Effects of Catalyst Activity Profiles on the Operating Conditions of an Industrial Polymerization Reactor

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Abstract
The aim of this paper is to analyze how different catalyst activity profiles influence the operating strategies of industrial reactors. Based on this analysis a method that can be used to transform information given by laboratory reactor experiments into a form which can be used to estimate the productivity of the catalyst and the quality properties of polymers under industrial conditions is proposed. The whole approach is demonstrated in case of the production of high-density polyethylene production.

Keywords: olefin polymerization, catalyst activity profiles, high-density polyethylene

1. Introduction
The wide range of end-use polyolefin products requires different and various technological properties from the polymers. This is why polymerization processes are carried out with different types of catalysts in different types of reactors. In case of high-density polyethylene the polymerization is usually catalyzed by Ziegler-Natta (ZN) or Phillips-type (PT) catalysts in stirred slurry-phase, loop or gas-phase fluidized bed reactors. In case of these catalysts the mechanisms of the elementary reactions and the rate constants of the partial reactions significantly differ from each other, which allows the production of polyolefin products with different properties.
The activity profile of a catalyst is basically determined by these elementary steps of polymerization reactions such as activation of catalyst, chain initiation, chain propagation, chain transfer, and chain deactivation. Hence, with the use of different types of catalysts different activity profiles can be observed in time.
The catalysts used for high-density polyethylene (HDPE) production can be sorted into two groups in activity profile point of view (Keii, 1972): a ‘buildup’ type and a ‘decay’ type. The so-called Phillips-type Cr-oxide catalysts belong to the buildup group whose characteristics are activating after a so-called induction period and slow deactivating process after that. Metallocene and ZN-type catalysts form the decay group, e.g. TiCl₄ on silica carrier with triethylaluminium cocatalyst, by which quick activating followed by deactivating process can be observed. These activity profiles can also be obtained by laboratory experiments performed in isotherm conditions and with constant component

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concentrations (Calabro, 1988, McDaniel 1991). Besides the type of metal atom, catalyst activity profile strongly depends on the type of the catalyst carrier, the preparation way, and the quality and quantity of the present cocatalyst, which are deeply analyzed by numerous works (Keii and Soga, 1986). Therefore, the developed activity profile can be influenced by several ways, so the more advantageous profile, which means specific mass of the polymer produced during the time period \(0 < t < T_{\text{polymerization}}\) can be a designable point of view by catalyst construction or selection.

Polyolefins are produced in continuous reactors, so the quantity and quality properties of the polymer product depend not only on the activity profile but also on the flow model of the reactor (residence time and its distribution). Residence-time distribution depends on reactor type and operating strategy. Zacca (et. al., 1996, 1997) analyzed the polymer product quality change as a function of change of the residence-time distribution. Wells (et al 2001) dealt with dynamic and stability property of tank and loop reactor used for high-density polyethylene production in case of catalysts with different activity profile.

The aim of this paper is to analyze how different catalyst activity profiles influence the operating strategies of industrial reactors. Based on this analysis a method that can be used to transform information given by laboratory reactor experiments into a form which can be used to estimate the productivity of the catalyst and the quality properties of polymers under industrial conditions is proposed.

The whole approach is demonstrated in case of the production of high-density polyethylene production. All simulation programs related to this paper were developed in Matlab.

2. First Principle Model of an Industrial Reactor

The reaction scheme of the polymerization process in case of different catalyst activity profiles shown in Table 1 enables us to describe the dynamic behavior of the polymerization and estimate the quality of the produced polymer (Wells et al 2001). The difficulty of the application of this approach arises in what way the rate constants of elementary reactions can be determined, because only the change of monomer decrease can be registered during the measurements performed in laboratory conditions, and the elementary reaction steps can be concluded from the product properties analyzed after stop of the reaction.

To get over these difficulties, consider the following assumptions:
1. active centers of catalyst particles have the same activity potential,
2. reaction rate of the propagation step is a function of catalyst age,
3. while reaction rates of the other elementary steps are independent from the catalyst age.

Based on these limitations, polymerization reaction rate can be formed by the following expression:

\[
    r_P(\tau) = g(\tau) \cdot k_P \cdot C(\tau) \cdot M \cdot M_{W,M} \tag{1}
\]

where \(g(\tau)\) is the density function of the activity profile, \(\tau\) and \(M_{W,M}\) mean the catalyst age and the molecular mass of the monomer, respectively.
Table 1 Chemical Reactions for Polymerization of Ethylene

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Chemical Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site activation by cocatalyst</td>
<td>$C_k + C_{cocat} \xrightarrow{k_{act,cocat}} P^k_0$</td>
<td>$r_{act,cocat} = k_{act,cocat} C_k C_{cocat}$</td>
</tr>
<tr>
<td></td>
<td>by monomer $C_k + M \xrightarrow{k_{act,M}} P^k_0$</td>
<td>$r_{act,M} = k_{act,M} C_k M$</td>
</tr>
<tr>
<td>Site transformation</td>
<td>$C_k \xrightarrow{k_{transf}} C_i$</td>
<td>$r_{transf} = k_{transf} C_k$</td>
</tr>
<tr>
<td>Chain initiation</td>
<td>$p^k_0 + M \xrightarrow{k_{init}} p^k_i$</td>
<td>$r_{init} = k_{init} p^k_0 M$</td>
</tr>
<tr>
<td>Propagation</td>
<td>$P^k_i + M \xrightarrow{k_{prop}} P^k_{i+1}$</td>
<td>$r_{prop} = k_{prop} P^k_i M$</td>
</tr>
<tr>
<td>Chain transfer by $H_2$</td>
<td>$P^k_i + H_2 \xrightarrow{k_{transf,H_2}} D^k_i + P^k_0$</td>
<td>$r_{transf,H_2} = k_{transf,H_2} P^k_i H_2$</td>
</tr>
<tr>
<td></td>
<td>by monomer $P^k_i + M \xrightarrow{k_{transf,M}} D^k_i + P^k_0$</td>
<td>$r_{transf,M} = k_{transf,M} P^k_i M$</td>
</tr>
<tr>
<td></td>
<td>by cocatalyst $p^k_i + C_{cocat} \xrightarrow{k_{transf,cocat}} D^k_i + P^k_0$</td>
<td>$r_{transf,cocat} = k_{transf,cocat} p^k_i C_{cocat}$</td>
</tr>
<tr>
<td>Spontaneous Site deactivation</td>
<td>$P^k_i \xrightarrow{k_{deact}} D^k_i$</td>
<td>$r_{deact} = k_{deact} P^k_i$</td>
</tr>
</tbody>
</table>

Figure 1. Comparison of Model Prediction to Data of Experimental for PE Production with Different Type of Catalysts

Based on measured data taken from literature, the identification of the above model was performed in case of ethylene polymerization with ‘buildup’ and also with ‘decay’ type of catalysts. The results of these identifications can be seen in Figure 1.

Let us do some simulation experiments in Continuous Stirred Tank Reactor (CSTR) with these activity profiles. Since the aim of this section is to analyze the effect of the activity profile, isotherm condition in the reactor and constant concentrations in the liquid phase are assumed.
So we have to deal with only the polymer phase and the catalyst. Because the activity profile of the catalyst particles changes with the age of the catalyst, the distribution function of the age of the catalyst particles has to be known. Balance equation that can be used to calculate of the mass of catalyst particles with different age can be expressed in the following form:

\[
\frac{\partial C(t, \tau)}{\partial t} + \frac{\partial C(t, \tau)}{\partial \tau} = F_{C, in} \cdot \delta(t - 0) - F_{C, out}(t, \tau)
\]

\(t = 0\) \(C(0, \tau) = C^0; \quad \tau \to \infty \quad C(t, \infty) = 0\)

The meaning of the right side of the equation 2 is that the age of the inlet catalyst particles is equal to zero, and the outlet polymer stream also carries its catalyst contain.

The balance equation of the polymer is the following:

\[
\frac{\partial D(t, \tau)}{\partial t} + \frac{\partial D(t, \tau)}{\partial \tau} = g(\tau) \cdot k_p \cdot M \cdot M_{W,M} \cdot C(t, \tau) - F_{D, out}(t, \tau) = R_p(t, \tau) - F_{D, out}(t, \tau)
\]

\(t = 0\) \(D(0, \tau) = D^0; \quad \tau \to \infty \quad D(t, \infty) = 0\)

The mass of the total polymer and catalyst in the reactor:

\[
D(t) = \int_0^t D(t, \tau) \cdot d\tau; \quad C(t) = \int_0^t C(t, \tau) \cdot d\tau
\]

If constant polymer mass is assumed in the reactor, then the output can be calculated by the following equations:

\[
F_{D, out}(t) = \int_0^t g(\tau) \cdot k_p \cdot M \cdot M_{W,M} \cdot C(t, \tau) \cdot d\tau
\]

\[
F_{D, out}(t, \tau) = \frac{D(t, \tau)}{D(t)} \cdot F_{D, out}(t)
\]

3. Estimation of Polymer Quality Properties Produced in Industrial Reactor

The above described model enables us to estimate the amount of the polymer produced by different flow model and catalyst activity profile and to determine the average productivity of the catalyst. However, for the estimation of the quality properties of the polymer there is a need to know the elementary reactions influencing these properties. In the analyzed case this means the relative relation between the chain transfer and propagation reactions shown in Table 1. This information can be obtained from experiments evaluated in laboratory batch reactor in different temperature and component concentrations for different length of time.

To present the proposed method, the characteristic values of these parameters have been obtained from the literature (Wells et al 2001).
3.1. Calculation of the Average Molecular Mass and Molecular Mass Distribution in case of Homopolymerization

The evolved molecular structure is determined by the relative rate between the chain transfer and propagation reactions. It can be formed according to the assumed reaction mechanism shown in Table 1 with different catalyst age:

\[ \beta(t) = \frac{R_{\text{chain transfer}}}{R_{\text{propagation}}} = \frac{k_{n,H_2} \cdot H_2 + k_{n,M} \cdot M + k_{n,\text{catalyst}} \cdot C_{\text{catalyst}}}{g(t) \cdot k_p \cdot M}, \]

and the molecular mass distribution of the produced homopolymer:

\[ w(r, \tau) = r \cdot \beta^2 \cdot \exp(-r \cdot \beta) \]

\[ w(r) = \frac{\int_0^\infty R_p(\tau) \cdot w(r, \tau) \cdot d\tau}{\int_0^\infty R_p(\tau) \cdot d\tau} \]

from which \( M_n, M_w, PD \) can be calculated (Soares et al, 1997).

3.2 Calculation of the Particle Size Distribution

Let the size distribution of the catalyst particles be denoted by

\[ w(r_{\text{cat}}) \]

\[ \int_0^{\infty} w(r_{\text{cat}}) \cdot dr_{\text{cat}} = 1 \]

The change of the size of the polymer particle produced by catalyst particle with size \( r_{\text{cat}} \) can be formed in the following:

\[ \frac{dr(t, \tau, r_{\text{cat}})}{dt} = \frac{g(t) \cdot k_p \cdot M \cdot M_w \cdot C(t, \tau, r_{\text{cat}})}{4 \cdot r(t, \tau, r_{\text{cat}})^2 \cdot \pi \cdot \rho_{\text{pol}}} \quad \text{for} \quad t = \tau = 0 \quad r = r_{\text{cat}}, \]

and the average size of polymer particle in a given time instant is:

\[ r(t) = \frac{\int_0^\infty D(t, \tau) \cdot \left[ \int_0^{\infty} w(r_{\text{cat}}) \cdot r(t, \tau, r_{\text{cat}}) \cdot dr_{\text{cat}} \right] \cdot d\tau}{\int_0^\infty D(t, \tau) \cdot d\tau} \]

4. Application of the model

Simulation studies were carried out for polymerization with buildup and decay type of catalyst in a CSTR type of reactor using the proposed model. Activity profiles of the catalyst can be seen in Figure 1. By changing the average residence time, the average productivity of the catalysts, the dispersity of the molecular mass distribution of the polymer (PD), and the average particle size (PS), have calculated assuming that the characteristic value of the catalyst particle size is 35 micron. The results can be seen in Table 2. It has to be noted that with the increase of the residence time the homogeneity of the polymer product (Table 2, PD) changes in a contrary direction by the two types of profiles. The cause of this phenomenon is that the rate of the catalyst particles with the same activity increases by the buildup profile if the residence time is increasing. The same phenomenon can be observed even by decay type of catalysts, but in case of
smaller residence time. The average particle size is increasing with the residence time as it is expected.

<table>
<thead>
<tr>
<th>Residence time (min)</th>
<th>Productivity kg polym./(g cat.-h)</th>
<th>PD Build-up</th>
<th>PD Decay</th>
<th>PS (mm) Build-up</th>
<th>PS (mm) Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>3.6</td>
<td>3.89</td>
<td>3.8</td>
<td>2.72</td>
<td>0.915</td>
</tr>
<tr>
<td>60</td>
<td>5.6</td>
<td>3.39</td>
<td>3.16</td>
<td>1.006</td>
<td>0.670</td>
</tr>
<tr>
<td>75</td>
<td>7.9</td>
<td>3.12</td>
<td>3.67</td>
<td>1.071</td>
<td>0.707</td>
</tr>
<tr>
<td>90</td>
<td>9.4</td>
<td>2.92</td>
<td>4.19</td>
<td>1.130</td>
<td>0.717</td>
</tr>
<tr>
<td>120</td>
<td>13.3</td>
<td>2.71</td>
<td>5.24</td>
<td>1.210</td>
<td>0.729</td>
</tr>
</tbody>
</table>

5. Conclusions

A new method has been proposed that is able to transform information from laboratory batch reactors into an interpretable form which can be used in case of continuous industrial reactors even when the catalyst activity changes. The applicability of this method has been demonstrated by a simulation study. In the near future we would like to prove the applicability of the proposed method also by processing measured data in laboratory and in industrial plants, and to expand the analysis to other application properties of the polymer powder. This method can be used not only to select the catalyst but also to design the product changes that often happen during the production, so it can give an opportunity to reduce the amount of the off-grade products and the involved costs.

References


