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Development of an Unsteady-State Model for Control of Polymer Grade Transitions in Ziegler-Natta Catalyzed Reactor Systems

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Summary: The dynamics of the activity and polymer growth in Ziegler-Natta catalysts has been well established in the literature.[1,2] The corresponding dynamic behaviour of the reactor system is predicted using a segregation model approach and the unsteady state model of residence time distribution previously developed.[3] The model is therefore able to predict reactor performance for a time-varying catalyst flow rate through the reactor, as well as time-varying concentrations of monomer, co-catalyst and chain termination agent. A method of determining grade transition policies by the use of the developed reactor models is then presented. It is demonstrated that the reactor productivity, catalyst efficiency, average chain length and polydispersity can be controlled by the catalyst flow rate and reactor monomer and hydrogen concentrations. The relationship between the required polymer product properties and the system flow rates is determined. Case studies are presented that evaluate various transition strategies for a specific polymer grades.

Keywords: computer modelling; polymer grade transitions; residence time distribution; unsteady state modelling; Ziegler-Natta polymerisation

Introduction

General attempts at modeling the behavior of reactors under unsteady-state modes of operation have been attempted during the previous two decades. At one stage, extended Kalman filters were used for state estimation of polymer reactors.[4] A more fundamental approach applied population balances describing nucleation, growth and aggregation of particles in constant volume batch systems.[5] In particular, a model of ethylene polymerization in a high pressure tubular reactor and found good agreement between prediction and measurement of conversion, molecular weight and long-chain branching for different reactor configurations and operating conditions.[6]

This lead to development of a dynamic reactor model that uses a multi-site kinetic scheme as its basis.[7] The lack of suitable on-line polymer property measurements was addressed by developing a scheme to predict polydispersity and density in an ethylene copolymerization reactor.[8] The modeling of fluidized beds was made simpler when it was shown that, in the absence of thermal gradients, there is virtually no effect of particle size and its distribution on fluidization quality for polyethylene and polypropylene particles.[9] The resulting simplified models allowed for investigation into grade transition strategies[10,11] and the introduction of industrially applicable analysis software.[12] Steady-state RTD was used together with a particle mass-transfer limitation model as well as catalyst deactivation to predict reactor performance.[13]

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These developments were restricted to the steady flows of catalyst through the reactor.

Compartmental models showed that imperfect mixing can change reactor steady states and stability that can lead to increased polydispersities as well as affecting copolymer composition and chain sequence length.[14] Independent studies[15] showed that imperfectly mixed reactors enjoy a substantially increased range of stable operation over perfectly mixed reactors, facilitating the grade transition process. The effect of RTD and catalyst poisoning and deactivation on copolymer content was found to be a narrowing of the copolymer distribution.[16]

Some attempts were made to model the effect of RTD under unsteady-state conditions for eventual application in product grade transitions.[17] Optimal grade transition strategies were discussed for multireactor systems[18] showing, in particular that controlling the reactor hydrogen concentration was an effective grade transition strategy.

In furthering the unsteady state model development for determining transition strategies, the earlier work in population balance modeling was extended to include particle energy balance effects.[19] A multicompartment population balance model was used to predict particle segregation phenomena and particle size distribution in a gas-phase olefin polymerization reactor.[20]

In summary, several researchers in more process control-oriented studies tend to favor empirical techniques such as dynamic matrix control rather than those based on fundamental models, which raise questions about the range of application of the resulting controllers. On the other hand, model predictive control studies usually involve estimation of kinetic parameters from plant data, which, for different reasons, also raises questions about the range of applicability.

A more rigorous method involves modelling particle behaviour from first principles and then predicting the performance of industrial reactors from the resulting particle model. The Residence Time Distribution (RTD) may be used to predict the performance of a reactor based on the performance of the particle by the use of the segregation model. However, the model of RTD under unsteady flow conditions has only very recently become available,[3] this, prior to that point, prediction of reactor performance during grade transition was limited to the case where catalyst flowrates are steady. The present article attempts to develop investigations into unsteady catalyst flowrates by the incorporation of the now available unsteady state RTD solution.

Model Development

In a stirred fluidized bed reactor used in Ziegler-Natta catalyzed propylene polymerization, the reactant phase contains TEA and gaseous monomer and hydrogen, whereas the polymer and catalyst constitute a solid phase. The reactor productivity and polymer product properties (average chain length and polydispersity) are predicted using the reaction kinetic scheme developed[21] and previously applied for ethylene polymerization.[22]

The composition in the reactant phase naturally depends on the entry and exit flowrates of the individual chemical components across the reactor as well as the rates of consumption within the reactor. The consumption rate depends on the catalyst activity, which itself is a function of the catalyst RTD in the reactor. Due to the fluidized nature of the reactor, since gas flow determines particle hydrodynamics, the material balances for both phases are strongly coupled, making the solution of even a single perfectly mixed reactor a complicated procedure. A computation scheme is presented here and used in the simulation of variations in catalyst flowrate as well as reactant phase composition.

Gas Phase Material Balances

The catalyst entry flowrate, reactor pressure, temperature are manipulated variables, whilst the concentrations in the reactor of ethylene, propylene, hydrogen and TEA are predicted via. the general material balances on the i-th component in the gas-phase given in Equation (1).

$$\frac{dc_i}{dt} = \frac{1}{V_g^R}(\dot{V}_{in}c_{i,in} - \dot{V}_{out}c_i) - r_i \qquad (1)$$

In Equation (1), c_i is the concentration of component i in the reactant phase [mol.m^{-3}], V_g^R is the volume of the reactant phase of the reactor [m^3], $\dot{V}_{in}$ and $\dot{V}_{out}$ are the volumetric entry and exit flowrates respectively [m^3.s^{-1}] and r_i is the consumption rate of component i due to reaction [mol.m^{-3}.s^{-1}]. Note that since perfect mixing is assumed in the gas phase, the concentrations of all gas phase species are assumed to be same everywhere, hence the CSTR model as reflected by Equation (1) is appropriate. The rate at which component i is consumed during the transformation of sites q to r on particles in the reactor of age θ at time t is given by Equation (2).

$$r_{i,st}^{q,r}(t,\theta) = k_{st,i}^{q,r}P_*^q(t,\theta)c_i(t) \qquad (2)$$

where $r_{i,st}^{q,r}$ has units of mol i.s^{-1}.kg-cat^{-1} and $P_*^q(t,\theta)$ is the concentration of active catalyst sites of type-q on particles of age θ at time t in the reactor, assumed to be approximately the same as the concentration of live chains attached to sites of type-q. During initiation, propagation and termination, the rates are given in Equation 3, 4 and 5 respectively.

$$r_{i,0}^q(t,\theta) = k_{0,i}^q P_*^q(t,\theta)c_i(t) \qquad (3)$$

$$r_{i,p}^q(t,\theta) = k_{p,i}^q P_*^q(t,\theta)c_i(t) \qquad (4)$$

$$r_{i,t}^q(t,\theta) = k_{t,i}^q P_*^q(t,\theta)c_i(t) \qquad (5)$$

The relationship between these intrinsic rates and the overall consumption rate is established in the next section.

Overflow Model

The mass of active catalyst present in the reactor determines the reactor productivity, hence the catalyst entry and exit flowrates must be known before the reactor's performance can be predicted. It is assumed here that the entry flowrate of the catalyst is a manipulated variable, and is hence a known time function. On the other hand, since the polymer grows on the catalyst particle, it is the exit flowrate of the polymer that determines the catalyst exit flowrate. In this section, a model is developed that relates these two, thus making it possible to solve the catalyst material balance over the reactor.

To determine the polymer exit flowrate, the polymerization rate, which depends on the gas phase concentrations, must first be known. In solving for the gas phase concentrations, and noting that gas phase components are consumed during reactions on the particles' surface, the particle RTD is needed to solve a model of the reactor. The particle RTD depends on the particle flowrates, which, as mentioned above, depends on the intrinsic rate itself. As such, the reactor hydrodynamics and intrinsic reaction rates are coupled.

We note that even though a particle grows rapidly due to polymer deposition, the catalyst mass within the particle remains unchanged with time. Catalyst mass is therefore an appropriate basis in developing the particle RTD in the reactor. For this reason, the dimensional RTD $w(t,\theta)$ [kg-cat.s^{-1}] is defined such that $w(t,\theta)\Delta\theta$ is as the mass of catalyst in the reactor in age range $[\theta, \theta + \Delta\theta]$ at time t.

The consumption rate of component-i can be predicted using the segregation model as shown in Equation 6.

$$r_i(t) = \int_0^\infty \left\{ w(t,\theta) \sum_m \left[\sum_n r_{i,st}^{q_m,q_n}(t,\theta) + r_{i,0}^{q_m}(t,\theta) + r_{i,p}^{q_m}(t,\theta) + r_{i,t}^{q_m}(t,\theta) \right] \right\} d\theta \qquad (6)$$

Clearly, in order to complete the material balance on the reactant phase components, the RTD $w(t,\theta)$ is required. This distribution can be obtained once the entry and exit flowrates of catalyst to/from the reactor are completely specified.

The tendency for the bed level to remain constant, and at the same level as the exit pipe, is interpreted here as an overflow situation. That is, the bed is well enough fluidized that particles at the same level as the exit pipe tend to leave the reactor. Noting that particles within the reactor are generally of a much greater volume and mass as compared with the fresh catalyst particles fed to the reactor, we conclude that even if the catalyst entry flowrate changes with time, the total bed volume will still be approximately constant.

If it is furthermore assumed that fluidized bed density is also constant, then clearly the total bed mass is constant. Only a negligibly small fraction of the bed mass is catalyst and reactant phase components that are sorbed into the particles; the vast majority is solid polymer. Since bed mass is constant and affected only by the mass of polymer, it is clear that any change in polymer bed mass is compensated for by the exit flowrate of polymer particles from the reactor such that a constant bed height is maintained. In order to understand this more clearly, the material general balance Equation 7 is written over the mass of the solid phase m_s (bed mass).

$$\frac{dm_s(t)}{dt} = \dot{m}_{s,in} - \dot{m}_{s,out} + \dot{m}_{s,gen} \tag{7}$$

where $\dot{m}_{s,in}$ is the entry flowrate of solids, $\dot{m}_{s,out}$ is the solids exit flowrate and $\dot{m}_{s,gen}$ is the rate of generation of solids in the reactor (all in [kg.s^{-1}]).

As mentioned previously, it may be assumed that since the pure catalyst particle mass is negligibly small as compared with the polymer particle mass, and so

$$\dot{m}_{s,in} = 0 \tag{8}$$

Furthermore, the observation of a constant bed level and the assumption of constant fluidized bed density results in zero accumulation of mass in the reactor. If so, Equation 9 must hold.

$$\dot{m}_{s,out} = \dot{m}_{s,gen} \tag{9}$$

Solid mass is generated when polymer is deposited onto the catalyst particles. Since the rate of initiation is negligibly small as compared with the propagation rate, the polymer deposition rate can be approximated by computing the overall monomer incorporation rate due to propagation as shown in Equation 10.

$$\dot{m}_{s,gen}(t) = MM_{mon} \int_0^\infty r_p(t,\theta)w(t,\theta)d\theta \tag{10}$$

where MM_{mon} is the molar mass of the monomer [kg.mol^{-1}], and $r_p(t,\theta)$ is the rate of propagation [mol-monomer.s^{-1}.kg-cat^{-1}]. In the case of co-polymerization, the monomer molar mass is the composition weighted average, where the composition of the monomer in the polymer is known from the relative reaction rates of monomer incorporation.

Catalyst Exit Flowrate

It is the catalyst rather than the polymer exit flowrate that is required to obtain the catalyst RTD function $w(t,\theta)$. Defining the quantity $\overline{\phi}_p$ to be the average polymer-to-catalyst mass ratio in the bed (kg-polymer/kg-cat), it becomes possible to relate the polymer exit flowrate $\dot{m}_{s,out}(t)$ to the catalyst exit flowrate $h_{out}(t)$ (see Equation 11).

$$h_{out}(t) = \frac{\dot{m}_{s,out}(t)}{\overline{\phi}_p(t)} \tag{11}$$

The average polymer-to-catalyst mass ratio may be determined by statistical averaging of the ratio function as given by Equation (12).

$$\overline{\phi}_p(t) = \frac{\int_0^\infty \phi_p(t,\theta)w(t,\theta)d\theta}{\int_0^\infty w(t,\theta)d\theta} \tag{12}$$

where ϕ_p (t,θ) is the polymer-to-catalyst mass ratio (kg-polymer/kg-cat) of for a particle of age θ in the reactor at time t. We shall refer to this development as the Overflow Model. The derivation of the function ϕ_p $(t,\theta)$is discussed in detail in the next section.

Equation (11) and (12) above reveal that in order to obtain the catalyst exit flowrate for the purpose of determining the catalyst RTD, the RTD itself is required. An

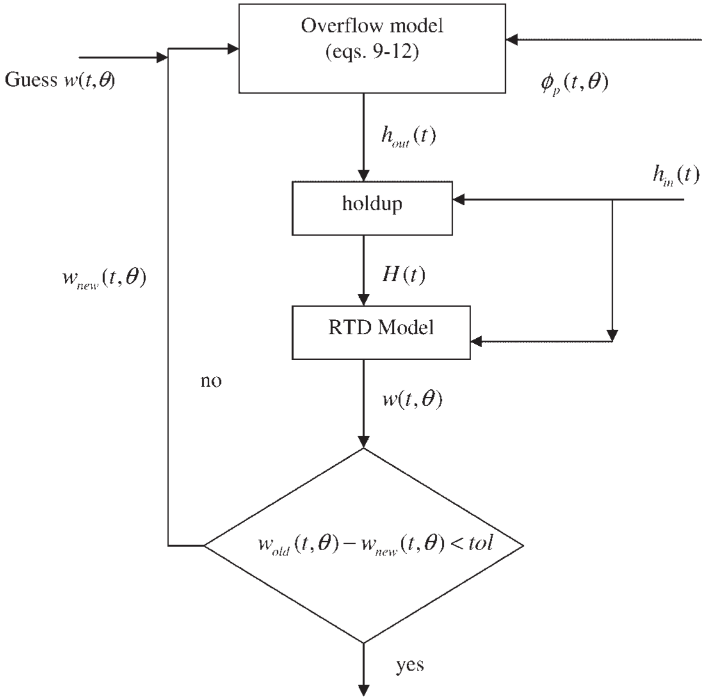

Figure 1.
Flow chart for solving for the catalyst residence time distribution under unsteady state mode of operation (pre-assumes function $\phi_p(t,\theta)$ is known).

iterative approach to solving these equations is presented as a flow chart in Figure 1.

Polymerization Kinetics

When solving for the catalyst RTD, the function ϕ_p (t,θ), which is effectively the mass of polymer accumulated in a particle of age θ at time t in the reactor, can be obtained by integrating the rate at which mass enters the particle by chain propagation across time range $[t - \theta, t]$ and age range $[0,\theta]$ as shown in Equation 13.

$$\phi_p(t,\theta) = MM_{mon}\int_0^{\theta} r_p(t-\theta+\theta',\theta')d\theta' \tag{13}$$

where the polymerization rate r_p is obtained as follows:

$$r_p(t,\theta) = \sum_q k_p^q P_*^q(t,\theta)c_M(t) \tag{14}$$

where $c_M(t)$ is the concentration of monomer in the reactor at time t [mol. m^{-3}]. The function $P_*^{qi}(t,\theta)$ (catalyst sites concentration [mol-site i/mol Ti]) is obtained as follows:

$$\underline{P}_*(t,\theta) = \exp(\mathbf{A}(t) - \mathbf{A}(t-\theta))\underline{P}_{*,0} \tag{15}$$

where

$$\frac{d\mathbf{A}}{dt} = \beta_{\mathbf{st}}^{\mathbf{T}}(t) - \mathrm{diag}\left[\sum_q \beta_{st}^{q,r}(t)\right] \tag{16}$$

The site transformation matrix $\beta_{st}^{q,r}(t)$ depends on all the concentrations in the reactant phase. In addition, the polymerization rate is directly proportional to monomer concentration $c_M(t)$. The function $\phi_p(t,\theta)$ can therefore be obtained only once the reactant phase concentrations in the reactor can be accurately measured or predicted. As established earlier, the reactant phase material balance can only be solved done once the RTD itself is known.

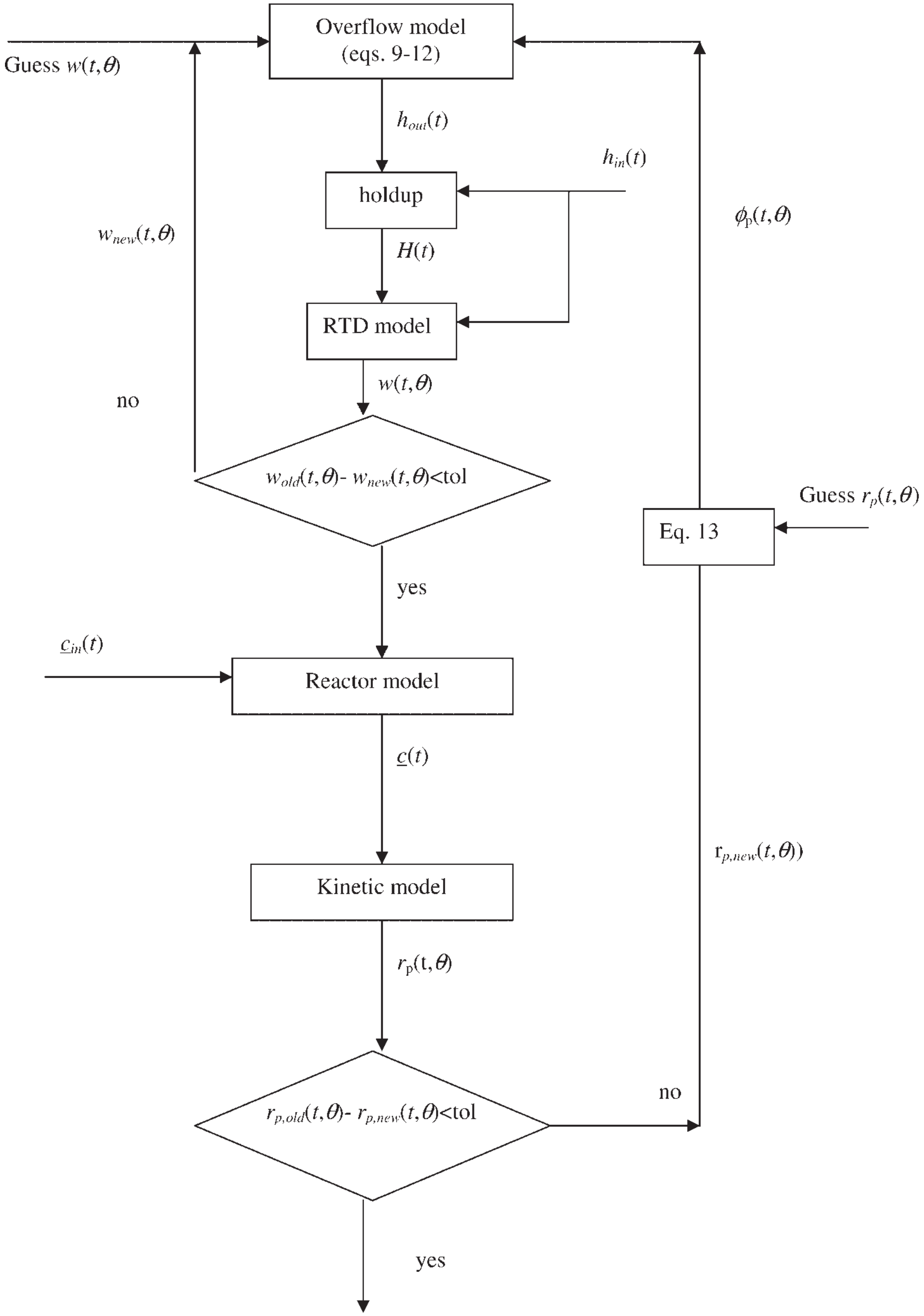

Figure 2.
Flowchart for convergence of the reactor material balance under unsteady state mode of operation.

In summary, it is clear that the reactant phase consumption model, the model of catalyst RTD as well as the model of particle mass increase are all strongly inter-related and cannot be solved separately. An iteration scheme is proposed in the following section for solving this highly coupled set of equations, with

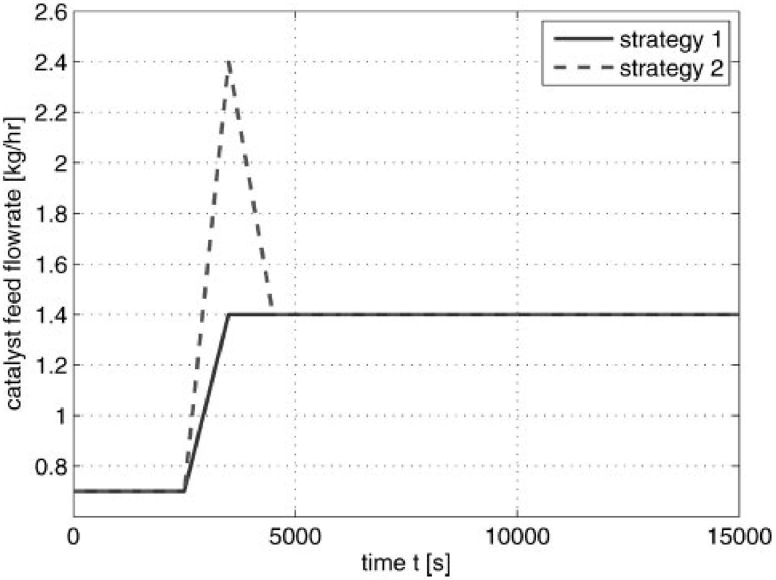

Figure 3.
Catalyst entry flow flowrate profile showing ramp increase (strategy 1) and overshoot increase (strategy 2).

the earlier scheme for converging the RTD incorporated as a nested loop (see Figure 2).

Numerical Solution Algorithm

In order to ensure that the iterations converge rather than diverge, and to reduce the time taken for convergence to be achieved, it is necessary to choose reasonable initial guesses for the RTD, the reactant concentrations as well as the average particle polymer-to-catalyst mass ratio. A reasonable guess for the reactant phase concentrations may be made by assuming first that the controller gain is sufficiently high that the concentration in the reactor is the same as the concentration setpoints chosen. If the concentrations are known, then the function $r_p(t,\theta)$ and hence $\phi_p(t,\theta)$ can be evaluated and the kinetics are considered to be solved.

Reasonable initial guesses are obtained for the residence time distribution by finding the steady state solution and by noting that at steady state, the mean residence time of the catalyst mass is the same as that of the solid particles, in the reactor. From this point on, steady state values will be denoted by the subscript 0. Equation 17 then holds.

$$\tau_0 = \frac{H_0}{h_0} = \frac{m_0}{\dot{m}_{0,out}} \tag{17}$$

where

$$m_0 = \int_0^\infty w_0(\theta)\phi_{p,0}(\theta)d\theta \tag{18}$$

and

$$\dot{m}_{0,out} = MM_{mon}\int_0^\infty w_0(\theta)r_{p,0}(\theta)d\theta \tag{19}$$

The normalized RTD may be related to the dimensional RTD as shown in Equation 20.

$$I_0(\theta) = \frac{w_0(\theta)}{H_0} \tag{20}$$

Equation (17)–(20) can be combined to give Equation 21.

$$\tau_0 = \frac{\int_0^\infty I_0(\theta)\phi_{p,0}(\theta)d\theta}{MM_{mon}\int_0^\infty I_0(\theta)r_{p,0}(\theta)d\theta} \tag{21}$$

The well known solution to steady state RTD for perfectly mixed reactors (Equation 22) then applies.

$$I_0(\theta) = \frac{1}{\tau_0}\exp\left(-\frac{\theta}{\tau_0}\right) \tag{22}$$

This function may be used as the initial guess for the RTD, following which the convergence algorithm proposed in Figure 2 may be employed.

Unsteady State Stimulation

In this section, we apply the convergence algorithm developed to demonstrate that it is possible to optimize a grade transition using the unsteady state model of polymerization developed in the previous sections. We consider the case in which the transition between two polymer grades can be determined by the catalyst flowrate, and present two possible transition strategies, the first being a simple ramp increase to a higher catalyst flowrate, the second being a temporary overshoot of this higher flowrate. The two strategies are shown in Figure 3.

The system responses to these inputs are given in Figure 4 and 5. Before comparing the two strategies, we note the following general trends observed in each case: The observed decrease in catalyst productivity is expected given that although polymer bed mass does not change, there is more catalyst in the bed after the increase in catalyst feed flowrate. As such, on average, there would be less polymer accumulated in the particles, which tends to decrease the catalyst productivity. Stated differently, the catalyst now flows through the reactor at a higher rate, has less time of exposure to the reaction conditions and hence accumulates a smaller polymer mass than prior to the increase. On the other hand, the monomer consumption rate increases due to the increased proportion of fresh catalyst in the reactor. Furthermore, since the Ti^{3+}.TEA sites are associated with a lower propagation-to-termination rate ratio, the average chain

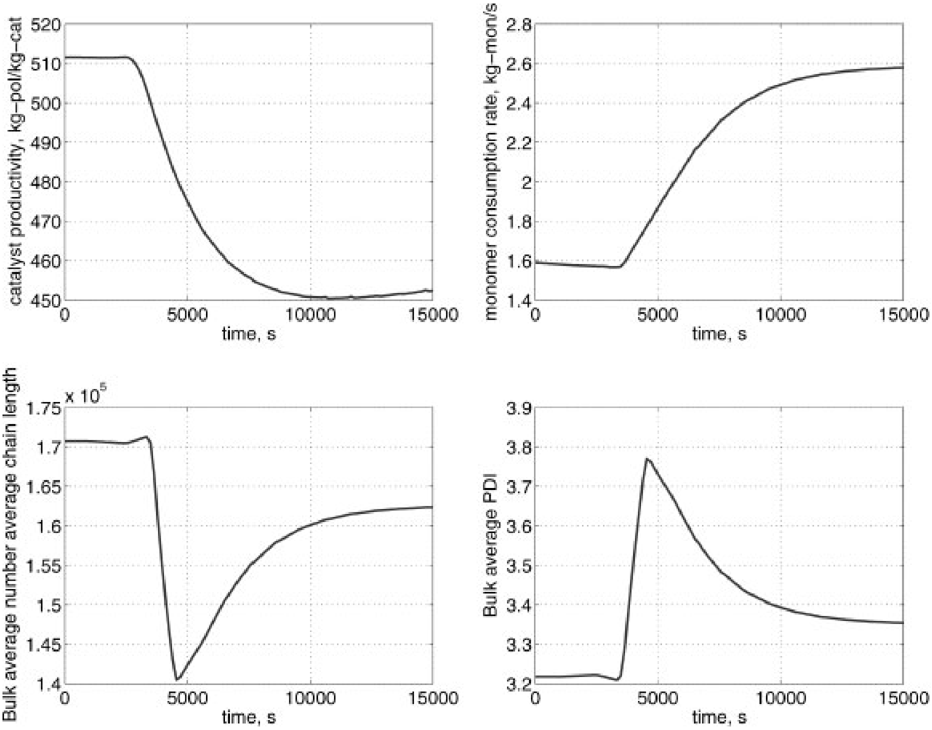

Figure 4.
System response to strategy 1.

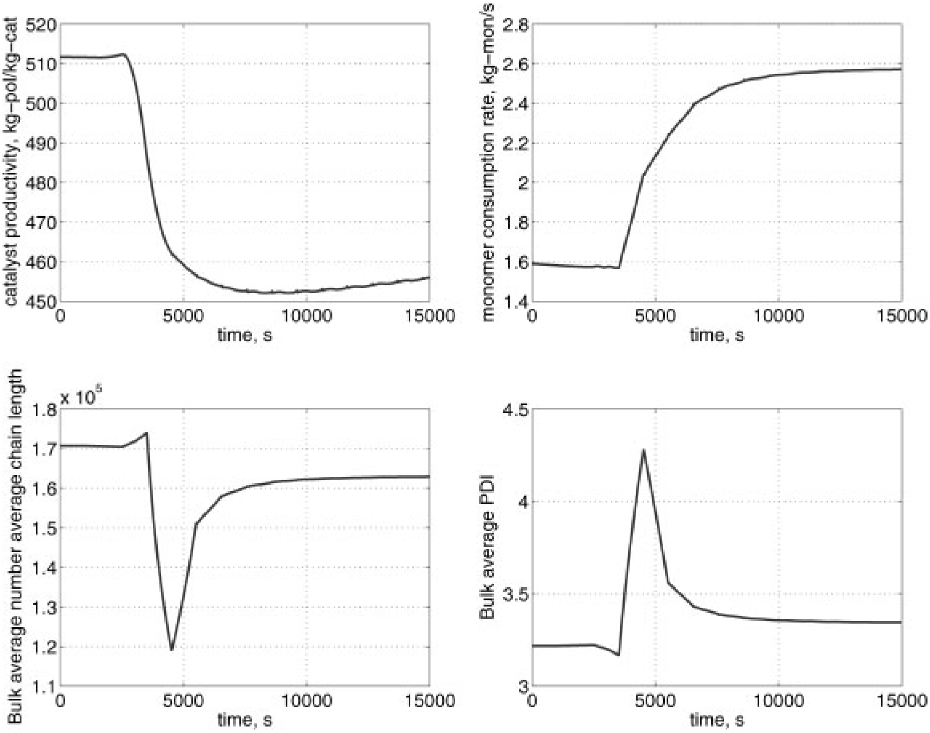

Figure 5.
System response to strategy 2.

length decreases once the catalyst feed rate increases, since it serves to increase the proportion of low-age particles in the reactor.

Comparing the system responses in each strategy (see Figure 4 and 5) it is clear that the overshoot strategy yields a faster return to steady operation and so is the better transition strategy. This result is to be expected since the period of overshoot may be considered the period during which system transients are accelerated toward achieving the final steady state.

Conclusions

A procedure for incorporating polymerization kinetics with the unsteady state RTD to predict the system performance is developed in this article. Through the introduction of the Overflow Model, it becomes possible to estimate the catalyst exit flowrate in response to the growth of polymer within the reactor. Numerical computation schemes are developed to overcome the complexity inherent in the strongly coupling among gas phase components material balances, the reactor residence time distribution and the intrinsic reaction rates. The resulting reactor model was then simulated under time-varying catalyst flow conditions.

A method of estimating a reasonable initial guess for the 2-D unsteady state residence time distribution is outlined. Two grade transition strategies involving the catalyst entry flowrate are simulated. The system response is characterised by the following main output variables: catalyst efficiency (the amount of polymer produced per mass of catalyst per unit time), the reactor monomer consumption rate/reactor productivity and the two crucial polymer properties, *viz.* number average chain length and polydispersity index. It is observed that an overshoot strategy can aid significantly in accelerating system transients so as to achieve the final steady state more rapidly than using a simple ramping approach.

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