Dynamic Optimization of an Emulsion Polymerization Process Using an Embedded Monte Carlo Model for Bimodal MWD

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Abstract
The molecular weight distribution (MWD) of polymers affects many end-use properties and is therefore a major production target. The desired MWD can also be multi-modal, which can be achieved by using chain-transfer agents. As these products are specialty chemicals, they are most often produced in semi-batch operation leading to inherent non-linear dynamics. By using dynamic optimization, production time can be reduced while producing the targeted quality. In this work, we consider the model-based dynamic optimization of an emulsion polymerization process to achieve a bimodal MWD while reducing the batch time. The degrees of freedom consist of the isothermal reactor temperature, feed rates of monomer, initiator and chain-transfer agent. We use a combined model consisting of a deterministic kinetic model and a stochastic Monte Carlo polymer architecture model. The kinetic model describes macroscopic variables, such as concentrations. Distinct chains are simulated in a polymer particle using the Monte Carlo model, and many particles are computed in parallel. The time-varying reaction rates used in the Monte Carlo model are computed in the kinetic model. By taking all simulated chains and their respective weights, the MWD can be constructed. A Monte Carlo approach is chosen as it allows to simulate properly the transfer to polymer and branching reactions. To solve the dynamic optimization problem, we select a derivative-free surrogate model based optimizer due to the stochastic nature of the Monte Carlo model. For the Monte Carlo model, gradients are not readily available. The results show a reduction of the batch time between 6.2 and 7.5 % compared to the base recipe while the product quality is satisfied.

Keywords: Dynamic Optimization, molecular weight distribution, derivative-free optimization, Monte Carlo simulation

1. Introduction
Polymers produced via emulsion polymerization have various applications such as paints, adhesives or drug delivery. For each use case, the polymer product should have usually different properties like viscosity, stickiness, etc. An important quality attribute of polymers is the molecular weight distribution (MWD), which can be narrow or broad, unimodal or bimodal. Due to strong competition among manufactures, optimal process operations can save cost and therefore protect operating margins. Especially polymer products are affected heavily by process operations, as they are known to be products-by-process (Asua, 2007). Therefore, optimal process operations must both increase the economic benefit and achieve the same customer demanded quality. Several authors have
addressed the problem of optimal control of polymerization processes. Sayer et al. (2001) use iterative dynamic programming to optimize the operations of a semicontinuous emulsion process with fixed batch time to reach a desired MWD in-silico. The MWD is computed via an adaptive collocation technique. Vicente et al. (2001) decompose the MWD into instantaneous MWD distributions over the global conversion, which is possible as only linear polymer chains are considered. They optimize the total process time. Vicente et al. (2002) also use iterative dynamic programming to achieve a desired composition and MWD, which is modeled by adaptive orthogonal collocation. They test the computed optimal feed rates in a lab scale reactor and achieve MWDs fairly close to the desired ones. Saliakas et al. (2007) optimize for minimal batch time and the deviation to the desired MWD is added as quadratic penalty to the objective function. Two models describing the MWD of the homopolymerization are compared, one model with fixed pivots and one using orthogonal collocation on finite elements. Pontes et al. (2011) model the MWD with orthogonal collocation for a continuous steady state operation and optimize operations for an economic objective function, consisting of the cost of raw materials and sale price of product.

All the works mentioned so far use deterministic models to describe the MWD. Despite the vast use of Monte Carlo models for polymerization systems, there is little work on the optimization with such models embedded. Gao et al. (2018) compare three derivative-free optimizers in case studies with a kinetic Monte Carlo process embedded. A free-radical polymerization is modeled which allows to describe microstructural aspects of the copolymer such as the dyad fractions. Ma et al. (2018) employ a steady-state Monte Carlo simulation in a derivative-free optimization environment. The chemical composition distribution is used as a micro-structural quality attribute. Overall the optimization problem consists of seven degrees of freedom. Mohammadi et al. (2018) use the outputs of a Monte Carlo model to train an artificial neuronal network which is optimized using a genetic algorithm to find optimum reaction conditions consisting of the monomer ratio, catalyst composition and chain shutting agent concentration.

In this contribution, a typical industrial setting is considered, where a given recipe should be optimized. The desired MWD is known from a reference batch. Using this recipe as starting point, an optimal process operation scheme is computed achieving the same MWD as quality while reducing the batch time. The contribution is structured as follows. In Section 2, the model and its extensions are briefly described. The dynamic optimization problem is formulated in Section 3 and its solution approach is presented. A case study with a bimodal MWD is dealt with in Section 4 and the contribution is summarized and conclusions are drawn in Section 5.

2. Model description and model extensions

The considered copolymerization is modeled by a hybrid model consisting of a deterministic kinetic model and Monte Carlo model describing the polymer chains described by Chaloupka et al. (2017) and shortly introduced here. The macroscopic variables, like concentrations, are solved using a deterministic kinetic model of the emulsion polymerization. Then, the computed trajectories of reaction rates are used in the Monte Carlo simulation, where each single particle is computed and individual chains are simulated. The Monte Carlo simulation is sped up by considering the propagation reaction separately. The models are implemented in Matlab. As it is assumed that the polymer particles do not influence each other, they can be computed easily in parallel. For this contribution, this model is extended by chain-transfer agent (CTA) and its related reactions. Therefore, bimodal distributions can be simulated and optimized. Chain
transfer agents increase the chain transfer reaction rate and lead in general to shorter chains. For a bimodal distribution, the CTA is added in a later stage to produce shorter chains while the long chains have already been generated. The new chain transfer reaction is added to the overall scheme:

\[ M_n^* + R - X \rightarrow M_n - X + R^* \]  

(1)

where \( M_n, R-X \), the superscript \(^*\) define a polymer chain with \( n \) monomeric units, the chain transfer agent and a radical, respectively. The parameters for the CTA kinetics are chosen from literature. An isothermal operation is assumed.

In the overall simulation scheme, the kinetic part cannot be parallelized in the same fashion as the Monte Carlo part. However, for different inputs, different ODE integrators compute the solution faster. Matlab offers six different integrators, each with different advantages and disadvantages. There is no additional cost to integrate the kinetic model with all available integrators in parallel and the simulations are stopped after the first result is available. All integrators use the same integration tolerances and the same model.

Compared to (Faust et al., 2019), a new binning strategy for the computed chains is applied which increases the exactness of the MWD calculation. Here, the computed polymer chains from all particles are taken and binned into the MWD. Therefore, the computation accuracy increases.

3. Dynamic optimization problem formulation and solution approach

The goal of the dynamic optimization is to find an operating scheme that minimizes the batch time while producing the desired MWD, which is given by the base recipe operation (2). In Faust et al. (2019) the reactor temperature, batch time, monomer and initiator feed are optimized. Here, the CTA feed is added to the degrees of freedom.

\[
\begin{align*}
\min_{\hat{m}_M(t), \hat{m}_I(t), \hat{m}_\text{CTA}(t), T_R, t_f} & \quad t_f \\
\text{s.t. kinetic ODE model} & \\
\text{stochastic MWD model} & \\
\int_0^{t_f} \hat{m}_M(t) dt &= n_{\text{M, total}} \\
T_R^{\text{min}} &\leq T_R \leq T_R^{\text{max}} \\
\varepsilon_{\text{MWD}}^{\text{max}} &\geq \sum_{k=1}^{N} (MWD(k) - MWD^{\text{ref}}(k))^2 \\
X^{\text{ref}} &\leq X(t_f)
\end{align*}
\]

(2a) (2b) (2c) (2d) (2e) (2f) (2g)

where \( \hat{m}_M(t), \hat{m}_I(t), \hat{m}_\text{CTA}(t), T_R, t_f \) refer to the monomer feed rate, initiator feed rate, CTA feed rate, reactor temperature and total time, respectively. \( \varepsilon_{\text{MWD}}^{\text{max}} \) denotes the absolute squared deviation to the reference MWD and is constrained in (2f). Constraint (2g) refers to the minimum conversion at the end of the batch.

In this work, the open source solver MaTSumoTo, developed by Müller et al. (2013), is used. A thin-plate spline with a polynomial tail is used as surrogate function. Matlab’s fmincon is used as local optimizer of the surrogate function. Two new sample points are
generated for each version of the surrogate function. If these two sample points are close to each other or close to already evaluated inputs, the search space is explored by maximizing the distance the evaluated points. As we optimize the surrogate with a local gradient-based optimizer, we can add constraints if we know the underlying function in terms of the degrees of freedom. Of course, the reformulation using penalties would not be necessary, if we have a functional expression of all constraints using the degrees of freedom. One could argue that at least the conversion constraint (2g) could be added as nonlinear constraint as it depends only on the evaluation of the ODE system. However, this would slow down the optimization of the surrogate with such an embedded ODE problem. Therefore, only the ratio feeds are used as linear inequality constraints (3b) to the optimization problem to be solved:

\[
\begin{align*}
\min_{x_j^M, x_j^I, \rho_j^{\text{real}}, \rho_j^{\text{total}}, \rho_{\text{CTA}}, t_j} & \sum_{k=1}^{N_k} (MWD(k) - MWD^\text{ref}(k))^2 + w_{\text{line}} \sum_{j} x_j^2 + w_{\text{ineq}} \sum_{j} (\min(0, X_j - X_j^\text{ref}))^2 \\
\text{s.t.} & \sum_{j=2}^{N} x_j^p \leq 1 \quad \forall p \in \{M, I, \text{CTA}\}
\end{align*}
\]  

4. Case study with bimodal target MWD

In this case study, a given reference batch recipe is optimized for batch time while achieving the same quality measures, such as the molecular weight distribution and the overall monomer conversion at the end of the batch. The desired bimodal molecular weight distribution is a result of the use of CTA.

The reference process operation takes 12600 seconds. The monomers are fed for the first 9000 seconds, and the CTA is fed from that time point on for one hour. The initiator feed is stopped after 7200 seconds. The problem is discretized using seven piecewise constant control profiles for each controlled feed rate. No CTA is fed during the first two control intervals, as it is known that the CTA will shorten the chains and the long chains will not be generated. Together with the reactor temperature and the total batch time, the problem consists of 20 degrees of freedom for optimization. The number of function evaluations is limited to 1000. In Table 1, an overview of the numerical results is given, both for the reference case and three optimization runs. As the model is stochastic and the optimization of the surrogate is started from random points, the optimization is started three times to check the consistency of the result. In total, 100 particles are simulated in parallel with the Monte Carlo model.

Compared to the reference, the batch time is reduced between 6.2 and 7.4% for the three runs by the optimization. The trajectories for different key states and inputs are shown in Figure 1. The reactor temperature is more or less unchanged compared to the reference, which is an indication that the quality is affected strongly by the reactor temperature. The reactor temperature difference between the runs is less than 0.2 K. In a pure batch time minimization with an inequality constraint on the overall conversion only, it is expected that the reactor is operated at the maximum allowed temperature. The overall conversions for the three runs differ in the first interval, but are relatively similar from that point on. The monomer feed for the optimized cases is higher than in the reference case leading to a faster reaction rate. Qualitatively, the optimized CTA feed very similar to the reference, only the total amount is increased.
Table 1 Numeric values of reference and optimization runs

<table>
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<th></th>
<th>Conversion [-]</th>
<th>Time [s]</th>
<th>Objective value</th>
<th>Time saving [%]</th>
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<td>Reference</td>
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<td>12600</td>
<td>1.68</td>
<td>-</td>
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<tr>
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<td>Run 2</td>
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<tr>
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<td>1.47</td>
<td>7.4</td>
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</table>

5. Summary and Conclusion

We presented an approach to optimize the process operation of a semi-batch reactor while achieving desired product specifications. The molecular weight distribution defines the product quality and is bimodal due to the use of chain transfer agent being added during the end of the batch. As the underlying model has embedded Monte Carlo simulations, a gradient-free optimization solver is used. A surrogate model is built from objective function evaluations, which consists of the objective and penalty terms for the nonlinear constraints where no algebraic function of degrees of freedom is known. Using random starting points, the surrogate model is optimized locally to generate new sample points and which are used to update the surrogate function. For the case study considered, the batch time is reduced between 6.2 and 7.2% while achieving the same polymer properties. The optimization problem formulation is flexible and does allow for integrated
product and process development. It can be tested whether for a given new molecular weight distribution, a process producing this quality can be found.

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