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Run-to-Run Adaptation of a Semiadiabatic Policy for the Optimization of an Industrial Batch Polymerization Process

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The problem of minimizing the batch time of the copolymerization of acrylamide and quaternary ammonium cationic monomers at the industrial level is considered. An adjustable model of the optimal solution is used in the optimization. The model consists of two arcs: The first is isothermal and limited by heat removal constraint, whereas the second is adiabatic. The switching time between the two arcs is the only free parameter that is adapted on a run-to-run basis using batch-end measurements. A batch time reduction of 35% is observed after three batches.

1. Introduction

Over the past several decades, the commercial use of cationic water-soluble polymers has grown remarkably. Cationic copolymers with acrylamide are used as flocculants in wastewater treatment or as fines retentates in paper making, to name just two applications, and constitute a market of 2 billion Euros per year. One way to produce these polymers is via batch inverse-emulsion copolymerization, which is one of the subtlest of all polymerization processes. Despite its relative complexity, batch inverse-emulsion polymerization is the method of choice whenever specifications on the conversion, particle size, or molecular weight distribution are stringent.[1] Because these processes use water instead of solvents, they are also of great interest for environmental reasons.[2] Note that, for this specific reaction, constraints are particularly stringent: Acrylamide is highly toxic, and its residual concentration has to be below 1000 ppm, whereas the copolymer is consumable.

Dynamic optimization represents the natural choice for reducing production costs while meeting operational and product quality constraints. For emulsion polymerization processes, optimal temperature profiles and/or monomer and initiator feed rate profiles have been determined off-line on the basis of a process model.[3−6] However, such an approach might not lead to optimality because of the presence of uncertainty. Industry typically deals with uncertainty by introducing a certain amount of conservatism that guarantees feasibility (i.e., constraint satisfaction), even in the worst scenario.[7,8] However, the performance might be rather poor. Hence, an important issue is the use of batch-end measurements to reduce this conservatism and improve performance.

In this paper, the dynamic optimization of an industrial batch copolymerization reactor is investigated. It is shown that the nominal solution, which is based on a tendency model, is potentially unfeasible in the presence of model mismatch and disturbances. Thus, it is proposed to use a simple *model of the solution*

obtained from the nominal solution and adapt it using measurements so as to satisfy the necessary conditions of optimality.[9,10]

The optimal temperature profile is approximated by a semiadiabatic profile consisting of two arcs: The first is isothermal and corresponds to the heat removal limitation, whereas the second is adiabatic and compensates the decrease in reaction rate by an increase in temperature. Hence, the input is parametrized using only one parameter, the switching time between the two arcs, which is updated in a batch-to-batch manner so as to minimize the batch time while enforcing a terminal constraint on the reactor temperature. The batch time is defined upon reaching the desired conversion. Experiments on a 1-ton reactor confirm the validity of the model of the solution and the efficiency of the run-to-run adaptation, leading to a 35% reduction in batch time.

This paper is organized as follows: Section 2 presents the industrial polymerization process in terms of the kinetic mechanism and common industrial practice. The formulation of the dynamic optimization problem and standard solution approaches are discussed in section 3. The semiadiabatic policy and its adaptation are presented in section 4, together with simulation and industrial experimental results. Section 5 concludes the paper.

2. Industrial Polymerization Process

2.1. Mechanism. We consider the inverse-emulsion copolymerization of acrylamide and quaternary ammonium cationic monomers, a heterogeneous water-in-oil polymerization process. 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 with, in addition, heterophase mass transfer and unimolecular macroradical termination with interfacial species.[11] The kinetic mechanism is derived from the mechanism of the emulsion homopolymerization of acrylamide.[12] 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, addi-

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Table 1. Principal Reactions of the Inverse-Emulsion Copolymerization Process

Oil-Phase Reactions
initiation by initiator decomposition
reactions of primary radicals
propagation reactions

Transfer between Phases of
initiator
comonomers
primary radicals

Aqueous-Phase Reactions
reactions of primary radicals
propagation reactions
unimacromolecular termination with emulsifier
reactions of emulsifier radicals
transfer to monomer
addition to terminal double bond
termination by disproportionation

tion 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 through the application of a quasi-steady-state approximation are presented in ref 11. The principal reactions can be summarized in Table 1.

At the industrial scale, other effects need to be considered. For example, the initiator efficiency and the efficiency of initiation by emulsifier radicals can vary significantly between batches because of the residual oxygen concentration at the outset of the reaction. Hence, chain-transfer agents and reticulants are added to the recipe to produce the desired average molecular weight because this characteristic is, together with the copolymer composition, one of the most important variables that influence the efficiency of the copolymer.[13] Although they have no influence on the conversion profile, these two additives modify the structure of the polymer and, consequently, its molecular weight distribution. For instance, transfer to the chain-transfer agent decreases the average molecular weight. Thus, it is quite complex to build a detailed model for the average molecular weight. Hence, a *tendency model* capable of predicting the conversion and the average molecular weight has been developed. Even though this tendency model uses the standard moment terminology for homopolymerization processes, the parameters were fitted to match the industrial reality in this copolymerization process. For reasons of confidentiality, this tendency model cannot be presented in this paper.

2.2. Common Industrial Practice. The aforementioned copolymerization process has, until very recently, been operated isothermally. The reactor temperature level is chosen on the basis of the following two characteristics:

Heat Removal Limitation. Because of the exothermicity of the reaction and the successive injections of initiator during the batch, it was observed that, for the chosen reactor temperature, the jacket temperature approaches its minimum value (see experimental results in Figure 1). Hence, there would be a high risk of runaway with higher reactor temperatures.

Molecular Weight Specification. The chosen reactor temperature meets the molecular weight specifications. Although a higher temperature in the early part of the batch would accelerate the reaction, it would also modify the structure and properties of the polymer, thus leading to shorter polymer chains and lower molecular weights. However, the reactor temperature is increased
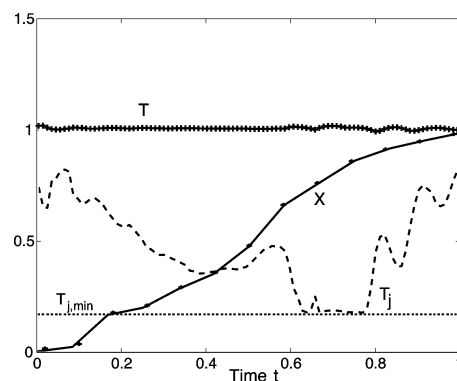

Figure 1. Profiles measured during isothermal operation: reactor temperature (T), jacket temperature (T_j), and conversion (X). The reactor temperature and the batch time have been normalized to 1.

at the end of the reaction (once conversion is above 98.5%) to enforce residual acrylamide consumption, without significant undesirable effects on the molecular weight.

3. Model-Based Optimization Strategies

The time needed to complete a batch exceeds the reaction time because one needs to consider the time to fill the reactor, the induction time, the time to clean the reactor, etc. However, minimizing the reaction time is the most efficient way to increase the productivity of the whole batch operation, because the duration of the filling and cleaning operations are typically fixed.

3.1. Minimum-Time Problem. The minimum-time problem can be formulated mathematically as the following dynamic optimization problem

$$\min_{t_f, T(t)} t_f \tag{1}$$

$$\text{s.t.} \quad \dot{x}(t) = F[x(t), T(t)], \quad x(0) = x_o \tag{2}$$

$$X(t_f) \geq X_{min} \tag{3}$$

$$\bar{M}_w(t_f) \geq \bar{M}_{w,min} \tag{4}$$

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

$$T(t) \leq T_{max} \tag{6}$$

where t_f is the final time to be minimized, $T(t)$ is the reactor temperature, x is the n-dimensional state vector, F represents the system equations, and x_o represents the initial conditions. The system is subject to constraints that can be divided in two categories:

Terminal Constraints: Inequalities 3 and 4. X_{min} is the lower bound on the final conversion $X(t_f)$, and $\bar{M}_{w,min}$ is the lower bound on the final mass-average molecular weight, $\bar{M}_w(t_f)$. The lower bound on the conversion is due to the fact that the monomer is toxic, and that on the average molecular weight guarantees the polymer quality.

Path Constraints: Inequalities 5 and 6. $T_{j,in,min}$ is the minimum value of the jacket inlet temperature $T_{j,in}(t)$, and T_{max} is the upper bound for the reactor temperature $T(t)$.

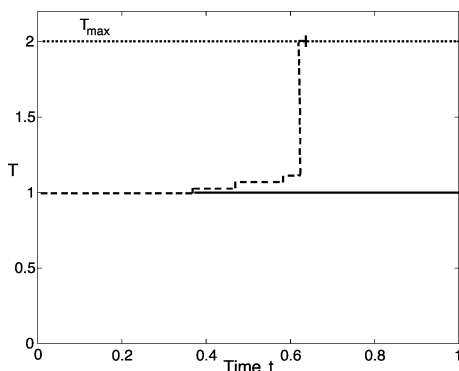For the sake of simplicity, $X_{min} = 98.5\%$ is considered. Above this conversion, the tendency model is no longer

Figure 2. Piecewise-constant optimal temperature profile (dashed line) compared to isothermal profile (solid line). Both the isothermal temperature level and the corresponding final time have been normalized to 1. The optimal temperature profile leads to a 37% reduction in batch time.

valid, because additional operations such as scavenging that are needed to ensure acrylamide total consumption are not modeled.

3.2. Nominal Optimization Based on the Tendency Model. The problem described by eqs 1−6 represents a dynamic optimization problem, the solution of which is typically obtained using a numerical optimization package. Numerical optimization based on a tendency model is performed with a piecewise-constant temperature profile. Five intervals of different but fixed lengths are considered. Intervals of different lengths are chosen so as to enable the adjustment of the reactor temperature profile to compensate for the decrease in reaction rate. The computed optimal reactor temperature profile is given in Figure 2.

The nominal solution consists of two arcs: The temperature is maintained constant during the first part of the batch and is then increased to its upper bound. These arcs can be interpreted as follows:

Heat Removal Limitation. Up to a certain level of conversion, the temperature is limited by the heat removal constraint. Because a long first arc is considered initially, the operation is isothermal and corresponds very closely to what is used in industrial practice. Also, this first isothermal arc ensures that the molecular weight constraint will be satisfied as it is mostly fixed by the chain-transfer agent concentration.

Intrinsic Compromise. The second arc compensates for the decrease in reaction rate by an increase in reactor temperature. Increasing the reactor temperature accelerates the reaction, but decreases the molecular weight. Even though the molecular weight decreases rather rapidly, this happens during a shorter time, which allows the molecular weight constraint still to be satisfied.

Note that the quality of the polymer is obtained during the first half of the reaction and is not modified significantly during the second part. This fact was confirmed through simulations with the tendency model and also through real experiments. Also, the polydispersity index and the cumulative number of consecutive cationic charges, which are other indicators of the copolymer efficiency, are not affected by the increase in reactor temperature.

3.3. Unfeasibility of the Nominal Solution. Even though the nominal profile allows for a 37% reduction in batch time, it cannot be implemented for the following reasons: (i) The heat removal constraint is nearly

reached between 40 and 75% conversion (Figure 1). Therefore, the risk of runaway is too high to allow any increase in reactor temperature at low conversion levels. (ii) The small temperature steps dictated by the nominal optimal solution cannot be implemented in view of the prevailing measurement noise and the modest performance of the cascade control loop.

The feasibility issue calls for the introduction of conservatism. For example, a reactor temperature policy that ensures feasibility for all possible situations could be computed. This method, which is referred to as robust optimization, has been studied extensively in the literature.[14] However, in this paper, a different approach is used, and it is discussed in the next section.

4. Semiadiabatic Policy for Optimization

4.1. Approximation of the Optimal Solution as a Semiadiabatic Policy. The optimal reactor temperature profile can be approximated as follows:

Heat Removal Limitation Approximated as an Isothermal Arc. The first part is approximated by an isothermal arc. The reactor temperature is maintained constant at the temperature corresponding to the isothermal policy. This arc satisfies the heat removal limitation. Furthermore, this temperature ensures that, during most of the reaction, a copolymer with the same average molecular weight as for the isothermal policy is produced.

Intrinsic Compromise Approximated as an Adiabatic Arc. The second part is approximated by an adiabatic arc. The reactor temperature control loop is opened, and the flow rate of the cooling fluid is set to zero. The heat generated by the reaction leads to an exponential temperature increase. It might in some way be "shocking" to propose that the reactor be left without control during this arc. Note, however, that the operators have a very efficient way of stopping the reaction in case of danger, which cannot be explained here for confidentiality reasons.

Note that the term "adiabatic" is used loosely here. The reactor zone could only be considered adiabatic if it did not exchange heat with the outside. Here, small amounts of heat are transferred to the jacket and also lost to the ambient. However, the term adiabatic is used for the sake of simplicity of terminology.

The reactor temperature can be parametrized using only one free parameter, the switching time between the isothermal and adiabatic arcs. The final time is determined when the desired conversion is reached.

4.2. Semiadiabatic Conservative Policy. Because of variations in the rate of reaction, a poor choice of the switching time can lead to a violation of the constraints on the molecular weight and maximum temperature. To guarantee feasibility, a conservative value of the switching time should be determined from the worst-case scenario. For instance, a certain amount of parametric uncertainty corresponding to what can be observed in industrial reactors should be introduced. As with the proposed input parametrization, the final reactor temperature depends only on the residual amount of reactants at the switching time between the two arcs; the worst case corresponds to the slowest possible rate of reaction. In our case, this conservative value is determined from operator experience.

4.3. Run-to-Run Adaptation of the Semiadiabatic Policy. Considering the proposed input parametrization, the optimization problem described by eqs
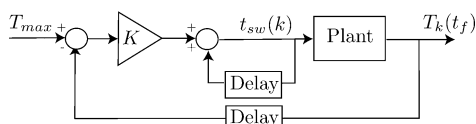
Figure 3. Adaptation scheme for the switching time.

1−6 can be rewritten as the following static optimization problem[10]

$$\min_{t_f, t_{sw}} J = t_f(t_f, t_{sw}) \tag{7}$$

$$\text{s.t.} \quad X_f(t_f, t_{sw}) \geq X_{min} \tag{8}$$

$$\bar{M}_{w,f}(t_f, t_{sw}) \geq \bar{M}_{w,min} \tag{9}$$

$$T_f(t_f, t_{sw}) \leq T_{max} \tag{10}$$

where X_f is final conversion, $M_{w,f}$ is the final weight-average molecular weight, and T_f is the final reactor temperature.

Note that path constraint 5 on $T_{j,in}(t)$ is assumed to be satisfied through the choice of the temperature level in the isothermal arc.

Because (i) the constraint on the molecular weight is less restrictive than that on the reactor temperature, (ii) the final time is defined upon meeting the desired conversion, and (iii) the terminal constraint on reactor temperature is active at the optimum, the necessary conditions of optimality (NCO) for the problem in eqs 7−10 reduce to

$$T(t_f) - T_{max} = 0 \tag{11}$$

$$\frac{\partial t_f}{\partial t_{sw}} + \nu \frac{\partial [T(t_f) - T_{max}]}{\partial t_{sw}} = 0 \tag{12}$$

where ν is the Lagrange multiplier for the constraint on the reactor temperature. The NCO consists of two parts: (i) the constraint part (eq 11) and (ii) the sensitivity part (eq 12). The idea used for adaptation is to enforce the two parts of the NCO using measurements.[10] In this example, enforcing the constraint part of the NCO provides the optimal value of t_{sw}, whereas the sensitivity part serves to compute the Lagrange multiplier ν. Because the value of ν is of no practical interest, only the adaptation of t_{sw} on a run-to-run basis using off-line measurements to satisfy the terminal constraints is considered.[14] The adaptation law reads

$$t_{sw}(k) = t_{sw}(k-1) + K[T_{max} - T_{k-1}(t_f)] \tag{13}$$

where $t_{sw}(k)$ is the switching time for the kth batch, K is the controller gain, and $T_{k-1}(t_f)$ is the value of the final (and maximal) reactor temperature for the $(k-1)$st batch. More details regarding the general run-to-run scheme can be found in ref 10. The adaptation is represented schematically in Figure 3.

The experimental results for the run-to-run adaptation on a 1-ton reactor are presented in Figure 4 and are also reported in Table 2. It is seen that, as the batch counter increases, the switching time decreases, the final reactor temperature increases, and the batch time decreases. Also note that T does not reach its upper bound because of the margin introduced to address the fact that run-to-run adaptation cannot handle within-batch disturbances.
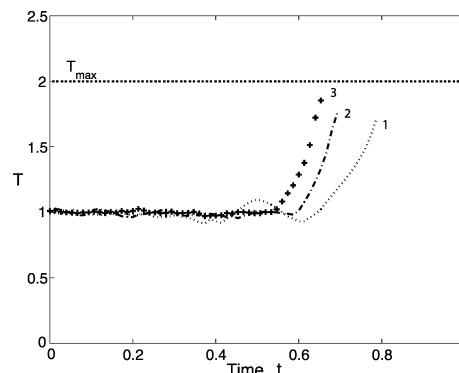

Figure 4. Adaptation of the semiadiabatic policy for batches 1 (dotted line), 2 (dash−dotted line), and 3 (solid line).

Table 2. Experimental Results

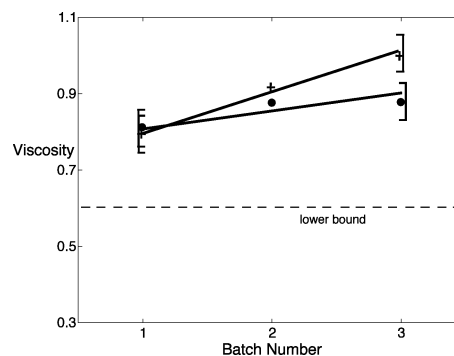| batch	strategy[a]	t_{sw}	$T(t_f)$[b]	t_f
−	isothermal	−	1.00	1.00
1	SA conservative	0.62	1.70	0.78
2	SA after 2 runs	0.58	1.78	0.72
3	SA after 3 runs	0.53	1.85	0.65

[a] SA = semiadiabatic. [b] $T_{max} = 2$.

Figure 5. Evolution of the measured product (+) and inverse (○) viscosities from batches 1−3. Brackets indicate the confidence levels of the measurements.

The conservative and adapted policies are, of course, more cautious than the nominal optimal one. Even though temperature is increased faster, this increase is initiated much later than in the nominal solution, thus reducing the risk of runaway at low conversion.

The fact that the molecular weight quality constraint is satisfied is supported by measurements of the product viscosity (i.e., the viscosity of the polymer at the end of the reaction) and of the "inverse" viscosity (i.e., the viscosity of the product sold to the customers), as shown in Figure 5. Because the acceptable range for both viscosities lies between 0.6 and 1.2, with a target value of 0.9, excellent product was made. The viscosity even seems to increase with the batch number. However, this increase is not significant with respect to the confidence of the viscosity measurements.

Several remarks are in order: (i) The temperature profile for all runs stays within bounds, i.e., no constraint violation. (ii) Run-to-run adaptation of the semiadiabatic policy is applicable to other recipes (for producing different but related polymers) provided that a feasible initial guess of the switching time and batch-end measurements of the reactor temperature exist. (iii) Run-to-run adaptation can reject variations that persist over several batches. (iv) Because no control is available during the second arc, within-run variations cannot be handled. Hence, this issue has been addressed by

introducing a margin on T_{max}. Furthermore, the control loop for the reactor temperature can be activated if necessary. (v) The reaction time reduction of 35% corresponds to a reduction of 10−15% of the time needed for the whole batch operation, which includes the time for filling of the reactor, the induction time, the reaction time, the time for additional operations, and the time for cleaning of the reactor.

5. Conclusion

Measurement-based adaptation of the reactor temperature profile has been investigated in the context of minimizing the reaction time for an industrial inverse-emulsion polymerization process. An optimal piecewise-constant policy is determined using a simple tendency model of the reactor. However, this solution is not applicable to industrial reactors because of the presence of uncertainty. Thus, a model of the optimal solution is obtained that consists of both an isothermal arc and an adiabatic arc, with the switching time between the two being the only free parameter. Run-to-run adaptation of the switching time was performed, leading to a batch time reduction of 35% in a 1-ton industrial reactor without any constraint violation.

Future research will include measurement-based optimization of the initiator concentration profile. Also, it is proposed that these techniques be applied to a variety of recipes and different reactor scales that are currently used such as 3-, 8-, and 12-ton reactors. Finally, a trajectory-following approach could be investigated for which an off-line-determined trajectory is followed using available on-line measurements.[15,16] This approach can bring the reactor to its active terminal constraint on temperature in a single batch and, in addition, is able to reject within-run disturbances via feedback.

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