

Trajectory Following for the Optimization of a Batch Polymerization Reactor

C. Welz, G. François, B. Srinivasan, D. Bonvin and D. Hunkeler^a

Laboratoire d'Automatique, École Polytechnique Fédérale
de Lausanne, CH-1015 Lausanne, Switzerland

^aAQUA+TECH Specialities S.A.

CP 28, CH-1283 La Plaine, Switzerland

Abstract

This paper considers the minimization of batch time for an industrial inverse-emulsion polymerization reactor in the presence of uncertainty. A first optimization study resulted in the current industrial practice of a semi-adiabatic profile (isothermal operation followed by an adiabatic one), where the switching time between the two modes of operation is updated to meet the terminal constraint on reactor temperature, as well as a constraint on residual raw material levels. However, such a procedure requires several batches for convergence and, in addition, cannot compensate the effect of the within-run disturbances. As an alternative, we propose following a temperature trajectory with respect to conversion, for which the conversion is estimated on-line based on temperature measurements. Simulation results show an improved performance compared to the run-to-run strategy, with the additional advantage that this reduction is obtained immediately, i.e. without having to wait for run-to-run convergence.

Keywords: Dynamic optimization, Measurement-based optimization, Batch reactor, Inverse-emulsion polymerization, Polyacrylamide.

1 Introduction

Reduction of production costs is a frequent objective in batch process operation. In many cases, this corresponds to the minimization of production time while satisfying operational constraints and quality specifications. In this paper, minimization of reaction time for the copolymerization of acrylamide and quaternary ammonium cationic monomers is studied. Numerical optimization, based on a process model, can be used to compute the optimal reactor temperature profile [1, 3]. However, since the rate of conversion can be highly uncertain in practice, open-loop application of the solution computed numerically leads to sub-optimality and/or infeasibility. This is the reason why the initial industrial practice at AQUA+TECH consisted of operating the process isothermally, followed by temperature steps to reduce residual monomer levels far below the legal limit of 1000 ppm.

In a first optimization study [3], it was noted that the optimal operation can be approximated by isothermal operation (in order to satisfy the cooling constraint), followed by adiabatic operation (where the temperature increases, thereby increasing the

reaction rate). With this semi-adiabatic strategy, the reactor temperature raises during the adiabatic phase and exhibits a maximal value that has to remain below a prescribed limit, exceeding which the polymer starts to coagulate. The switching time between the two phases is crucial for respecting this constraint, and much can be gained by keeping this temperature constraint active [8].

Enforcing a terminal constraint is a difficult task. One possibility is via run-to-run control by using only batch-end measurements [3]. This approach has now become the current industrial practice at AQUA+TECH. However, it is slow in the sense that it requires several runs to converge. Also, it cannot handle disturbances occurring during the batch. Hence, the problem addressed here is that of using *on-line measurements* to guarantee the satisfaction of a *terminal constraint*, thereby ensuring feasible and near optimal operation for each batch.

The approach proposed is to follow a feasible trajectory that steers the system to the desired constraint at final time [10]. In the process under study, the reactor temperature follows a pre-defined trajectory. Also, since the final time is free (it needs to be minimized), the trajectory is defined with respect to conversion, which is estimated using a simple calorimetric approach.

The paper is organized as follows: Section 2 describes the optimization problem and presents the current industrial operating strategy, i.e. semi-adiabatic operation with run-to-run adaptation. Section 3 proposes following a trajectory based on conversion estimates for keeping the terminal temperature constraint active. Simulation results are presented in Section 4, and conclusions are drawn in Section 5.

2 Industrial Batch Polymerization Process

2.1 Polymerization Mechanism

The inverse-emulsion copolymerization of acrylamide and quaternary ammonium cationic monomers, a heterogeneous water-in-oil polymerization process, is considered. Nucleation and polymerization are confined to the aqueous monomer droplets, with each dispersed particle behaving as a segregated polymerization reactor. The polymerization follows a free-radical mechanism. Two reactions need to be considered in addition: heterophase mass transfer, and unimolecular macroradical termination with interfacial species [4]. The kinetic mechanism is derived from the mechanism of inverse-emulsion homopolymerization of acrylamide [5]. Primary radicals are produced by initiator decomposition in the oil phase. Propagation occurs in both the oil and aqueous phases (after transfer between phases of primary radicals, radicals and monomers). Unimolecular termination with interfacial emulsifier, transfer to monomer, addition to terminal double bonds, reactions of emulsifier radicals and termination by disproportionation are the other reactions that occur in the aqueous phase. A detailed kinetic mechanism and a derivation of the kinetic model by applying quasi steady-state approximation are presented in [4]. Since it is quite complex to build a detailed model for the average molecular weight, a *tendency model* that is able to predict the conversion and the average molecular weight has been developed for the purpose of simulation. The model parameters were fitted to match the industrial reality in this copolymerization process. For reasons of confidentiality, this tendency model is not presented in this paper, and all numerical values are normalized.

2.2 Optimization Problem

The optimization problem consists of minimizing the reaction time t_f by adjusting the jacket inlet temperature $T_{j,in}$ while satisfying terminal constraints on conversion $X(t_f)$ and average molecular weight $\bar{M}_w(t_f)$, and path constraints on $T_{j,in}(t)$ and the reactor temperature $T_r(t)$:

$$\min_{t_f, T_{j,in}(t)} t_f \quad (1)$$

$$\text{s.t.} \quad \dot{x}(t) = F(x(t), T_{j,in}(t)), \quad x(0) = x_o \quad (2)$$

$$X(t_f) \geq X_{des} \quad (3)$$

$$\bar{M}_w(t_f) \geq \bar{M}_{w,des} \quad (4)$$

$$T_{j,in}(t) \geq T_{j,in,min} \quad (5)$$

$$T_r(t) \leq T_{r,max} \quad (6)$$

where x is the state vector, F the system equations, and x_o the initial conditions.

2.3 Semi-Adiabatic Operation

The numerical solution to Problem (1)-(6) is approximated by semi-adiabatic operation, consisting of two intervals (Figure 1) [3]: a) an isothermal interval ($T_r(t) = T_{r,iso}$) where, up to a certain level of conversion, the temperature is limited by the heat removal constraint, and b) an adiabatic interval characterized by an increase of the reactor temperature up to its upper bound $T_{r,max}$.

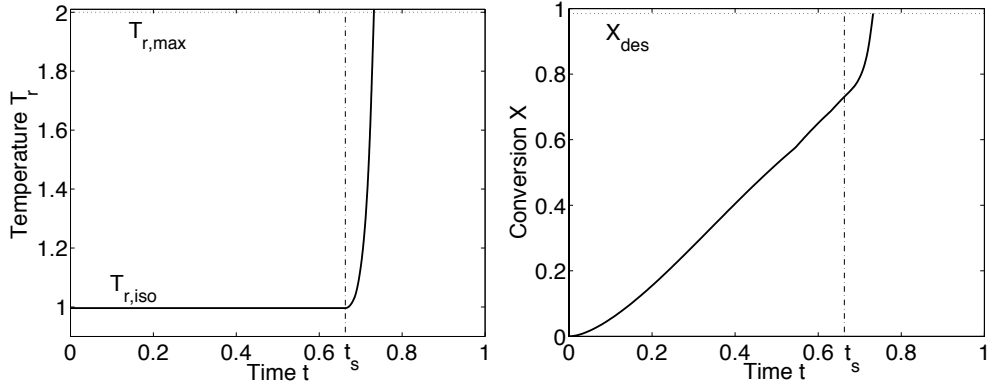


Figure 1: Approximation of the optimal solution with isothermal and adiabatic intervals separated by the switching time t_s : Reactor temperature T_r and corresponding conversion X . Both the isothermal temperature $T_{r,iso}$ and the corresponding final time t_f have been normalized to 1.

Since, after a certain level of conversion, the rate of reaction decreases, the reactor temperature can be increased in order to shorten the reaction time, while still meeting the terminal specification on average molecular weight [3]. It is important to note that the quality of the polymer (desired molecular weight) is obtained during the first half of the reaction and is not modified significantly during the second part. This fact was confirmed in simulation using the tendency model and also in real experiments [3].

2.4 Run-to-Run Adaptation of the Semi-Adiabatic Profile

With semi-adiabatic operation, the reactor temperature upper bound is only active at the final time. Consequently, this constraint will be considered as a terminal constraint in the following. Keeping it active is the essential objective in the operating strategies presented in the following sections. The other constraints are implicitly satisfied, i.e. the terminal constraint on conversion is kept active by stopping the batch at the desired conversion $X = X_{des}$, and the terminal constraint on the average molecular weight is met implicitly due to the sufficiently long isothermal interval.

The constraint on $T_r(t_f)$ depends essentially on the switching time t_s between isothermal and adiabatic operations. Switching too early to adiabatic operation may lead to runaway situations, since there will be too much monomer left in the reactor ready to be consumed. Thus, in the presence of uncertainty, a conservative switching time has to be chosen, which results in the terminal constraint not being active.

In order to reduce the batch time, the following run-to-run adaptation scheme is proposed to compensate for disturbances that remain constant over several batches (batch-wise correlated disturbances) [3]:

$$t_{s,k} = t_{s,k-1} + K [T_{r,max} - T_{r,k-1}(t_f) - b_{r2r}] \quad (7)$$

where K is the run-to-run gain. A backoff $b_{r2r} > 0$ has to be added to the temperature measurement in order to guarantee feasibility in the presence of within-run perturbations and measurement noise [8]. This backoff creates an offset towards more conservative switching times, and thus longer batch times.

3 Trajectory Following

3.1 Meeting a Terminal Constraint via Trajectory Following

Keeping the terminal constraint active via run-to-run adaptation is straightforward, though it has two problems: (i) within-run perturbations, which could be large in many cases, cannot be handled, and (ii) it requires several runs before convergence, which implies that a few non-optimal runs are necessary. This is a problem when the number of runs of the same product is limited.

Therefore, the problem addressed here is that of meeting terminal constraints within a single run. Model-based methods use a mechanistic [6] or statistical [2] model on-line in order to predict the value of the constrained quantity at final time. Then, the input is computed via optimization to enforce the terminal constraint. Instead of predicting the constrained quantity at final time based on a model, the idea used here is to follow a trajectory [10]. If the constrained quantity can be measured on-line, i.e. not only at the end of the batch but also during the batch, it is possible to track a reference trajectory whose main purpose is to guarantee meeting the terminal constraint at final time.

It is interesting to note the twist in idea – instead of the model being adapted to provide a good prediction of the system trajectory, the input is adjusted so that the system follows a reference trajectory. Since this reference trajectory leads to the active terminal constraint, the system will be steered towards the terminal constraint.

In more concrete terms for the process under study, the idea is to follow a reference for the reactor temperature. This reference is obtained from the semi-adiabatic strategy with the reactor temperature constraint active at final time, i.e. $T_r(t_f) = T_{r,max}$.

Since the final time is not fixed, the trajectory cannot be defined with respect to time. On the other hand, the final time is determined upon attaining the desired conversion, $X(t_f) = X_{des}$. So, X , instead of time, is used as the monotonous variable to parameterize the temperature trajectory. The active terminal constraint $T_{r,max}$ is met by tracking the reactor temperature reference as a function of conversion $T_{r,ref}(X)$, with $T_{r,ref}(X_{des}) = T_{r,max}$. Hence, the system is steered to the desired constraint $T_{r,max}$ at final time, since $T_{r,ref}(X(t_f)) = T_{r,ref}(X_{des}) = T_{r,max}$ by construction.

3.2 Estimation of Conversion

Since conversion is not measured directly, it has to be estimated on-line. It can be computed as a function of the rate of heat production in the reactor, which can be obtained from measurements of the jacket outlet temperature $T_{j,out}(t)$ and the reactor temperature $T_r(t)$. It is assumed here that the jacket temperature equals the jacket outlet temperatures. The rate of heat production $Q_{reac}(t)$ is obtained from an energy balance as follows [7, 9]:

$$Q_{reac}(t) = UA(T_r(t) - T_{j,out}(t)) + mc_p \frac{dT_r(t)}{dt} \quad (8)$$

where U is the overall heat transfer coefficient between the reactor and the jacket, A the effective heat exchange surface, mc_p the heat capacity of the reactor contents. These variables are assumed to be constant. The derivative $dT_r(t)/dt$ is calculated by differentiation of a fourth-order polynomial fitted using a least-squares approach.

The conversion is obtained from the heat of reaction by integrating the conversion rate:

$$\hat{X}(t) = \frac{1}{(-\Delta H)V(M_{10} + M_{20})} \int_{\tau=0}^t Q_{reac}(\tau) d\tau \quad (9)$$

where V is the reactor volume, ΔH the reaction enthalpy, and M_{10} and M_{20} the initial monomer concentrations.

A backoff $b_{track} > 0$ in the conversion estimate $\hat{X}(t)$ is considered:

$$T_{j,in}(t) = G [T_{r,ref}(\hat{X}(t) - b_{track}) - T_r(t)] \quad (10)$$

where G is the operator representing the controller. Backoff in \hat{X} pushes the rise in temperature to the safe side. The reason for using a backoff in \hat{X} rather than in T_r is as follows: During the first isothermal period, no backoff should be used, whereas a backoff is necessary when the temperature begins to rise. Therefore, instead of introducing a varying backoff in temperature, the easier option of introducing a constant backoff in conversion is preferred.

4 Simulation Results

In order to obtain a realistic simulation scenario with the tendency model, the following uncertainty is considered:

- Parametric uncertainty on reaction rate: 20% variation of the copolymerization propagation rate, due to inhibitors which are invariably present, as well as a composition drift during the reaction for processes non semi-batch in monomer addition.
- Parametric uncertainty on the rate of initiator efficiency: 100% equally-distributed variation, changed every run.
- Perturbation of the cooling water flowrate: 10% equally-distributed multiplicative noise, changed every 0.06 time units in normalized time.
- Measurement noise on the reactor temperature T_r and the cooling jacket outlet temperature $T_{j,out}$: normally-distributed additive noise with variance 0.01

The reaction rate is set to the value corresponding to the most exothermic reaction kinetics, though this value is considered to be unknown to the optimization strategies. In order to be representative, the values for the batch time and the maximum temperature are averaged over 20 realizations of measurement noise and perturbations.

4.1 Isothermal Operation

The reactor temperature T_r is kept at the constant value $T_{r,iso}$ during operation. A standard PI controller with a constant feedforward value T_r^{ff} is utilized:

$$T_{j,in}(t) = T_r^{ff} + K_p \left((T_{r,iso} - T_r(t)) + K_i \int_0^t (T_{r,iso} - T_r(\tau)) d\tau \right) \quad (11)$$

where the parameters $K_p = 0.2$ and $K_i = 0.023$ were tuned manually. The reactor temperature is kept at the normalized temperature $T_{r,iso} = 1$. The small deviations that are seen on Figure 2 are due to initiator addition in the course of the batch.

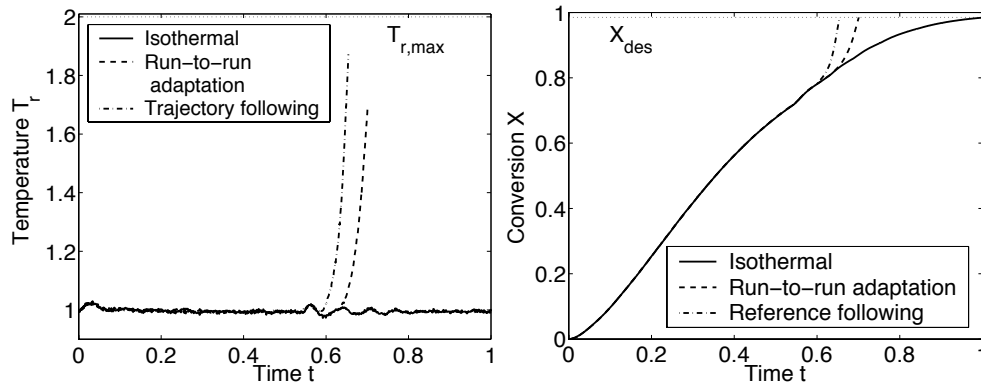


Figure 2: Comparison of three operation modes: Reactor temperature (normalized) and conversion as functions of normalized time t .

4.2 Semi-Adiabatic Strategy with Run-to-Run Adaptation

The gain in the run-to-run update law (7) is $K = 0.057$, representing a compromise between robustness and performance. The necessary backoff $b_{r2r} = 0.225$ from the

reactor temperature constraint at final time is determined such that the same is satisfied in 99% of the batches. Starting with a conservative switching time, the batch time can be reduced to 68% of its isothermal value after 5 runs. Since this run-to-run adaptation scheme cannot handle within-run disturbances, an important backoff from the active reactor temperature constraint is needed.

4.3 Trajectory Following

The tracking scheme with conversion estimation and generation of the reference temperature trajectory is shown in Figure 3.

The lookup table that yields the desired reactor temperature $T_{r,ref}$ for a given conversion is generated from a feasible solution of conversion and reactor temperature profiles (Figure 1). The same PI-controller parameters as in (11) are used to adjust the jacket temperature according to (10).

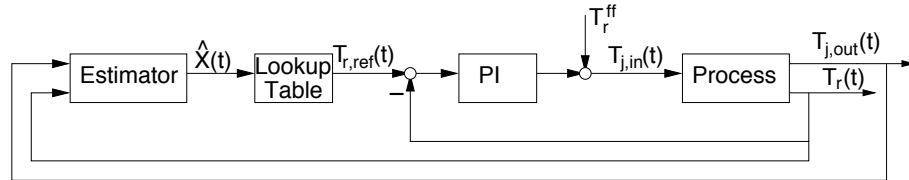


Figure 3: Tracking scheme with a PI controller and estimation of the conversion $X(t)$.

With this strategy, the conservatism that had to be introduced in the semi-adiabatic strategy can be reduced and requires a backoff $b_{track} = 1.6\%$ from the conversion estimate. Figure 2 shows that $T_r(t_f)$ gets closer to $T_{r,max}$ than in the run-to-run case. By compensating within-run disturbances, the batch time can be reduced to 66% of the isothermal strategy (Table 1).

Strategy	t_f (normalized)	$T_r(t_f)$ (normalized)
Isothermal	1.00	1.00
Semi-adiabatic, t_s adapted run-to-run	0.68	1.76
Trajectory following	0.66	1.87

Table 1: Comparison of three operation modes: Batch time and final reactor temperature (averaged over 20 realizations).

5 Conclusion

This paper has considered the optimization of an industrial batch polymerization process in the presence of uncertainty. Three operating modes are compared: maximal isothermal operation, semi-adiabatic operation with run-to-run adaptation and near semi-adiabatic operation with trajectory following.

The semi-adiabatic strategy consists of isothermal operation followed by adiabatic operation. Batch time can be reduced significantly over successive batches by adapting the switching time between the two operating modes. However, the adaptation

requires several batches to converge and necessitates a certain amount of conservatism to accommodate within-run disturbances. Following a temperature trajectory with respect to conversion (estimated from on-line temperature measurements) further reduces batch time. This reduction is obtained in a single run, which makes this strategy especially attractive. In addition, the feedback inherent to the tracking scheme helps reject within-run disturbances.

References

- [1] G. Arzamendi and J.M. Asua. Monomer addition policies for copolymerization composition control in semicontinuous emulsion copolymerization. *J.Appl.Polym.Sci.*, 38:2019–2036, 1989.
- [2] J. Flores-Cerrillo and J.F. MacGregor. Within-batch and batch-to-batch inferential-adaptive control of semibatch reactors: A partial least squares approach. *Ind.Eng.Chem.Res.*, 42:3334–3345, 2003.
- [3] G. Francois, B. Srinivasan, and D. Bonvin. Run-to-run adaptation of a semi-adiabatic policy for the optimization of an industrial batch polymerization process. *Ind.Eng.Chem.Res.*, 2004. submitted.
- [4] D. Hunkeler and A.E. Hamielec. Mechanism, kinetics and modelling of inverse-microsuspension polymerization: 2. Copolymerization of acrylamide with quaternary ammonium cationic monomers. *Polymer*, 32(14):2626–2640, 1991.
- [5] D. Hunkeler, A.E. Hamielec, and W. Baade. Mechanism, kinetics and modelling of the inverse-microsuspension homopolymerization of acrylamide. *Polymer*, 30:127–142, 1989.
- [6] K.S. Lee and J.H. Lee. Model predictive control for nonlinear batch processes with asymptotically perfect tracking. *Comp.Chem.Eng.*, 21:873–879, 1997.
- [7] H. Ni, K. Debelak, and D. Hunkeler. Fuzzy logic supervised ANN feedforward control for a batch polymerization reactor. In *American Control Conference*, volume 3, pages 1777–1781, Seattle, USA, June 1995.
- [8] B. Srinivasan, D. Bonvin, E. Visser, and S. Palanki. Dynamic optimization of batch processes: II. Role of measurements in handling uncertainty. *Comp.Chem.Eng.*, 27:27–44, 2003.
- [9] O. Ubrich, B. Srinivasan, P. Lerena, D. Bonvin, and F. Stoessel. The use of calorimetry for on-line optimisation of isothermal semi-batch reactors. *Chem.Eng.Science*, 56:5147–5156, 2001.
- [10] C. Welz, B. Srinivasan, and D. Bonvin. Combined online and run-to-run optimization of batch processes with terminal constraints. In *ADCHEM'04*, pages 55–62, Hong-Kong, January 2004.