Dynamic Modelling & Optimization of AN/Bd (NBR) Emulsion Copolymerization in a Continuous Reactor Train

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1. Introduction

LARGE scale production of commodity rubbers such as styrene-butadiene (SBR) or nitrile-butadiene (NBR) is done using a continuous process. Due to the specific end-use requirements of the polymer products the reactor train must be carefully controlled, so that product quality is maintained and, at the same time, raw materials, off-spec product, and reaction time are minimized. These variables all translate to making a product as cheap and as fast as you can, while maintaining quality standards set by the customer.

Apart from developing and validating a model for the industrial production of NBR, a second goal of this project is to investigate control and optimization strategies that are practical enough to be applied in an industrial environment. More specifically the present work will investigate the system behaviour of a train of reactors by manipulating various ingredient feed flows (monomer, CTA, emulsifier), and then suggest practical methods/policies to control the system while meeting a specific objective.

Though, many different strategies can be suggested, from an off-line perspective, industry desires precise control over the polymer properties in real-time. This stresses the need for appropriately selected soft-sensors, which use on-line process measurements and a mechanistic model to optimally estimate unmeasurable state variables.

2. Optimization Methodology

THE design criteria/objectives include maximum conversion, minimum cross-linked product, and minimum off-spec product. These objectives are obtained by applying multiobjective optimization techniques (e.g. mixed-integer dynamic optimization) for various process/product constraints (e.g. realizable flow rates & feasible molecular weights, branching frequencies, and copolymer composition)

Design variables are those that can be manipulated to satisfy the objective function. Though the temperature, pressure and residence time are the reactor design variables, certain constraints are applied in order to realize a feasible process. The primary design variables in the current optimization are the feed flow ratios of the monomers, feed flow rate of chain transfer agent/surfactants, and mean residence time (both in case of same size and variable size CSTR's). These variables are manipulated to satisfy the objective function.

3. Optimization Examples

TWO particular optimization scenarios that are of industrial interest are:

1. How should the feed flow rates be controlled in order to minimize composition drift?
2. How should the feed flow rates be adjusted during a grade change so that off-spec product is minimized?

Example 1: Grade Change

The change of polymer grade can be optimized by reducing the off-spec material produced during the transient period between nominal steady-states (i.e. between t_1 & t_2). Typically optimal molar flow rates of monomer and CTA into each reactor are found in order to meet the required copolymer composition, molecular weights and branching specifications. One example of an optimization formulation is as follows:

$$\min_{F_A^{[n]},F_B^{[n]},F_T^{[n]}} \int_{t_1}^{t_2} G^{[n]}(t)dt \quad (1)$$

$$t_1 = \max t_{SS_1} \quad (2)$$

$$t_2 = \min t_{SS_2} \quad (3)$$

$$\text{subject to: } \begin{array}{l} \overline{F}^{[n]}_{A,ss_k,min} \le \overline{F}^{[n]}_A(t) \le \overline{F}^{[n]}_{A,ss_k,max} \\ \overline{MW_w}^{[n]}_{ss_k,min} \le \overline{MW_w}^{[n]}(t) \le \overline{MW_w}^{[n]}_{ss_k,max} \\ \overline{PDI}^{[n]}_{ss_k,min} \le \overline{PDI}^{[n]}(t) \le \overline{PDI}^{[n]}_{ss_k,max} \\ \overline{BN_3}^{[n]}_{ss_k,min} \le \overline{BN_3}^{[n]}(t) \le \overline{BN_3}^{[n]}_{ss_k,max} \\ \overline{BN_4}^{[n]}_{ss_k,min} \le \overline{BN_4}^{[n]}(t) \le \overline{BN_4}^{[n]}_{ss_k,max} \end{array}$$

In this example the objective is to minimize polymer production $G(t)$ by minimizing the transition between the steady states of each grade.

Example 2: Composition Control

Using mechanistic models for semi batch and CSTR reactors, the copolymer composition in the final reactor can be controlled by following several policies. These policies include:

- maintaining a constant molar ratio of the monomers (i.e. $N_1/N_2 = \alpha$), by manipulating the flow rate of the more reactive monomer
- manipulating the flow rates of monomers such that the concentrations of monomers in the reactor are constant
- manipulating the monomer flow rates based on the amount of consumption by reaction

Studies have been performed with the above strategies in the past but the optimal conditions were obtained based on a single value objective function that corresponds to the entire processing time. In our study, the optimal flow profiles will be obtained by performing a dynamic optimization where the objective function is minimized at every time step.

4. Typical Model Simulations

THE following figures show model simulations for a continuous reactor train. CSTR simulations were performed using a residence time of 60 minutes per reactor and a start up procedure full of water with all ingredients fed to the first reactor. Additionally, CTA and monomer were fed at a constant rate to downstream reactors in order to demonstrate the effect on molecular weight, chain branching and copolymer composition.

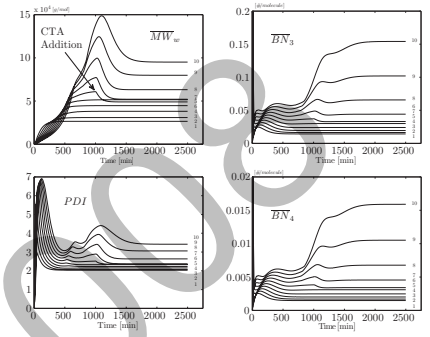

Figure 1: *CSTR train simulation with the addition of CTA to the 6^{th} reactor, (a) weight average molecular weight, (b) tri-functional branching, (c) polydispersity (d) tetra-functional branching*

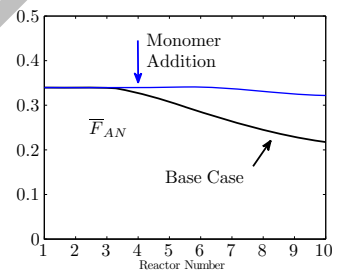

Figure 2: *CSTR train simulation - effect of copolymer composition with the addition of AN to the 4^{th} reactor*

Evident from Figure 1 is the effect of a step change in CTA inflow on polymer quality indicators. Figure 2 shows the steady state response, in each reactor, of the AN cumulative copolymer composition to a step change in AN inflow. A constant step in the inflow rates is clearly not an optimal solution; thus the proposal of a stepwise or continuous flow rate trajectory is desired.

5. Process Control Considerations

DESIGN of process control systems for trains of CSTR's is a challenging task. The control system parameters or the controller parameters (K_c, τ_I, and τ_D in the case of a PID controller) are functions of the process parameters such as the time constant (V/q) of the reactors. Since the manipulative variables in the present system will be the flow rate of the feed streams, whenever there are set point and regulatory changes, the corresponding time constants will change which would force one to tune the PID controller every time. This problem could be overcome by conventional gain scheduling or with the design of an additional system component called an adaptive gain compensator.

Following is an example of the design procedure to model the gain of the compensator (K_h):

- The closed loop gain is equal to the product of the individual gains in the control system

$$K_L = K_m K_c K_v K_h K_{fp} \frac{\partial q_v}{\partial X_v} K_{p1} K_{p2} \dots K_{pn}$$

- The closed loop gain, K_L is usually a function of process time constants which in turn means is a function of any of the process flow rates. With,

$$K_m = g_1(q),\ K_{fp}\frac{\partial q_v}{\partial X_v} = g_2(q),\ K_{pn} = h_n(q)$$

- Now the compensator gain can be derived as follows

$$K_h = \frac{f_1(q)}{K_c K_v g_1(q) g_2(q) h_1(q) h_2(q) \dots h_n(q)}$$

The incorporation of this proposed compensator into the feed back control system would improve the performance of the control system while not disturbing the conventional controller settings.

6. Concluding Remarks

GRADE changes are quite often made in the polymer industry to produce a variety of polymers. The strategies for optimizing the transition time for each successive grade change will be developed. This will lead to the minimization of off spec product and consequently reduce operational costs. In addition, several control policies will be implemented to achieve a desired copolymer composition where optimal feed flow rates are maintained with the constraints on molecular weights, polydispersity, and branching number.

The proposed compensator could improve the performance of the feed back control system compared to that of the conventional off-line control methods. The in turn could give good quality control in the emulsion polymerization system which is our primary objective while the characteristics of the proposed compensator have to be further studied.

7. Nomenclature

$\overline{BN}_{3,ss_k}$	Maximum or minimum tri-functional branching at steady state k
$\overline{BN}_{4,ss_k}$	Maximum or minimum tetra-functional branching at steady state k
$F_A^{[n]}, F_B^{[n]}, F_T^{[n]}$	Molar flow of AN, Bd and CTA
$\overline{F}_{A,ss_k}$	Maximum or minimum AN copolymer composition at steady state k
k	Index of steady state
K	Gains for loop L, measurment m, controller c, valve v, flow process, fp
$\overline{MW}_{w,ss_k}$	Maximum or minimum weight average molecular weight at steady state k
N_j	Total number of moles of monomer j
n	Reactor number
q	Volumetric flow rate
t_1, t_2	Time of steady state 1 and 2 during a grade change
X	Valve stem position

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