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Mathematical modeling of a continuous solution polymerization reactor: case-study MMA polymerization

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Abstract *In this paper, the dynamics of the free radical polymerization of methyl methacrylate (MMA) in a cooling jacketed continuous reactor were investigated. The modeling stage has been conducted regarding several underlying phenomena so to obtain the most accurate model as we can. Like most of the chemical processes, the mathematical model exhibits high interaction and nonlinearity. To control this system several methods can be implemented to control the system. However, the design of an efficient and reliable control strategy requires, in most cases, the linearization and decoupling of the model equations. In this first part of a paper series the process model is developed and validated prior to the implementation of a fuzzy control strategy.*

Keywords: Solution polymerization, molecular weight distribution, modeling

Introduction:

Continuous polymerization reactors are commonly encountered in chemical industry. With an increasing demand for high-quality polymers, it is necessary to build a control strategy to enable a better control of the properties of the polymer product and minimize the production of off-spec polymers particularly during the start-up or grade change operations. However, polymerization processes are difficult to control effectively due to their complexity as well as the severe nonlinearity and interactivity exhibited by their process models [1-3]. As a result, several kinds of nonlinear control strategies have been developed for polymerization processes.

Product quality is a much more complex issue in polymerization than in more conventional short chain reactions. The molecular structure of the polymer is so sensitive to operating conditions that any disturbance in feed conditions, mixing, reactor temperature and initiator concentration can affect the critical molecular properties such as molecular weight, polymer composition distributions, etc. The requirement of an accurate process model for the optimal quality control is very important. To do so we considered all inherent underlying phenomena in order to build a reliable model of the process. The process model of the free radical polymerization of methyl methacrylate (MMA) in a cooling jacketed continuous reactor is used as a case-study [4-6]. The mathematical model of process, developed here, exhibits a highly non-linear interactive behavior.

DEVELOPEMENT OF THE PROCESS MODEL

Let us consider a reactor where methyl methacrylate (MMA), initiator and the Solvent are continuously introduced. This reactor is assumed to be a jacketed, well-mixed tank. A coolant flows through the jacket to remove the heat of copolymerization. Polymer, solvent, unreacted monomer and eventually initiator flow out of the reactor to a separator.

The reaction kinetics are based on the "terminal model" and assumed to follow the free radical polymerization mechanism, including chain transfer reactions to both solvent and monomer, termination by coupling and termination by disproportionation.

The temperature dependence of the rate constants is assumed to follow the Arrhenius law. The kinetic data used for the plant model of this study are taken from the literature.

From the general free radical polymerization mechanism we obtain the reaction rates as follows:

The initiator:

$$R_I = 2 f_i k_d I$$

The solvent:

$$R_s = k_s \left(\frac{2 f_i k_d I}{k_{tc} + k_{td}} \right)^{0.5} S$$

The monomer (MMA):

$$R_M = -\frac{dM}{dt} = (k_p + k_{trm}) M \left(\frac{2 f_i k_d I}{k_{tc} + k_{td}} \right)^{0.5}$$

Reactions heat rate:

$$\Delta H_T = (-\Delta H) k_p \left(\frac{2 f_i k_d I}{k_{tc} + k_{td}} \right)^{0.5} M$$

The mass balances for the different compounds are given by

$$\frac{d(IV)}{dt} = q_I I_f - qI - R_I V$$
$$\frac{d(MV)}{dt} = q_M M_f - qM - R_M V$$
$$\frac{d(SV)}{dt} = q_S S_f - qS - R_S V$$

The energy balances for reactor and jacket can be formulated, respectively, as follows:

$$\frac{d(V\rho C_p T)}{dt} = q_M \rho_M C_{pM} (T_f - T) + q_I \rho_I C_{pI} (T_f - T) + q_S \rho_S C_{pS} (T_f - T) + V \Delta H_T - U_r A_r (T - T_j)$$
$$\frac{d(V \rho_c C_{pc} T_j)}{dt} = \rho_c C_{pc} q_f (T_{jin} - T_{jout}) + U_r A_r (T - T_j) - U_j A_j (T_a - T_j)$$

To build up an accurate model as possible it is necessary to introduce molecular weight distribution equations. To do so, it is not necessary to solve the infinite number of equations for the concentrations of polymer chains of different lengths. Instead, the method of moments is adopted to calculate the number-average molecular weight (M_n) and the weight-average molecular weight (M_w). The definitions of the moments are as follows:

$$G_k = \sum_{n=1}^{\infty} n^k R_n(t), \qquad F_k = \sum_{n=1}^{\infty} n^k P_n(t) \qquad k = 0,1,2$$

where G_k and F_k are the kth moments of living and dead polymer concentrations, R_n and P_n, respectively.
One can derive balance equations for the first three moments of the living and dead polymer concentrations as follows:

$$\frac{d(G_0V)}{dt} = -qG_0 + \left(2fk_dI - k_tG_0^2\right)V$$
$$\frac{d(G_1V)}{dt} = -qG_1 + \left[2fk_dI + k_pMG_0 - k_tG_0G_1 + (k_{trm}M + k_{trs}S)(G_0 - G_1)\right]V$$
$$\frac{d(G_2V)}{dt} = -qG_2 + \left[2fk_dI + k_pM(G_0 + 2G_1) - k_tG_0G_2 + (k_{trm}M + k_{trs}S)(G_0 - G_2)\right]V$$
$$\frac{d(F_0V)}{dt} = -qF_0 + \left[0.5(k_t + k_{td})G_0^2 + (k_{trm}M + k_{trs}S)G_0\right]V$$
$$\frac{d(F_1V)}{dt} = -qF_1 + \left[(k_tG_0 + k_{trm}M + k_{trs}S)G_1\right]V$$
$$\frac{d(F_2V)}{dt} = -qF_2 + \left[(k_{td}G_0 + k_{trm}M + k_{trs}S)G_2 + k_{tc}\left(G_0G_2 + G_1^2\right)\right]$$

where the number and weight-average molecular weights are defined by the following equations:

$$M_w = w_M \frac{(G_2 + F_2)}{(G_1 + F_1)}$$
$$M_n = w_M \frac{(G_1 + F_1)}{(G_0 + F_0)}$$

Conclusions:

Modeling of continuous stirred tank reactor of MMA solution polymerization has been conducted in conjunction with several considerations. The mathematical model based on eleven equations is in fact highly interactive and nonlinear witch in turn imply a linearization and decoupling strategy.

The mathematical model has been improved by adding the equations of the molecular weight distribution moments, which have been obtained from equations of moments. In spite of dealing with more complex model, this approach enables the control or the optimization of the number average and average molecular weights.

From a practical point of view the key control objectives of the copolymerization reactor are:

The linearization
The compensation of interaction
The preclusion of input multiplicity
The robustness of the controller (i.e., tolerance to modeling and tuning errors)

Previous works indicate that the input multiplicity issue, should be the central point in the study of the solution copolymerization control problem.

Notations:

I	: initiator concentration, kmol /m^3
I_f	: initiator feed concentration, kmol /m^3
M	: monomer 1, 2 concentrations, kmol /m^3
M_f	: monomer 1, 2 feed concentrations, kmol /m^3
q_M	: monomer 1, 2 feed rates, m^3/s
q_S, q_I	: solvent and initiator feed rates, m^3/s
q	: output flow rate, m^3/s
R_M	: monomer reaction rate, kmol /m^3.s
R_I,R_S	: initiator and solvent reaction rate, kmol /m^3.s
S	: solvent concentration, kmol /m^3
S_f	: solvent feed concentration, kmol /m^3
T, T_f, T_j	: reactor, feed-rate and cooling temperatures, K
T_{jin}, $T_{j\,\mathrm{out}}$	: input and output cooling liquid, K
V	: reactor volume, m^3
U	: overall heat transfer coefficient, kJ/m² .s.K
ρ, ρ_c	: average densityof the reactor mixture, kg/ m^3
ρ_M, ρ_S, ρ_I	: density of monomer, solvent and initiator kg/ m^3

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Appendix:

Kinetic scheme for free-radical polymerization of MMA

Initiation :

$$I \xrightarrow{k_d} 2\dot{R}$$

$$\dot{R} + M \xrightarrow{k_a} R\dot{M}_1$$

Propagation :

$$R\dot{M}_1 + M \xrightarrow{k_p} R\dot{M}_2$$

$$R\dot{M}_{n-1} + M \xrightarrow{k_p} R\dot{M}_n$$

Chain transfer to monomer :

$$R\dot{M}_n + M \xrightarrow{k_{trm}} RM_n + \dot{M}$$

Chain transfer to Solvent :

$$R\dot{M}_n + S \xrightarrow{k_{trs}} RM_n + \dot{S}$$

Termination by combination :

$$R\dot{M}_n + R\dot{M}_n \xrightarrow{k_{tc}} RM_{n+m}R$$

Termination by disproportionation :

$$R\dot{M}_n + R\dot{M}_m \xrightarrow{k_{td}} RM_{n'} + RM_{m'}$$