# Application of Input Trajectory Optimisation of Ziegler-Natta Catalysed Gas-Phase Olefin Polymerisation Reactor Systems

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**Summary**: In this work, an alternative formulation of the Population Balance Model (PBM) is proposed to simplify the mathematical structure of the reactor model. The method is based on the segregation approach applied to the recently developed unsteady state Residence Time Distribution (RTD). It is shown that the model can predict the performance of a reactor system under unsteady flow and composition conditions. Case studies involving time-varying catalyst flowrates, reactor temperature and reactor pressure were simulated and found to predict reactor performance with reasonable accuracy. The model was used to propose a grade transition strategy that could reduce transition time by as much as two hours.

**Keywords:** computer modelling; reactor engineering; residence time distribution; Ziegler-Natta polymerization

## Introduction

The performance of the gas-phase Ziegler-Natta catalysed olefin polymerization reactor depends on certain key properties of the particles, namely: 1) due to potential mass transfer limitations, the particle size, which will vary during polymerization, 2) due to site transformation and the grow of polymer on the particle, the time of exposure of the particles to the reaction environment and 3) due to potential concentration-time changes in the reactor, the composition and chain length characteristics of the polymer developed.

In situations where the properties of the fluid element (in this case, the particle) determine the system performance, Hulbert and Katz (1964) showed in their landmark paper that the most appropriate modelling tool is the Population Balance Equation. Various attempts have been made ever since to predict the performance of polymerization reactor systems by this method.

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In developing an unsteady state reactor model for the eventual purpose of simulating grade transitions,[6] applied the residence time distribution theory to predict reactor performance of loop, continuous stirred tank, horizontal stirred bed and fluidized bed technologies. However, given that the population balance models were suitable for predicting steady state operation, it was not possible for grade transitions to be considered for variations in catalyst flowrate.

The modeling of fluidized beds was made simpler by the findings of[2] who showed that there is virtually no effect of particle size and its distribution on fluidization quality for polyethylene and polypropylene particles. Generally, it was found that the most important factors that governed grade transition performance were reactor design, residence time distribution of the polymer and monomer-phase. Ohshima *et al.* (1994) also demonstrated the successful development of optimal grade transition strategies using model-based control, with the model being validated using plant data.

Although there is no shortage of interest in applying population balances

to modelling these reactor systems, the approach is plagued in each case by the same basic problems: for even a small number of properties, the Population Balance Equation (PBE) is a high-dimensional partial differential equation that is difficult to solve even numerically. We seek in the present work to develop an alternative method that allows for predicting system performance in a simpler way while utilizing a Population Balance framework.

## Reactor Model Development

It is clear that the unsteady state RTD is a key component of the reactor model. The solution is[4] given by equation 1.

$$I(t,\theta) = \frac{h_{in}(t-\theta)}{H(t-\theta)} \exp\left(-\int_{t-\theta}^{t} \frac{dt'}{\tau_{in}(t')}\right) \quad (1)$$

where $I(t, \theta)$ is the residence time distribution with respect to age $\theta$ at time $t$ in the reactor, $h_{in}(t)$ is the entry flowrate to the reactor at time $t$, $H(t)$ is the holdup in the reactor at time $t$ and $\tau_{\text{in}}$ is the mean residence time based on the entry flowrate as defined in equation 2.

$$\tau_{in}(t) = \frac{H(t)}{h_{in}(t)} \quad (2)$$

If the inlet and exit flowrates $h_{in}(t)$ and $h_{out}(t)$ are known, then the holdup can be determined from the overall material balance given by equation 3.

$$\frac{dH}{dt} = h_{in}(t) - h_{out}(t) \quad (3)$$

The inlet flowrate $h_{in}(t)$ is the catalyst inlet mass flowrate to the reactor at time $t$, and is considered to be a specified time function, whilst $h_{out}(t)$ is the catalyst mass exit flowrate. The latter is much harder to determine, since, in the gas phase fluidized systems, the catalyst is carried out with the polymer particles. Even if the particle mass exit flowrate is fixed (which, in the unsteady state mode of operation, it doesn't have to be), the catalyst loading per particle is an unknown function quantity, hence there is no direct way of determining the exit flowrate of catalyst from the reactor.

We recognize that the exit flowrate of polymer may vary if the reaction conditions such as monomer concentration, reactor temperature and even amount of catalyst held up in the bed vary with time. However, in the fluidized systems, it is generally found that the mass of particles (including both polymer and catalyst) is constant since the exit pipe is at a fixed position, causing the polymer powder to ''overflow''. As such, if the bed density is approximately constant, then the mass of polymer in the bed is also approximately constant. The mass in the reactor at any given time may be determined from the overall material balance represented by equation (4).

$$\frac{dm_s(t)}{dt} = \dot{m}_{s,in} - \dot{m}_{s,out} + \dot{m}_{s,gen} \quad (4)$$

If the internal mass is fixed, the accumulation term is zero. The later generations of the Ziegler-Natta catalyst are highly active; the mass of the polymer developed per particle is usually far greater than the mass of the catalyst itself, hence the inlet mass flowrate of catalyst is negligibly small in comparison with the rate of polymer growth. The development then simplifies to equation 5.

$$\dot{m}_{s,out} = \dot{m}_{s,gen} \quad (5)$$

In other words, since no polymer flows into the reactor, the rate at which polymer flows out of the reactor at any given point in time is identical to the rate at which polymer is produced in the reactor. Solid polymer 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 propagation as given by equation 6.

$$\dot{m}_{s,gen}(t) = MM_{mon} \int_0^\infty r_p(t,\theta) w(t,\theta) d\theta \quad (6)$$

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$^{-1}$]

 

and 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 dimensional RTD $w(t,\theta)$ is simply $I(t,\theta)H(t)$. 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. Equation 7 is used to determine the polymerization rate $r_p$.

$$r_p(t,\theta) = \sum_q k_p^q P_*^q(t,\theta) c_M(t) \tag{7}$$

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

$$\underline{P}_*(t,\theta) = \exp(\mathbf{A}(t) - \mathbf{A}(t-\theta))\underline{P}_{*,0} \tag{8}$$

where

$$\frac{d\mathbf{A}}{dt} = \boldsymbol{\beta}_{\mathbf{st}}^{\mathbf{T}}(t) - \mathrm{diag}\left[\sum_q \beta_{st}^{q,r}(t)\right] \tag{9}$$

The site transformation function $\beta_{st}^{q,r}(t)$ is the sum of the transformations from each of the potential transformation reactions due to attack of the each of the species in the system that may attack a catalytic centre. The exact dependence assumed in the work is defined in equation 10 (Notation adapted from[3]).

$$\beta_{st}^{q,r} = k_{st,Sp}^{q,r} + \sum_i k_{st,M_i}^{q,r}[M_i]^{\alpha_{M_i}} + k_{st,H}^{q,r}[H]^{\alpha_H} + k_{st,Al}^{q,r}[Al]^{\alpha_{Al}} \tag{10}$$

Equations 7–10 therefore represent all the information required to evaluate the right hand side of equation 6 which then allows for the determination of the polymer exit mass flowrate (see equation 5). To translate this to the the catalyst exit flowrate, however, a relationship between the particle polymer mass and catalyst mass must be developed.

If we propose the definition $\overline{\phi}_p$ as the average polymer-to-catalyst mass ratio in the bed (kg-polymer/kg-cat), then the polymer exit flowrate $\dot{m}_{s,out}(t)$ may be related to the catalyst exit flowrate $h_{out}(t)$ as shown in equation 11.

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

where the average polymer-to-catalyst mass ratio may be determined from equation 12.

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

The function $\phi_p(t,\theta)$ is the polymer-to-catalyst mass ratio (kg-polymer/kg-cat) of polymer on a catalyst particle of age $\theta$ in the reactor at time $t$ and may be determined from equation 13.

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

This completes the set of information required to solve the reactor model. Since the RTD is needed to evaluate equation 12 before the catalyst exit flowrate can be determined, the system is coupled, and is best solved by iteration.

## Simulation Results

### Case 1: Catalyst Flowrate

In the first simulation, the entry flowrate of the catalyst to the reactor is increased by a factor of 2 over a 20 min period (approximately), as shown in Figure 1.

System response is illustrated in Figure 2. The decreased 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 individual particles, which tends to decrease the catalyst productivity. On the other hand, the total monomer consumption rate increases due to the increased proportion of fresh catalyst in the reactor. Since the $Ti^{3+}$.TEA sites are associated with a lower propagation-to-termination rate ratio, the average chain length

 

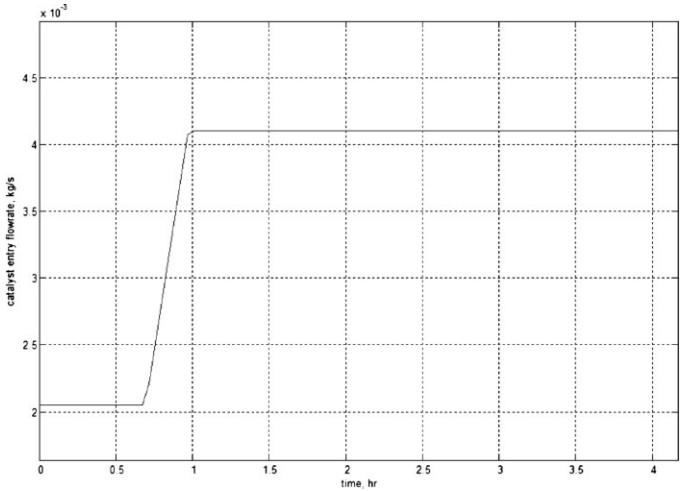


***Figure 1.***
System inputs for a variation in catalyst feed flowrate.

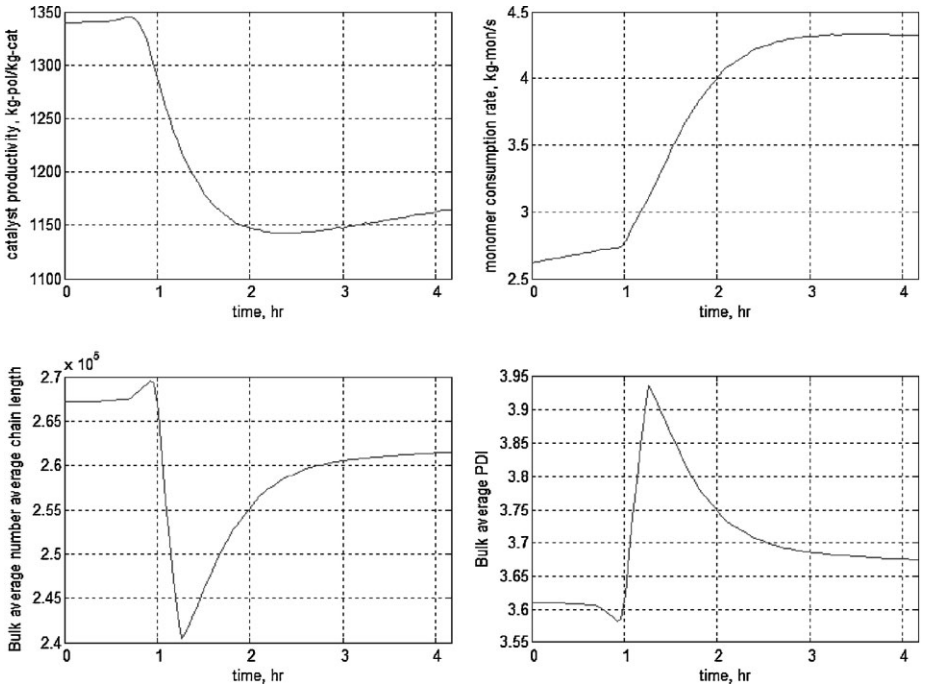


***Figure 2.***
System performance for a variation in catalyst feed flowrate.

decreases once the catalyst feed rate increases, since it serves to increase the proportion of low-age particles in the reactor. The predicted system dynamics are therefore consistent with our understanding of the process behaviour.

**Case 2: Reactor Pressure**

The reactor pressure is increased from 1 atm to 2 atm over a period of 20 min in the next case. The concentrations of ethylene, propylene and hydrogen increase correspondingly.

 

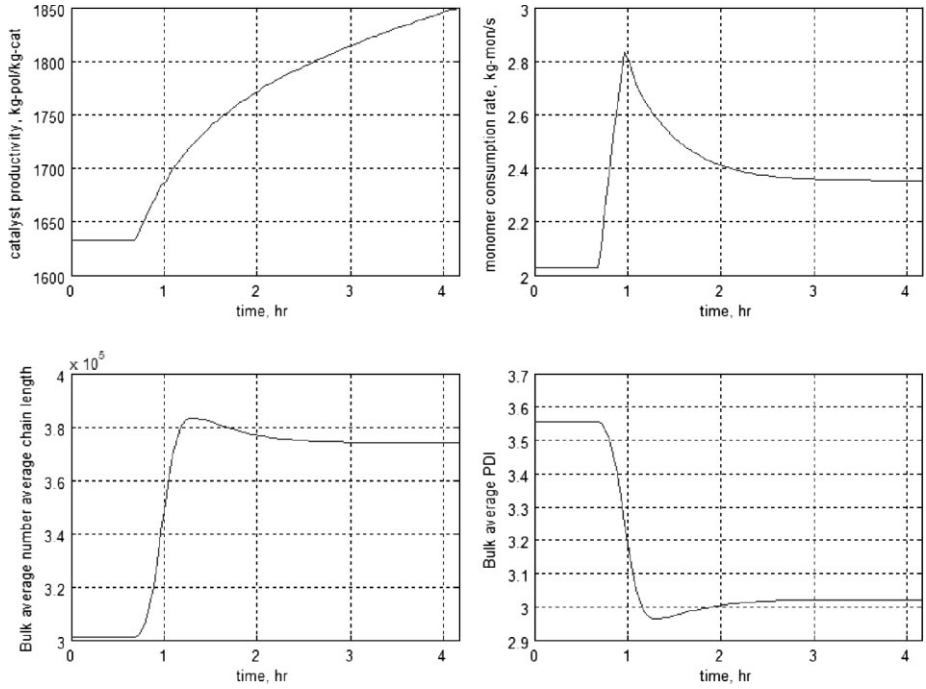


***Figure 3.***
System performance for a variation in reactor pressure.

Due to the increased monomer concentration, the productivity of the catalyst increases (see Figure 3). However, the overall reactor productivity increases sharply initially and thereafter decreases as a result of the increased catalyst removal rate, which tends to decrease the overall bed activity. Although both the monomer and hydrogen concentrations increase, there is an overall increase in the propagation to termination rate ratio, which results in the average chain length increasing with time. The PDI, however, is found to decrease.

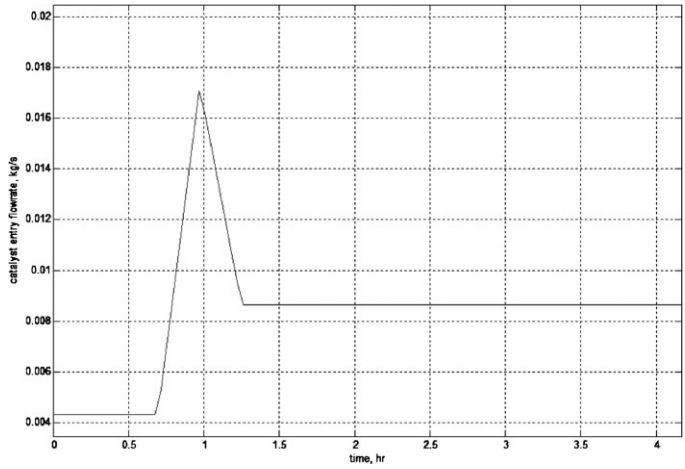


***Figure 4.***
System inputs for an overshot catalyst entry flowrate.

 

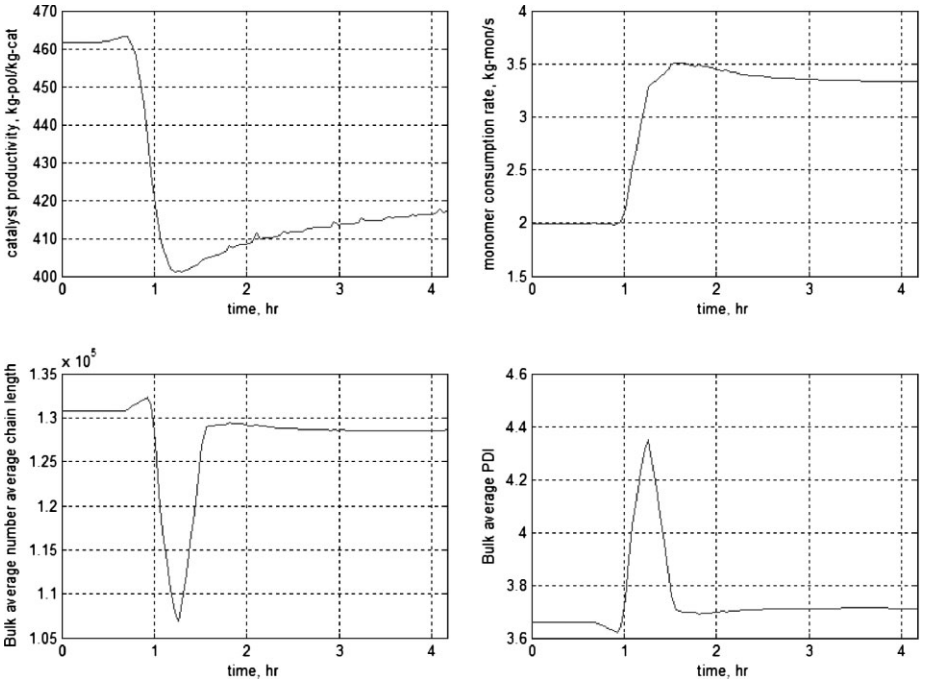


***Figure 5.***
System outputs for an overshot catalyst entry flowrate.

**Trajectory Optimization**

Since the model simulation appears to give reasonable predictions of reactor performance, we now consider using it to optimize the input trajectories with a view to reducing the grade transition time. In the following such case, we simulate an oveershoot strategy. In this approach, we wish to double the catalyst flowrate, but we wish to avoid upsetting the system performance for as great a period of time as observed in case 1 (see Figure 2). As such, we briefly overshoot the catalyst flowrate before bringing it to twice the original flowrate (see Figure 4).

It is evident from Figure 4 that the system steady state is achieved within a far shorter time period when using the catalyst flowrate overshoot (compare with Figure 2). The model may therefore be used to evaluate grade transition strategies and possibly adapted for the purpose of model-based control.

## Conclusion

An approach of Population Balancing has been adopted in modelling the Ziegler-Natta catalysed gas phase olefin polymerisation reactor system. A novel approach that avoids the need to solve the Population Balance Equation was proposed. The new method, however, places heavy reliance on the Residence Time Distribution theory and on a measurement of the feed property distribution to the reactor.

In the case of the RTD, the recent advances in predicting the unsteady state mode of operation were exploited for the purpose of optimising grade transition time. The model was first evaluated for ramped increases of catalyst flowrate, reactor temperature and reactor pressure. The predictions were found to correspond to expected dynamic trends. An overshoot optimisation strategy was proposed and compared against the ramped catalyst

 

flowrate case study. It was observed that the transition time could be reduced by almost two hours.

We therefore propose that the new formulation affords input trajectory optimisation investigations that may well make model based control feasible.

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