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Simulating Cumulative Distributions under Transient Conditions in Well-Mixed, Continuous and Batch Polymerization Reactors

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Summary: Instantaneous property methods are applied to the simulation of cumulative distributions of polymer chain architecture in well-mixed, continuous and batch reactors. We show how cumulative distributions can be simulated under transient conditions using a general convolution integral and suitable output from a dynamic reactor simulation package such as POLYRED™. We also show how the state equations that describe a polymerizing system can be augmented for direct simulation of these distributions. Examples of the impact of catalyst kinetics, reactor operating policies, and process upsets on the molecular weight distribution of bimodal high molecular weight polyethylene produced in well-mixed, stirred-bed gas-phase reactors are simulated for a binary transition-metal catalyst system.

Keywords: cumulative distribution; instantaneous distribution; mixed-catalyst; simulations; molecular weight distribution / molar mass distribution

Introduction

Multi-modal molecular weight and chemical composition distributions have become increasingly important product design features in commercial polyolefin resins. Mixed-catalyst systems[1-4] represent a major advance in meeting these market performance needs with the lowest capital investment cost; for mixed catalysts, however, product structure and quality is a complex function of reactor operating conditions and the kinetic response of the individual catalysts comprising these systems,[5-6] especially under transient conditions. The simulation of the probability distributions that describe the detailed architecture of multi-modal polyolefins provides a useful

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means for exploring this complex dependence and for evaluating strategies to achieve superior product consistency and aim-grade performance.

A simple method is presented for simulating cumulative distributions of polymer chain architecture under transient conditions in well-mixed, continuous and batch polymerization reactors using an extension of 'instantaneous property' methods, and output from a suitable dynamic reactor simulation package such as POLYRED™. We also show how these distributions can be simulated directly if the state equations that describe a well-mixed polymerization reactor are augmented properly. The cumulative size exclusion chromatogram (SEC) of bimodal high molecular weight polyethylene produced by a binary catalyst system in a well-mixed, stirred-bed gas-phase reactor is simulated using a simplified kinetic model derived from pilot plant and laboratory data. Two examples are presented to illustrate the effect of hydrogen drift during polymerization in a laboratory-scale, semi-batch reactor, and the impact of reactor startup and a simple process upset during polymerization in a continuous pilot-scale reactor.

Theory

Instantaneous property or distribution methods were originally developed and applied to predicting the evolution of cumulative polymer properties and distributions in the presence of composition drift in batch and semi-batch polymerization reactors.[7-8] More recently, these methods have been adapted to simulate the evolution of cumulative distributions during polymer particle growth,[9] and to model the dependence of polymer properties on the distribution of particle size and residence time in olefin polymerization reactors.[10-12]

Instantaneous distributions, as the name implies, describe the relative number or mass-weighted frequency with which numerable chain structural elements, x, occur jointly, marginally, or conditionally in polymer molecules produced in a polymerization reaction during a short period of time, say between ξ and $\xi + \Delta\xi$. The instantaneous distribution of these random structural characteristics can be written as $h(x,\theta(\xi))$, where the elements of the vector $\theta(\xi)$ are time-dependent distribution parameters that are functions of the kinetics and mechanism of polymerization and reactor conditions. For convenience, we will assume that h is a mass-weighted distribution.

It follows from elementary statistical theory that the *cumulative* (or *mixture*) distribution $g(x,t)$ for polymer anywhere in a well-mixed batch or semi-batch reactor at time t can be obtained from convolution of the instantaneous distribution h with the instantaneous mass-rate of polymerization, $P_R(\xi)$,

$$g(x,t) = \frac{\int_0^t P_R(\xi) \cdot h(x, \theta(\xi)) \cdot d\xi}{W_b(t)} \tag{1}$$

$W_b(t)$ is the polymer or bed mass in the reactor at time t. In well-mixed continuous reactors, polymer is discharged at the reactor outlet with time-dependent mass flow rate, q_o. Consequently, some of the polymer produced at time ξ is discharged before time t, and does not contribute to the cumulative distribution of x. By multiplying $P_R(\xi)$ by $w(\xi,t)$, the mass-fraction of polymer produced at time ξ, that remains in the reactor at time t,

$$w(\xi,t) = \exp\left[-\int_\xi^t \frac{q_o(\varphi)}{W_b(\varphi)} d\varphi\right] = \exp\left[-\int_\xi^t \frac{d\varphi}{\tau}\right] \tag{2}$$

where $W_b(\varphi)$ is the mass of the polymer bed in the reactor at time φ, and $q_o(\varphi)/W_b(\varphi)$ is the inverse of the instantaneous residence time τ, eqn (1) can be modified to account for the mass-residence time distribution of polymer in well-mixed continuous reactors. The integrand in eqn (2) is the inverse of the instantaneous mass-mean residence time of polymer in the reactor, and the integral is the number of reactor *bed turnovers* (BTOs) in the interval (ξ, t). The convolution integral for a well-mixed, continuous reactor, generalized to accommodate the presence of a well-characterized polymer bed at time t_0, or a steady-state condition with known $g(x,t)$, can be written as—

$$g(x,t) = \frac{W_b(t_0) \cdot g(x,t_0) \cdot \exp\left(-\int_{t_0}^t \frac{d\varphi}{\tau}\right)}{W_b(t)} + \frac{\int_{t_0}^t P_R(\xi) \cdot h(x,\theta(\xi)) \cdot \exp\left(-\int_\xi^t \frac{d\varphi}{\tau}\right) \cdot d\xi}{W_b(t)} \tag{3}$$

When $q_o = 0$, eqn (3) has as its limiting case the cumulative distribution that results from polymerization in a well-mixed, batch or semi-batch reactor.

Eqn (3) can also be obtained as the analytical solution of the differential equation for the time-dependence of $g(x,t)$, which can be derived from material balance considerations—

$$\frac{dg(x,t)}{dt} = \frac{P_R}{W_b} \cdot \left[h(x,\theta(t)) - g(x,t)\right] \tag{4}$$

For multi-site-type and mixed catalysts,

$$h(x,\theta(\xi)) = \sum_k S_k(\xi) \cdot u_k(x,\theta_k(\xi)) \tag{5}$$

where the linear coefficients in eqn (5) are the instantaneous ‘splits’ or weight fractions, S_k, of polymer produced by each of the catalyst sites. The molecular architecture of the polymer formed by the *k-th* site is governed by a mass-weighted instantaneous distribution of x, $u_k(x,\theta_k(\xi))$, where $\theta_k(\xi)$ is a vector of time-dependent distribution parameters that are functions of the kinetics and mechanism of polymerization and reactor conditions. The functional form of u_k will usually be the same for each catalyst site.

Cumulative distributions can be simulated using the convolution integral in eqn (3) and suitable output from a dynamic reactor simulation package. Alternatively, if reactor simulation source code is available, these distributions can be simulated directly by augmenting the state equations for the system with the system of equations formed by evaluating eqns (4) and (5) at discrete values of x.[10]

Other approaches to computing cumulative molecular weight or chain length distributions under transient conditions using discrete weighted residual methods[14-16] have been described in the literature; PREDICI, based on the discrete Galerkin h-p-method developed by Wulkow, for example, is available commercially.[15]

Mixed-Catalyst Kinetic Model

The simulation of cumulative distributions using the convolution integral in eqn (3) will be illustrated with a binary catalyst system designed to produce bimodal high molecular weight, high-density polyethylene in a single reactor. The model system is comprised of a single-site catalyst (LMW) that produces low molecular weight polymer, and a three-site catalyst (HMW) that produces high molecular weight polymer. These catalysts are characterized by different chain propagation and deactivation rates, and chain transfer kinetics: the single-site catalyst is long-lived in comparison with the multi-site catalyst, and chain transfers preferentially with hydrogen; it also chain transfers *via* monomer in the absence of sufficient hydrogen. The multi-site HMW catalyst chain transfers exclusively *via* monomer. An SEC of the bimodal polyethylene produced by this model catalyst under suitable steady-state conditions is shown in Figure 1.

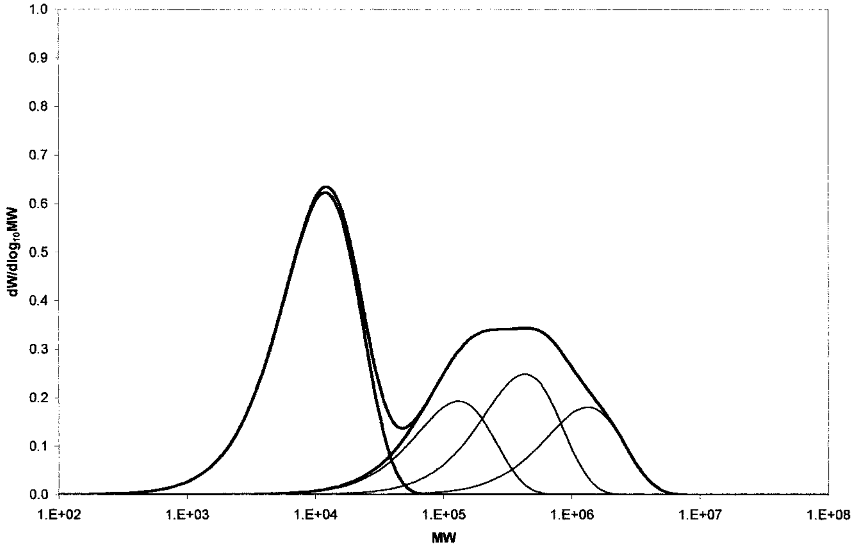

Figure 1. Simulated SEC of model bimodal high molecular weight polyethylene. The weight fraction, or HMW split, of polymer produced by the HMW catalyst is 0.5

Additional simplifying assumptions made to keep the number of model parameters within manageable limits include:

1. The system is modeled as a homopolymerization;
2. Propagation rates are first-order in monomer;
3. Rate constants for chain initiation and chain propagation are equal;

4. The rate constant for chain transfer *via* monomer is the same for all four catalyst sites;
5. The deactivation rate constant is the same for all three HMW catalyst sites; and
6. Catalyst enters the reactor pre-activated.

With these assumptions, estimates of the kinetic parameters for the model catalyst system described above can be obtained from pilot plant and SEC data. The values summarized in Table 1 are based on monomer and hydrogen concentrations at active catalyst sites estimated using Stern's correlation.[17]

Table 1. Model kinetic parameters

Parameter	Type	Catalyst	Value
ϕ^{LMW} (*mole/mole-catalyst*)	Catalyst composition	LMW	0.33
ϕ_1^{HMW} (*mole/mole-catalyst*)	Catalyst composition	HMW Site 1	0.45
ϕ_2^{HMW} (*mole/mole-catalyst*)	Catalyst composition	HMW Site 2	0.18
ϕ_3^{HMW} (*mole/mole-catalyst*)	Catalyst composition	HMW Site 3	0.04
k_p^{LMW} $(L\text{-}mole^{-1}\text{-}sec^{-1})$	Propagation	LMW	2.80×10^3
$k_{p,1}^{HMW}$ $(L\text{-}mole^{-1}\text{-}sec^{-1})$	Propagation	HMW Site 1	2.48×10^3
$k_{p,2}^{HMW}$ $(L\text{-}mole^{-1}\text{-}sec^{-1})$	Propagation	HMW Site 2	8.16×10^3
$k_{p,3}^{HMW}$ $(L\text{-}mole^{-1}\text{-}sec^{-1})$	Propagation	HMW Site 3	25.30×10^3
k_{CTH} $(L\text{-}mole^{-1}\text{-}sec^{-1})$	Chain transfer to hydrogen	LMW	4.24×10^4
k_{CTH} $((L\text{-}mole^{-1})^{0.5}\text{-}sec^{-1})$	Chain transfer to hydrogen	LMW	3.86×10^2
k_{CTM} $(L\text{-}mole^{-1}\text{-}sec^{-1})$	Chain transfer to monomer	LMW and HMW Site 1, 2, 3	1.064
k_d^{LMW} (sec^{-1})	Deactivation	LMW	9.63×10^{-5}
k_d^{HMW} (sec^{-1})	Deactivation	HMW Site 1, 2, 3	5.78×10^{-4}

The catalyst composition parameters in Table 1 are the mole fractions of each site type for a model catalyst system with a loading of 4.125×10^{-6} *mole-active-cat/gm-cat*. Two rate constants for chain transfer to hydrogen are given in Table 1—one for use when chain transfer is first order in hydrogen, and one for use when the rate of chain transfer is proportional to the square root of the hydrogen concentration.[18] The latter has been used in the examples simulated for this paper.

Examples

The simulation of cumulative distributions with POLYRED is a two step process beginning with the configuration and testing of a simulation model for the polymerization reaction system of interest. Pre-selected simulation variables required for evaluation of eqn (3) are written to files at uniformly spaced increments of time after each simulation; the data in these files are used to compute the cumulative distribution(s) of interest in user-written, post-processing routines. For the examples presented here, the convolution integral in eqn (3) has been evaluated using MATLAB™ scripts written for that purpose.

The POLYRED simulation variables used for evaluation of eqn (3) for molecular weight distributions are shown below in Table 2 for gas-phase, transition-metal-catalyzed olefin polymerization in stirred-bed reactors.

Table 2. POLYRED CSBR simulation variables

Convolution Term	**POLYRED Variable(s)**	**Definition**
ξ, φ	Time (*sec*)	Elapsed time.
$P_R(\xi)$	Rate_M[i] (*gms/sec*)	The instantaneous mass-rate of polymerization of monomer, i. $P_R(\xi)$, the total mass-rate of polymerization is obtained by summing the contribution of each monomer.
$S_k(\xi)$	w_inst_S[k]	The instantaneous weight fraction of polymer produced by catalyst site type, *k*.
$q_o(\varphi)/W_b(\varphi)$	QMass_O ÷ MassBed (*sec*$^{-1}$)	The instantaneous bed turnover rate used in the evaluation of $w(\xi,t)$. QMass_O is the outlet stream mass flow rate, and MassBed is the total mass of the reactor bed.
$W_b(t)$	WtFrPol_O × MassBed (*gms*)	Mass of polymer in the reactor bed. WtFrPol_O is the weight fraction of polymer in the outlet stream and reactor bed.
$M_{N,k}$	LMWnS[k]	Number average molecular weight of live polymer produced by catalyst site, *k*.

In practice, instantaneous distributions for each catalyst site type, $u_k(x,\theta_k(\xi))$, are evaluated at discrete values of x. In the univariate case, a discrete approximation for $g(x,t)$ is obtained by computing the convolution integral at each value of x using numerical quadrature. In the examples presented here, x is molecular weight discretized along a uniformly spaced, 301-point, base-10 logarithmic grid from 10^2 to 10^8, and u_k for SECs is given by,

$$u_k(x,\theta_k(\xi)) = MW \cdot W_k(MW) \cdot \ln(10) \tag{6}$$

where $W_k(MW)$ is the instantaneous mass-weighted Schultz-Flory distribution for the molecular weight of polymer generated by catalyst site *k*,

$$W_k(MW) = \frac{MW}{M_{N,k}^2}\exp\left[-\frac{MW}{M_{N,k}}\right] \tag{7}$$

and $M_{N,k}$ is the instantaneous number average molecular weight of polymer produced by catalyst sites of type *k*. The number average molecular weight of live polymer at each site type, LMWnS[k], is used for $M_{N,k}$ to simulate the cumulative SECs in the examples below.

Semi-Batch, Laboratory-Scale Gas-Phase Polymerization. In Example 1, polymerization is carried out at 85 °C in a 1.25 liter laboratory reactor in which hydrogen has been batch charged, and ethylene is fed on demand to maintain reactor pressure. The initial molar H_2/C_2 ratio is 0.0013, and the ethylene partial pressure is 220 psig. Sufficient catalyst is batch charged to produce approximately 90 grams of polymer in 30 minutes. Figure 2 shows the depletion of hydrogen during the run and the corresponding increase in the molecular weight of polymer produced by the LMW catalyst, while Figure 3 shows how the instantaneous SEC of LMW polymer changes with time.

SECs of bulk reactor polymer were computed using eqn (3). Figure 4 shows how the SEC (or molecular weight distribution) of polymer in the reactor changes as the polymerization proceeds, while Figure 5 shows how the polymer produced by each of the catalysts contributes to the final product. The unimodal character of the final polymer, which is a consequence of hydrogen depletion during polymerization, is noteworthy. For metallocene catalysts that do not generate in-situ hydrogen, drift of this magnitude should be expected in small-scale reactors, complicating the interpretation of results from mixed-catalyst trials. In this example, hydrogen is consumed at a relatively high rate to generate the LMW polymer fraction.

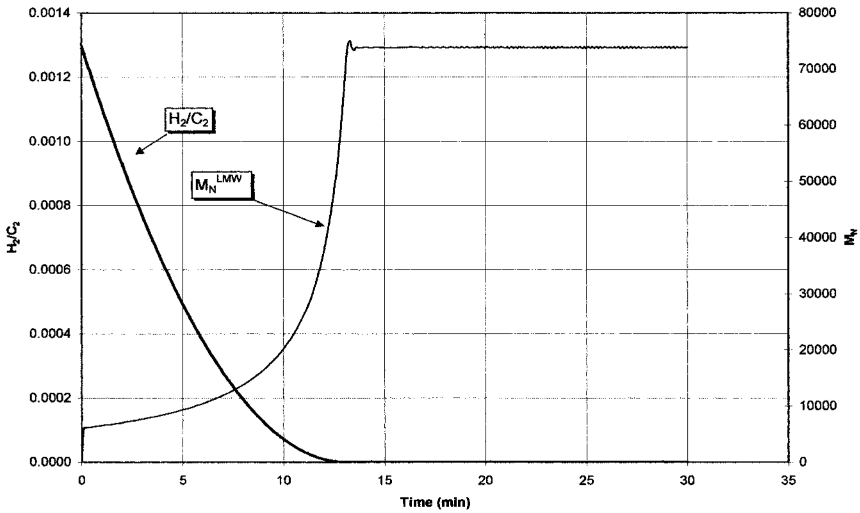

Figure 2. Effect of hydrogen drift on the instantaneous number average molecular weight of LMW polymer

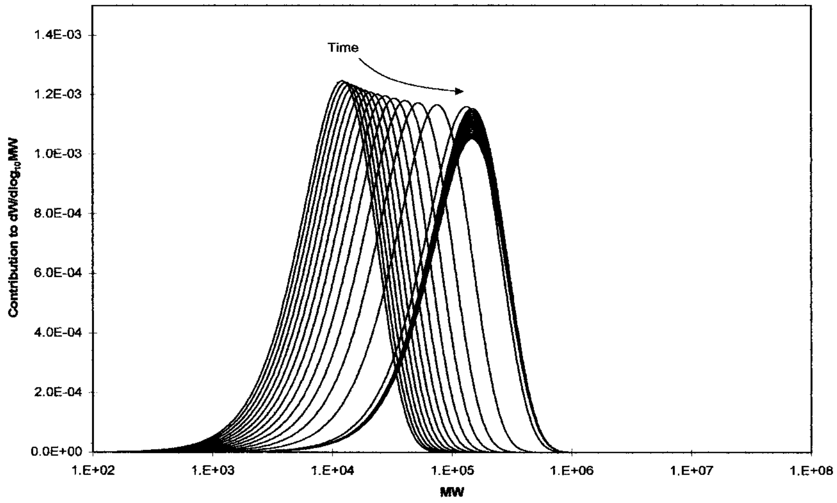

Figure 3. Simulated SECs of instantaneous LMW polymer as a function of time

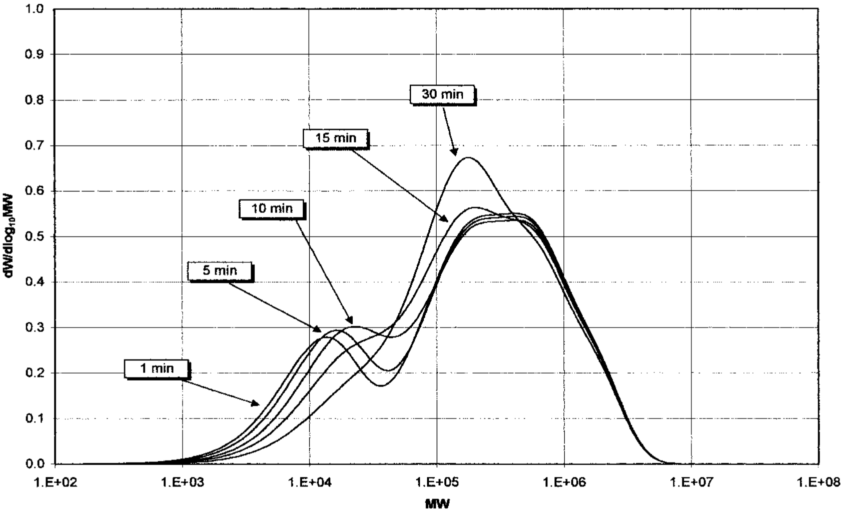

Figure 4. Simulated SECs of bulk semi-batch reactor resin during polymerization

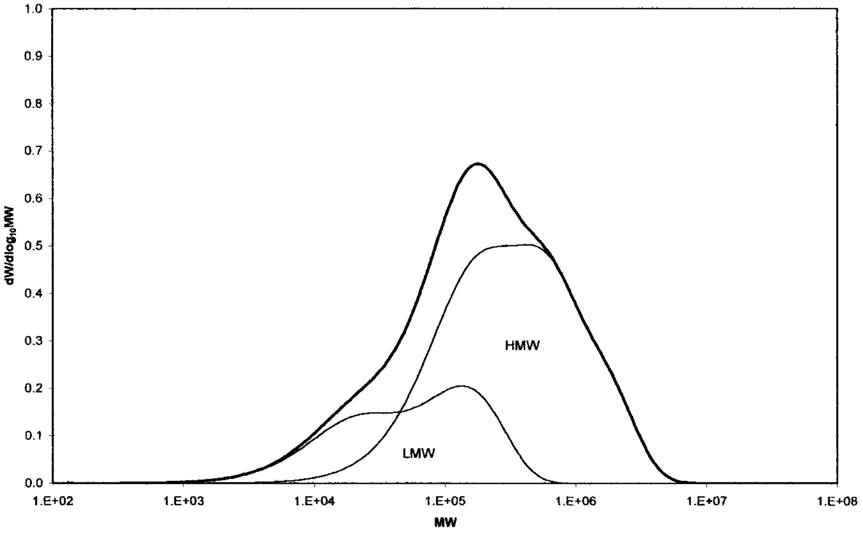

Figure 5. Simulated SEC of final semi-batch product showing HMW and LMW components

Continuous, Pilot-Scale Gas-Phase Polymerization. In Example 2, the model catalyst system summarized in Table 1 is fed to a continuous pilot-scale reactor with an initial 120 lb polyethylene bed. During the 48 hour run, ethylene partial pressure is controlled at 220 psig, hydrogen is fed to maintain the gas-phase molar H_2/C_2 ratio at 0.0013, and reactor temperature is controlled at 85 °C. Bed level is controlled at a constant reactor volume fraction of ~ 0.5. Under steady-state conditions at a production rate of 30 lbs/hr and a residence time of 4 hrs, the desired high molecular weight, high-density bimodal product is produced with an HMW split of ~ 0.50. Two events are studied:

1. Reactor startup with a 120 lb resin bed consisting of the desired product; and
2. The effect of a half-hour interruption of catalyst feed, 36 hours into the run.

In this example, all the features of eqn (3) are employed—the reactor is started with a well-characterized seed bed with known cumulative molecular weight distribution, and the effect of the interruption of catalyst feed is studied starting from a steady-state condition just prior to the disturbance.

The major features of the run are captured in Figure 6, which shows how the HMW split of the bimodal polymer changes during startup, and in response to an interruption in catalyst feed. The cumulative molecular weight distributions of polymer produced by each of the two catalysts in this model do not change with time during the run because reactor pressure and H_2/C_2 ratio are controlled at their set points. In this example, only HMW split is affected by the interaction between reactor dynamics and catalyst kinetics. For reference, the variation in residence time during the run is shown in Figure 7.

During reactor startup, HMW split increases rapidly from its initial value of 0.50, reaching a maximum of ~ 0.54 after 2.88 hours. It takes another 17 hours before the split returns to the desired value. This excursion in split during startup, in spite of an initial bed consisting of the desired bimodal product, may seem surprising. It is, however, a natural consequence of the large disparity in catalyst half-lives (2 hours for the LMW catalyst *vs.* 20 minutes for the HMW catalyst) in the model mixed-catalyst system.

Simulated SECs of polymer in the startup bed, 2.88 hours after start up, and at the peak of the catalyst feed disturbance have been computed using eqn (3) and are shown in Figure 8.

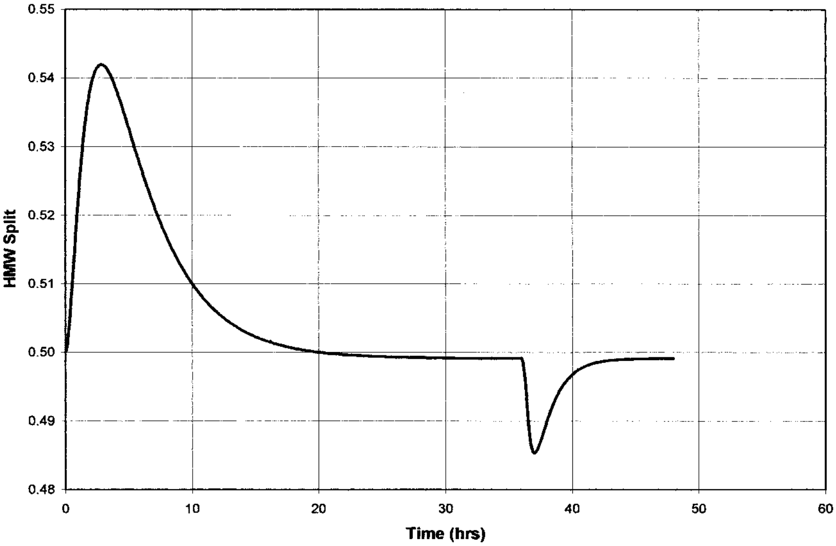

Figure 6. HMW split during start up and following a disturbance in catalyst feed rate

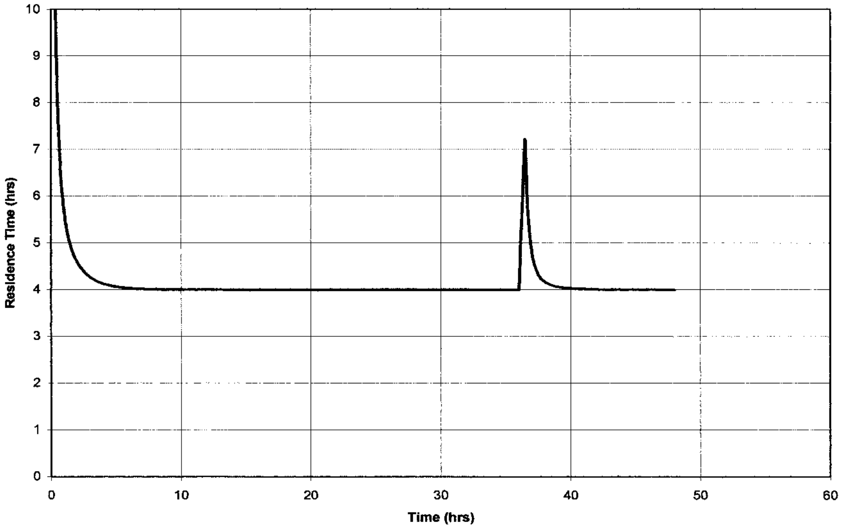

Figure 7. Reactor residence time during start up and following a disturbance in catalyst feed rate

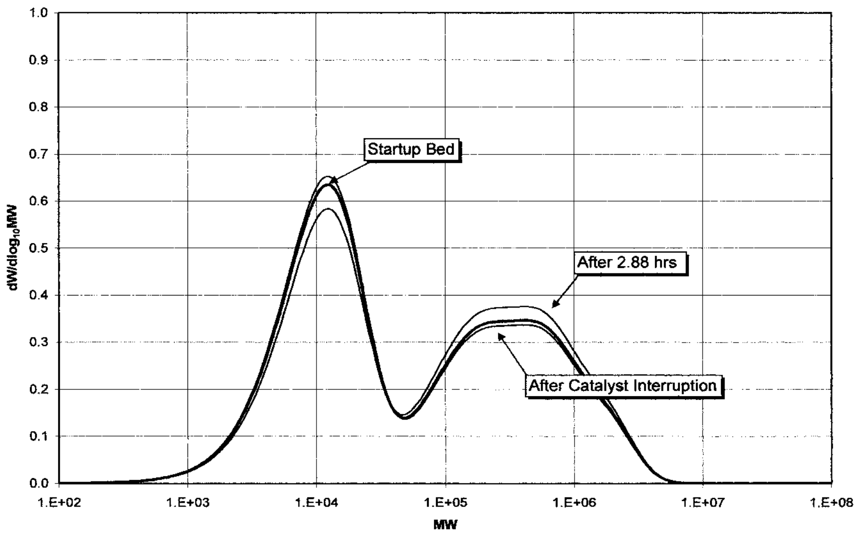

Figure 8. Simulated SECs of bulk reactor resin

Conclusions

Cumulative distributions can be computed in a two-step process using a convolution integral and suitable output from existing reactor simulation codes, or more directly by augmenting the system state equations. These methods:

- are not restricted to steady-state operation—residence time and bed weight may vary—allowing the study of the effect of a wide range of transient phenomena on polymer quality, including process disturbances and upsets, and product grade transitions; and
- are not restricted to distributions of polymer structure—they can be applied to any polymer property for which a mixing rule can be written in a form that is a linear function of mass.

The convergence properties of these methods, however, have not been rigorously investigated, which is true in general of instantaneous property methods. These methods also require computable instantaneous distributions for structural characteristics of interest.

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