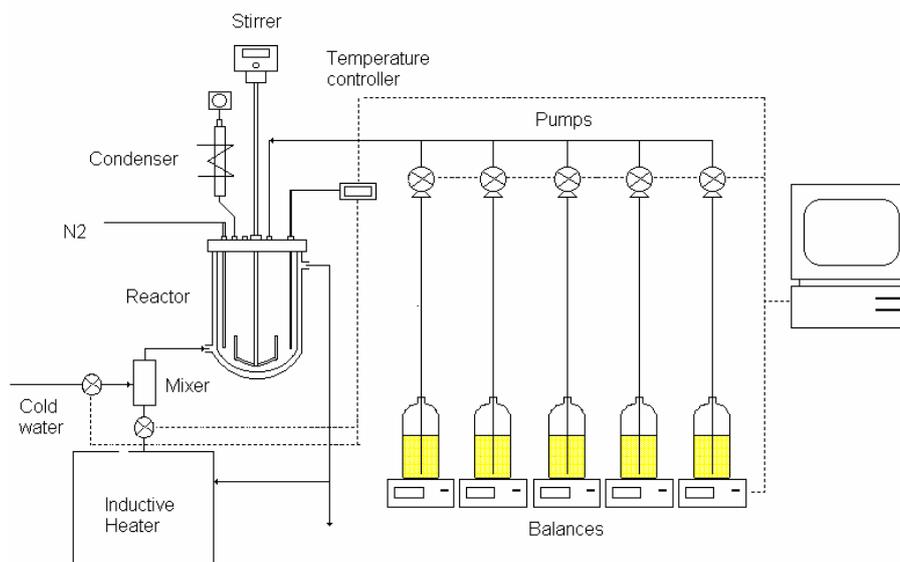


Fig. 1. Experimental set-up.

IV. RESULTS

In order to carry out the optimization, the process was divided into 5 discrete time intervals. During the first four intervals the less reactive monomer was fed to the reactor and at the last interval this feed rate was set equal zero. The more reactive monomer was fed according to the NLA controller during all intervals in order to keep a constant polymer composition. The manipulated variables in the first four intervals were the temperature profile (reactor temperature set-point profile for the PID controller) and the flow rate of the less reactive monomer (the amount of less reactive monomer fed at each interval is the same, although the length of each interval is variable) and in the last interval just the reaction temperature could be manipulated. To keep the safety of the operation, the maximum set-point temperature allowed for the intervals where the less reactive monomer was fed was 70°C and for the last interval, when monomer concentration was lower, the maximum set-point temperature was set to 75°C. The maximum reaction temperature was kept in 1°C higher than the maximum set-point-temperature.

To ensure that all batches would present the same final average particle size (this is a usual requirement of latex producers) the first step of the reaction (particle nucleation step or seed production step) was not considered for optimization as different reaction temperatures or monomer concentrations would lead to different numbers of nucleated particle. This stage corresponded to the first 30 minutes of the reaction when just the initial charge was present in the reactor. Therefore, the optimization procedure started only 30 minutes after reaction had begun. The mathematical model of the emulsion polymerization was used to simulate the first 30 minutes of reaction during which the nucleation step takes place. In this case, isothermal conditions were assumed. At the end of this period the value of process variables were stored and used as initial conditions for the optimization.

To initialize the optimization procedure, initial values were assigned for the time length of each interval and for the temperature set-point. The feed rate of the less reactive monomer (VA) and the more reactive monomer (BA) were assumed to be constant and low enough to ensure starved conditions. Both monomers were fed during 120 minutes. The reaction temperature was assumed to be constant throughout the polymerization reaction and equal to the temperature used to produce the polymer particle seeds (60°C). Such initial conditions (constant temperature profile and starved conditions) lead to a constant polymer composition, although they also lead to a large reaction time (>260 minutes) as it is possible to observe in Fig. 2. Figure 2 also shows a good agreement between the mathematical model and the experimental results for instantaneous conversion (conversion related to monomer already fed to the reactor at that exactly time) and overall conver-

sion (conversion related to the total amount of monomer fed to the reactor at the end of the reaction).

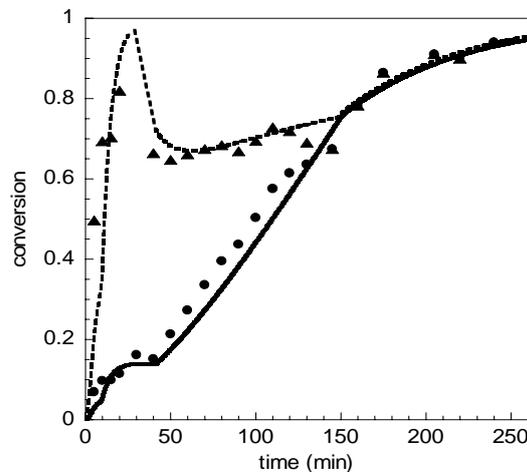


Fig. 2. Evolution of conversion for Run 1 - non-optimized reaction. Legend: experimental (dots) and mathematical model results (lines). Instantaneous conversion, (▲) and (---); overall conversion, (●) and (—).

It was used for the optimization procedure 64 random combinations of manipulated variables (length of the time interval and set-point temperature) for each interval and 4 iterations (the objective function did not reduce significantly between iterations 3 and 4). Figure 3 shows the optimal set-point temperature and feed flow rate trajectories calculated by the IDP procedure. The NLA controller calculated BA feed flow rate every 15s. In order to reduce the lines of the formulation implemented in the computer that controls monomer feed flow rates and temperature set-points, time intervals of 4, 7 and 10 minutes were implemented where BA feed flow rates were kept constant. As it can be observed in Fig. 3a, the amount of BA fed at each time interval has been preserved. Figure 3b shows that the set-point temperature was set most part of time equal to the maximum set-point temperature allowed. Although, at 62 minutes the adiabatic temperature reached the maximum temperature allowed, it means that VA could not be fed faster at that interval and also at the previous intervals, as the adiabatic temperature takes into account the reactor temperature and the total amount of monomer that remains unreacted in the reactor at that exactly time. As the PID controller implemented in the model was very effective (the parameters of the controller were adjusted and the refrigerant fluid flow rate was considered constant), it was not observed any significant overshoot and the maximum reaction temperature was not reached. A significant reduction in reaction time might be observed (from 260 minutes to 90 minutes of overall reaction time) after the implementation of optimal trajectories.

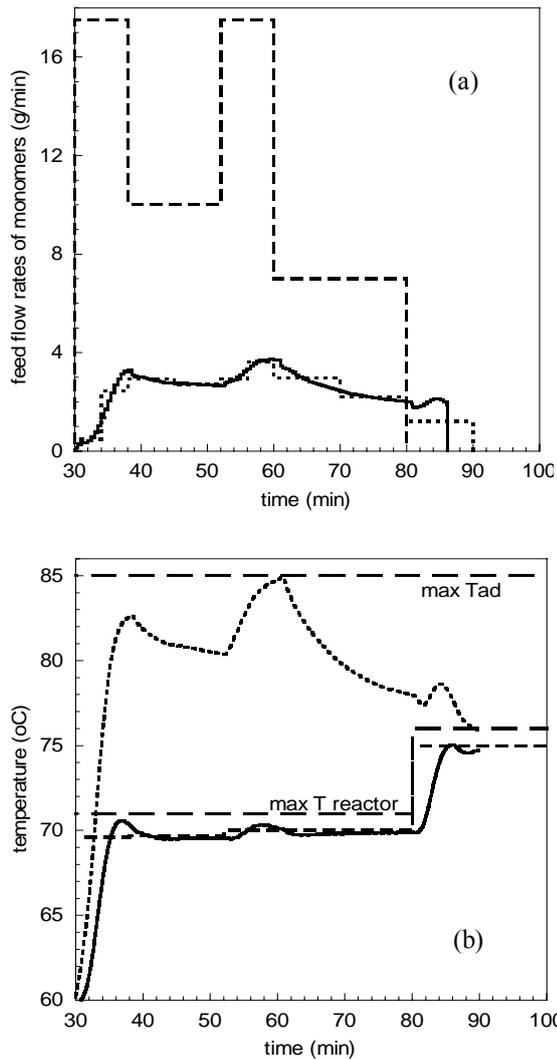


Fig. 3. Optimal set-point temperature and feed flow rate trajectories calculated by IDP procedure (Run 2). (a) VA feed flow rate (----); BA feed flow rate calculated by the NLA controller (□□); BA feed flow rate implemented (—). (b) optimal set-point temperature (----); adiabatic temperature (· · ·); reactor temperature (□□).

Keeping the number of polymer particles constant during the monomer feeding period is very important to assure that the final latex would have a certain particle diameter. Figure 4 shows that the number of particles did not change significantly after the particle nucleation period during Run 2. This indicates that there was not any significant renucleation (or coagulation) and the desired average particle diameter was reached. Therefore, the number of polymer particles was controlled just at the nucleation step and the optimal trajectories did not interfere with the number of particles. The number of polymer particles can interfere on the reaction rate due to the compartmentalized nature of emulsion polymerization. Analyzing the number of particles predicted by the model, 4.8×10^{14} particles/g of latex, and the average number of particles during the experimental reaction it is possible to verify that they were very simi-

lar (the simulated optimal final average particle diameter was 100 nm and the experimental data was 106 nm) showing a good agreement between simulated results and experimental data.

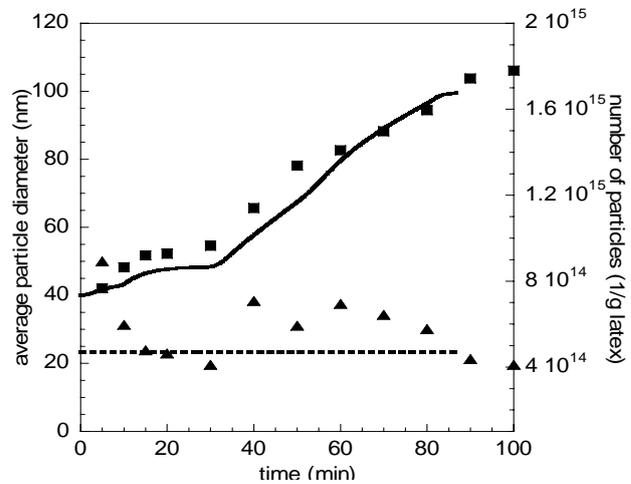


Fig. 4. Evolution of average particle diameter and number of polymer particles for Run 2. Legend: experimental (dots) and mathematical model results (lines). Average particle diameter, (■) and (—); number of particles, (▲) and (---).

Figure 5 presents the evolution of the simulated optimal overall conversion and simulated cumulative copolymer composition and those obtained during the experiment following the optimal trajectories (Run 2). A reasonable agreement between model and experimental data might be observed. Nevertheless, observing the overall conversion it is possible to note that experimental polymerization rate was faster than that predicted by the mathematical model. It is important to note that the behavior of Runs 1 and 2 should be the same during the first 30 minutes (nucleation step). Although, analyzing Fig. 2 and Fig. 5 it is possible to observe that experimental conversion did not present exactly the same behavior between both reactions and Run 1 presented a much more similar behavior to the simulated conversion.

The cumulative copolymer composition was kept during most part of the time at the desired composition (0.80 VA weight fraction), as can be observed in Figure 5. This means that optimal trajectories calculated by the mathematical model were successfully implemented for the copolymer composition control.

The slightly faster reaction rate observed experimentally in Run 2 was, probably due to the slightly higher experimental reactor temperature in comparison with the simulated temperature. The main reason for that were the overshoots in the reactor temperature, demonstrating that the parameters of the PID controller were not well adjusted in Run 2. As the parameters were the same for both reactions and the overshoots and the average reactor temperature at Run 1 were lower than those registered during Run 2, it is possible to infer that some disturbance might have interfered in the reactor

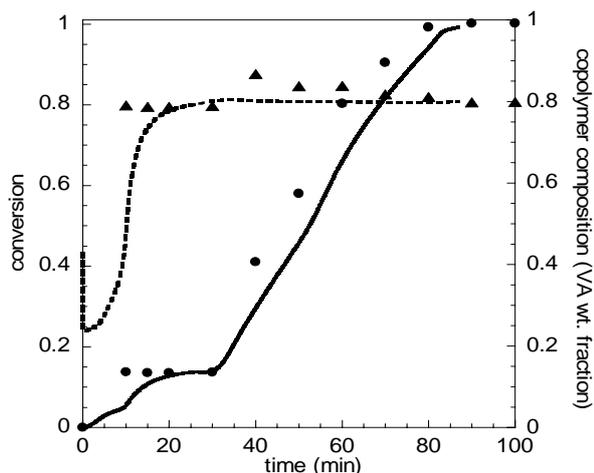


Fig. 5. Evolution of overall conversion and cumulative copolymer composition for Run 2. Legend: experimental (dots) and mathematical model results (lines). Overall conversion, (●) and (-); cumulative copolymer composition, (▲) and (----).

temperature control performance (*i.e.*, the flow rate of cold water that may vary randomly depending on the use of cold water by other utilities in the lab). This kind of disturbance is very similar to those found in industry where the flow rates of steam and cold water may vary depending on their use by other facilities. Nevertheless, it is important to emphasize that the IDP optimization procedure was able to minimize the reaction time keeping a constant copolymer composition. The mathematical model also predicted quite well the evolution of conversion and number of particles for both reactions.

V. CONCLUSIONS

Iterative Dynamic Programming (IDP) was used to minimize the reaction time of a semicontinuous emulsion copolymerization obtaining a copolymer with constant composition and taking the safety aspect into account. IDP was used to calculate optimal trajectories for the less reactive monomer feed flow rate and for the reactor set-point temperature.

The real-time implementation of the optimal trajectories was successfully carried out resulting in a significant reduction in reaction time (from 260 minutes to 90 minutes) and the copolymer composition was close to the desired value. Note that the success of real-time implementation is due to the goodness of the mathematical model and the lack of non-modeled disturbances during the real-time experiment. Even with the disturbance observed between the experiments regarding the reactor temperature control, the mathematical model predicted quite well the experimental behavior showing that the disturbances were not very significant.

The mathematical model used to represent emulsion polymerization reactions was based on a detailed process model derived from first principles and included the energy balance of the reactor and of the jacket, and also the dynamics of the reactor temperature control. This aspect is extremely important when regarding the implementation of such strategies in an industrial reactor, where the limitations of the heat removal capacity of the reactor are, usually, much higher than a lab scale reactor, and the optimal profiles calculated by the model must take it into account.

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