Design and Operation of Copolymerisation Reactors through Modelling and Nonlinear Analysis

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Abstract

The development of an appropriate model for copolymerisation reactors that can describe the process behaviour over the complete range of conversion contributes to a better understanding of the polymerisation process, helps to avoid unsafe operating conditions and to develop operational and optimizing control strategies. The aim in this work is to study the design and operational issues of a copolymerisation reactor through a systematic model-based (open-loop) nonlinear analysis. The performance of two first-principles models are compared with respect to the steady state and dynamic behaviour of the polymerisation process. The analysis highlights the influence of the reaction mechanism, the transport phenomena, the process design and operating conditions on the polymer grade and the production rate.

Keywords: Polymerisation process, process design, nonlinear analysis, simulation.

1. Introduction

The production of synthetic polymers is one of the most important worldwide industries. Each year more than 100 million tons of synthetic polymers are produced worldwide (Ray and Villa, 2000). Copolymerisation processes are commonly preferred since the combination of two monomers allows the obtaining of specific desired physical, chemical and mechanical properties of the final polymer product.

From an industrial perspective, the main achievements during the production process are to maintain or improve the product quality; to reduce the process time, the cost of production and energy consumption; to increase productivity; to reduce waste emissions; while maintaining acceptable ranges of operability (safety and stability). Therefore, the knowledge of the instantaneous copolymer product characteristics (composition, molecular weight, solid fraction, etc.) during the production process is important for enhancing industrial competitiveness (through efficient operation and control, flexible design and optimal cost). To achieve this, several challenges need to be overcome since the copolymerisation processes are complex due to their highly non-linear behaviour, the existence of steady state multiplicity, tendency to instability, the strong input-output coupling, and the extreme sensitivity to changes in operation conditions.

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Mathematical model development often represents a bottleneck in the creation of model-based strategies for automation of polymerisation processes. Recent model-based control studies for continuous solution copolymerisation reactors (Bindlish and Rawlings, 2003; Maner and Doyle, 1997) have used a simplified model (Congalidis et al., 1989) that is valid only in a region of low conversion, where an important product behaviour (the get-effect) is not observed and consequently, does not also predict steady state multiplicity. Hence, a first task in this work was to develop a more general process model that can describe the reactor behaviour over the complete conversion range, so that the design of operational strategies can be fully analysed.

Two first-principles models have been investigated: the first one corresponds to the model presented by Congalidis et al. (1989) that covers the low conversion region, while the second model has been derived in this work and covers the complete range of conversions. The steady state (multiplicity existence and stability) and dynamic behaviour are studied to identify the roles played by the reaction mechanism, the transport phenomena and operational variables with respect to the polymer grade (i.e. composition, conversion and molecular weight) and the production rate. Finally, the application of the developed model is highlighted through a case study (the solution copolymerisation of methyl methacrylate - vinyl acetate) where the optimal operating point with a desired quality target is determined.

2. Modelling of the solution copolymerisation reactor

2.1 Process description

Consider a CSTR where a solution copolymerisation process takes place. Two monomers (A and B), an initiator (I), a solvent (S) and a transfer agent (T) are fed to the reactor. An inhibitor (Z) may enter as an impurity. The heat generated by the exothermic polymerisation reactions is removed by means of a coolant jacket. The copolymerisation is carried out by a free-radical mechanism represented by the 27 reactions (Congalidis et al, 1989), which are classified as: 7 initiation, 4 propagation, 4 transfer to monomer, 2 transfer to solvent, 2 transfer to agent, 6 (both coupling and disproportion) termination, and 2 inhibition reactions.

2.2 Mathematical models

2.2.1 Model 1

Model 1 is taken from Congalidis et al. (1989), including corrections given by Maner and Doyle (1997). The assumptions in this model were: the reactor is perfectly mixed, density and heat capacity of the reaction mixture are constant, the cooling fluid temperature is uniform, the reaction volume is constant and there is no gel effect. The reactor model equations (given in Congalidis et al., 1989) were derived from the mass balances for all component concentrations (c_k), the monomer concentrations in the dead copolymer (λ_i), the reactor energy (T_r), and the moments of the molecular weight distribution of the dead copolymer (ψ_i^p). This model can be only applied at the low conversion region (below conversions around 20-30%) where the gel effect does not play an important role and the medium viscosity remains moderate.

2.2.2 *Model 2*

Several modifications were considered in order to obtain a more general and appropriate model to cover the complete range of conversion. Starting from *Model 1*, we included the following phenomena: (a) gel effect correlations (Pinto and Ray, 1995a), (b) composition dependent (linear) models for physicochemical properties (density and heat capacity) of the reaction mixture, (c) a correction in the mass balances taking into account the volume shrinkage due to changes in the density, and (d) the heat transfer coefficient dependence on the mixture viscosity and reactor mixing. Then *Model 2* takes the following form:

$$\frac{dc_k}{dt} = \frac{Q_f c_{k,f} - Q_e c_k}{V_r} - R_k, \qquad c_k(0) = c_{k0}; \qquad k = a,b,i,s,t,z \tag{1}$$

$$\frac{d\lambda_k}{dt} = \frac{Q_f \lambda_{k,f} - Q_e \lambda_k}{V_r} + R_k, \qquad \lambda_k(0) = \lambda_{k0}; \qquad k = a,b \tag{2}$$

$$\frac{dT_r}{dt} = \frac{\sum_{i=a,b} \sum_{j=a,b} \left(-\Delta H_{pij}\right) k_{pij} c_j c_{i\bullet}}{\rho_r C_{pr}} + \left(\frac{C_{pf} T_f}{C_{pr}} - T_r\right) \frac{Q_f \rho_f}{V_r \rho_r} - \frac{U_r S_r \left(T_r - T_j\right)}{V_r \rho_r C_{pr}}, \quad T_r(0) = T_{r0} \tag{3}$$

$$\frac{d\psi_i^p}{dt} = \frac{Q_f \psi_{i,f}^p - Q_e \psi_i^p}{V_r} + R_{\psi,i}, \qquad \psi_i^p(0) = \psi_{i0}^p; \qquad i = 0,1,2 \tag{4}$$

$$\frac{dV_r}{dt} = Q_e - Q_{out}, \qquad V_r(0) = V_{r0} \tag{5}$$

Where Q_f is the volumetric feed rate, Q_e and Q_{out} are the volumetric feed and exit rates corrected due to density changes, V_r is the reactor volume, T_f and T_j are the feed and jacket temperatures, R_k are the reaction rates, k_{ijk} and ΔH_{pij} the kinetic constants and heats of propagation rates, ρ and C_p are density and the heat capacity of the polymeric mixture (subscript f for feed and r for reactor), respectively. The outputs of interest are the instantaneous polymerisation rate (G_{pi}), the molar fraction of monomer A in the dead polymer (Y_{ap}), the weight-average molecular weight (M_w) and the overall monomer conversion (c_m) defined as:

$$G_{pi} = \left(R_a M_a + R_b M_b\right) V_r, \qquad Y_{ap} = \lambda_a / \left(\lambda_a + \lambda_b\right) \tag{6}$$

$$M_w = \psi_2^p / \psi_1^p, \qquad c_m = \left(c_{af} + c_{bf} - c_a - c_b\right) / \left(c_{af} + c_{bf}\right) \tag{7}$$

If the reactor operates at low conversions (implying no gel effect, and constant density, heat capacity and viscosity) and constrained to constant volume (i.e., $Q_f = \underline{Q_e} = Q_{out}$ and $dV_r/dt = 0$), then *Model 2* [Eqs. (1) - (7)] is reduced to *Model 1* (Congalidis et al., 1989).

2.3 MMA-VA copolymerisation data

Models 1 and *2* can be applied to any solution copolymerisation system. As a case study, the copolymerisation of methyl methacrylate (MMA: monomer A) and vinyl acetate (VA: monomer B) is considered, using AIBN (I) as initiator, benzene as solvent (S), acetaldehyde as transfer agent (T) and no inhibitor. All kinetic and physicochemical parameters required to solve *Model 1* were reported in Congalidis et al. (1989) and some corrections for energy activities E_i, E_{pbb} and E_{xbt} were given by Maner and Doyle (1997). The solution of *Model 2* requires additional data that can be found elsewhere, for instance see: Pinto and Ray (1995a) for the gel effect correlations, Brandrup and Immergut (1975) for physicochemical data, Fujita et al. (1960) for viscosity correlation, and Bondy and Lippa (1983) for heat transfer correlation. As a base case the following operation conditions, reported by Congalidis et al. (1989), are considered: $\{G_{a,f}, G_{b,f}, G_{i,f}, G_{s,f}, G_{t,f}, G_{z,f}, \lambda_{a,f}, \lambda_{b,f}, \psi^p_{0,f}, \psi^p_{1,f}, \psi^p_{2,f}, T_j, T_f\}$ = {0.3 kg min^{-1}, 1.5 kg min^{-1}, 0.003 kg min^{-1} , 0.6 kg min^{-1}, 0.045 kg min^{-1}, 0, 0, 0, 0, 0, 336 K, 353 K}. The reactor design parameters are: $V_r = 1.0$ m^3 and $S_r = 4.6$ m^2.

3. Nonlinear Process analysis

3.1 Computer-aided modelling framework

ICAS-MoT (Sales-Cruz and Gani, 2003) has been used in this work to construct, analyse, solve and validate the models. After validation, the generated model-code from *ICAS-MoT* has been used in open-loop dynamic simulation studies and in the determination of the optimal condition of operation. The available futures of *ICAS-MoT* allow these calculations to be made by the model developer/user without the need for any programming. Consequently, the time saved in model implementation and programming is used in model-based process analysis. Table 1 gives some of the model statistics.

Table 1. MMA-AV copolymerization reactor: Model statistics.

	Number of					
Model	*Total Equations*	*ODEs*	*State variables*	*Fixed variables*	*Non-adjustable parameters*	*Adjustable parameters*
Model 1	115	18	18	17	39	2
Model 2	154	19	19	18	54	27

3.2 Steady state behaviour

First, the base case was reproduced as can be seen in Table 2, where the outputs evaluated at steady state are reported and compared. Actually, the steady states calculated from both models are similar, but there are some differences (for *Model 2*) in the calculated values for T_r and M_w, which are mainly due to the incorporation in *Model 2* of the dependence of the gel effect and the heat transfer coefficient on conversion.

Table 2. Outputs evaluated at the steady-state for the base case.

Outputs	Congalidis et al (1989)	*Model 1*	*Model 2*	Units
G_{ip}	23.3	23.327	23.065	kg h^{-1}
Y_{ap}	0.56	0.5591	0.5627	molar fraction
M_w	35000	34993.6	48453.6	kg kmol^{-1}
c_m	0.2	0.2027	0.2003	molar fraction
T_r	353.1	353.016	343.726	K

Then, bifurcation diagrams were constructed to analyse the existence of the steady state multiplicity around the reference operating point. Several bifurcation parameters were investigated ($G_{i,f}$, $G_{z,f}$, T_j, V_r). For instance, there is no multiplicity when varying T_j, but there is multiplicity with ignition-extinction zones when varying $G_{i,f}$, $G_{z,f}$ and V_r (see Figure 1 where the result for $G_{i,f}$ as bifurcation parameter is shown). According to Figure 1, *Model 1* indicates that there is no multiplicity, while *Model 2* predicts input multiplicity. The base case (Point A) is just in the limit where both models have a unique stable steady state. Nevertheless, a slight increase on $G_{i,f}$ can induce to steady state multiplicity into *Model 2* (for instance changing from point A to point B). These results confirm that *Model 1* should succeed only in the region of low c_m values (including the base case – point A).

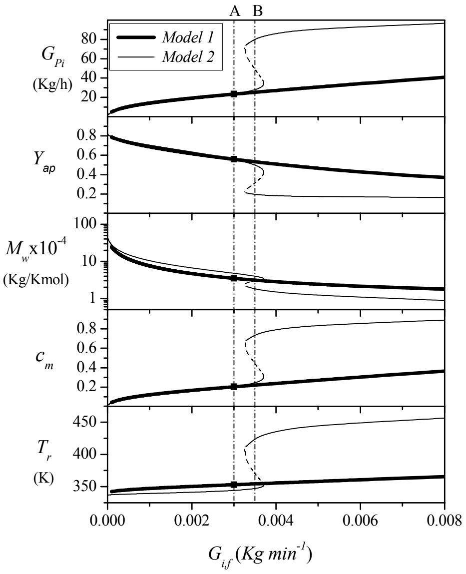

Figure 1. Multiplicity of steady states.

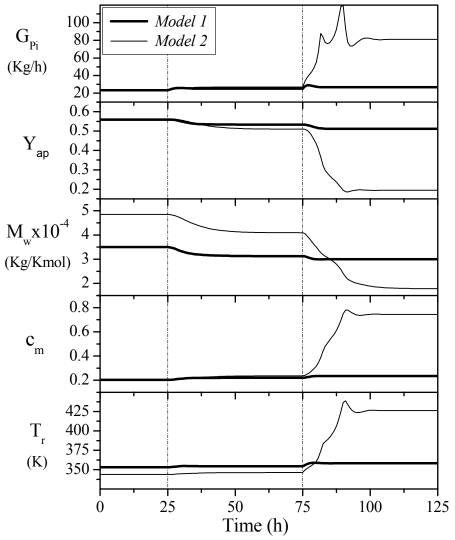

Figure 2. Dynamic behaviour under step changes.

3.3 Dynamic behaviour

Step changes at different times have been considered to highlight the process behaviour at low and high conversions. Figure 2 presents a scenario where the initial conditions are the ones corresponding to the base case (point A in Fig. 1), then at t = 25 h, $G_{i,f}$ is increased from 0.003 to 0.0035 kg.min^{-1} (point B in Fig. 1) so that now the process motion is in the multiplicity region. Then T_j is modified slightly from 336 to 339.5 K at t = 75 h, which causes the models to respond differently. *Model 1* predicts small changes in the final steady state (at t = 125 h), while *Model 2* forces the polymerisation process to reach its ignition-type steady state. Therefore there is a significant influence of T_{j} and $G_{i,f}$ on the process polymerisation, resulting in a high dependence on the gel effect and modifying meaningfully the polymer grade and production rate. Consequently, use of *Model 1* under these conditions is a limitation.

3.4 Operating point design

To illustrate the applicability of *Model 2* and the use of *ICAS-MoT*, the determination of the optimal condition of operation (u) required to produce a copolymer with same polymer grade (composition and weight-average molecular weight) as that of the base case, as well as the same production rate but at a higher conversion (assume 50% instead of 20%) is considered. An optimisation problem is formulated as (where $\bar{y}$ is the desired output):

$$\min_{\mathbf{u}} J = \sum_{i=1}^{5}\left[\left(y_i - \bar{y}_i\right)/\bar{y}_i\right]^2 \tag{10}$$

Subject to the *Model 2* (steady state) and constrains $u_{min} \leq u \leq u_{min}$. *ICAS-MoT* uses the model in an optimization loop where a SQP (Successive Quadratic Programming) – based algorithm is used to minimize Eq. (10). The resulting optimised variables were $u = \{G_{a,f}, G_{b,f}, G_{i,f}, G_{s,f}, G_{t,f}, G_{z,f}, T_j\} = \{0.2467, 0.4930, 0.0025, 0.5132, 0.0024, 0, 352\}$ (G in kg min^{-1} and T in K), and with product grade as: $y = \{G_{pi}, Y_{ap}, M_w, c_m, T_r\} = \{$23.04 kg h^{-1}, 0.5605, 35087 kg kmol^{-1}, 0.4990, 363.4 K$\}$.

4. Conclusions

The results illustrate that through a validated model-based non-linear analysis it is possible to design, understand the main characteristics, select the operations conditions and define the main variables to be controlled for copolymerisation processes. The models, modelling tools and the case study highlight the role of computer-aided model-based analysis that can provide the engineer not only with a better understanding of their process but also to obtain feasible operational strategies, improved monitoring, fault detection and optimization control tasks.

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