Abstract: Polyethylene (PE) is one of the most widely used polymers in chemical industry. In all the PE processes, high-pressure autoclave process is generally considered as the most profitable segment of the polyethylene business worldwide in recent years. Depending on different grades of the product, reactor zone temperatures in this autoclave process can be in the range 150-230°C and pressure in the range of 1500- 2000 kg/cm². In this paper, rigorous dynamic model of an industrial ethylene and vinyl acetate (EVA) copolymerization reactor will be established. Industrial operating condition data of seven product grades with melt index ranging from ones to over four hundred will be used as fitted or test data to obtain the key kinetic parameters in the model. The predicted outputs of melt index, vinyl acetate wt. % in polymer, and polymer production rate will be compared to plant data. Copyright © 2005 IFAC

Keywords: Autoclave process; Polyethylene; EVA copolymerization reactor; Free-radical copolymerization; Melt index.

1. INTRODUCTION

Polyethylene is one of the most widely used polymers in chemical industry. In all the polyethylene process, high-pressure autoclave process is generally considered as the most competitive and the most profitable segment of the polyethylene business worldwide in recent years. The autoclave process is extremely flexible in producing various specialty products. Also, products from autoclave process can be used in variety of high-value sensitive applications because of no residue of metal-base catalyst which is commonly used in other polyethylene processes is present in this polymer. In this paper, rigorous modeling of an industrial high pressure ethylene and vinyl acetate (EVA) copolymerization autoclave reactor will be established.

Rigorous modeling of a high-pressure ethylene and vinyl acetate copolymerization reactor in the literature is relatively scarce in comparison with the free-radical polyethylene (PE) reaction. Zabisky et al. (1992) reviewed the kinetic model for PE and EVA polymerization in a high-pressure tubular reactor. Chan et al. (1993) using several continuous stirred tank reactor (CSTR) or plug-flow reactor segments in series to model the autoclave reactor. In their paper, pseudo kinetic rate constants are used to allow for copolymerization. Sarmoria et al. (2000) developed a mathematical mixing model that describes high-pressure polymerization of ethylene and ethylene-vinyl acetate. The resulting moment model is able to calculate conversions, average molecular weights, long chain branching and melt indexes at any point in the reactor. Brandolin et al. (2001) further developed a mathematical model able to describe the complete molecular weight distributions of polyethylene and ethylene-vinyl acetate copolymers obtained in high pressure autoclave reactors.

In this paper, reactor simulation including detailed polymerization reaction mechanism and also
dynamic component balance and energy balance will be established for an industrial autoclave reactor. Industrial operating condition data of seven product grades with melt indexes ranging from ones to over four hundred will be used as fitted or test data to obtain the key kinetic parameters in the model. The predicted outputs of melt index, vinyl acetate wt. % in polymer, and polymer production rate will be compared to plant data.

The organization of the paper is as follows. The detailed rigorous dynamic model of an industrial autoclave reactor is given in Section 2. Simulation results of the fitted model in comparison with the plant data is shown in Section 3. Some concluding remarks are drawn in Section 4.

2. PROCESS MODELING

The overall process of this industrial ethylene-vinyl acetate copolymerization process can be seen in Figure 1. In this paper, the detailed dynamic model of the autoclave reactor will be developed. The autoclave reactor is modeled as seven constantly-stirred zones with flow from top zone down. Back-mixing flow from lower zone upward is also allowed. The combined feed (INL) including ethylene, vinyl acetate, chain modifier, and inert is fed into the first five zones. The peroxide initiator and solvent (INI) is fed into three of the seven zones. The temperatures of these three zones are controlled by the initiator flow addition rate. The detailed segmented model of this autoclave reactor is shown in Figure 2.

For each zone, the dynamic component balance and energy balance are simulated with the free-radical polymerization kinetic mechanism as below:

\[ \frac{d[X_j]}{dt} = \sum F_{j,n}^\text{INL} [X_j]_{j,n} - \sum F_{j,n}^\text{OUT} [X_j]_{j,n} + V_j r_j \]  

\[ \frac{dT_j}{dt} = \sum \rho_{j,n} F_{j,n} C_p T_{j,n} - \sum \rho_{j,n} F_{j,n} C_p T_{j,n} + V_j \rho_j \Delta H r_j \]

In the two equations above, \( j \) is the reactor zone number and [\( X \)] means the concentration of each component. The overall mass balance of each zone is assumed to be at quasi steady state with the total inlet flow to each zone includes possible feed flow rate into this zone, possible initiator feed into this zone, the outlet flow from the above zone, and the back-mixed flow from the zone below as in the following Eqn. (3):

\[ \sum F_{j,n}^\text{INL} [X_j]_{j,n} = F_j^\text{INL} [X_j]^\text{INL} + F_j^\text{OUT} [X_j]^\text{OUT} + \left(1 - \alpha_{j-1} \right) F_{j-1,n} [X_j]_{j-1} + \alpha_{j+1} F_{j+1,n} [X_j]_{j+1} \]

In this equation, \( \alpha \) is the fraction of total zone outlet flow back into the above reactor zone.

The kinetic mechanism includes the following elementary reactions: decomposition of initiators, propagation, chain transfer to monomer, chain transfer to modifier, chain transfer to polymer, termination by disproportionation, termination by combination, and \( \beta \)-scission of terminal radicals. Pseudo kinetic rate constants are used to allow for copolymerization. The detailed kinetic mechanism can be seen below:

Initiation:

\[ I \overset{k_i}{\longrightarrow} 2R_i(0) \]

\[ R_i(0) + M \overset{k_i}{\longrightarrow} R_i(1) \]

Propagation:

\[ R_i(x) + M \overset{k_p}{\longrightarrow} R_i(x+1) \]

Termination by combination:

\[ R_i(x) + R_j(y) \overset{k_{tc}}{\longrightarrow} P_{i+j-1}(x+y) \]

Termination by disproportionation:

\[ R_i(x) + R_j(y) \overset{k_{td}}{\longrightarrow} P_i(x) + P_j(y) \]

Chain transfer to monomer:

\[ R_i(x) + M \overset{k_{cm}}{\longrightarrow} P_i(x) + R_i(1) \]

Chain transfer to modifier:

\[ R_i(x) + T \overset{k_{ct}}{\longrightarrow} P_i(x) + R_i(0) \]
Chain transfer to polymer:
\[ R_i(x) + P_j(y) \xrightarrow{K_{p}} P_j(x) + R_{j+1}(y) \]

\( \beta \)-scission of terminal radicals:
\[ R_i(x) \xrightarrow{K_{p}} P_j(x - 1) + R_1(y) \]

In the kinetic mechanism above, subscript \( i \) stands for the number of long chain branches, \( x \) is the chain length measured as number of monomer units in the chain. Each kinetic rate constant is a pseudo kinetic rate constant. For example:

\[ K_p = k_{p1} f_1 + k_{p2} f_2 + k_{p2} f_2 + k_{p2} f_2 \quad (4) \]

where \( f \) and \( \phi \) are defined as:

\[ f_1 = \frac{M_1}{M_1 + M_2}, \quad f_2 = 1 - f_1 \quad (5) \]

\[ \phi_1 = \frac{k_{p21} f_1}{k_{p21} f_1 + k_{p22} f_2}, \quad \phi_2 = 1 - \phi_1 \quad (6) \]

with \( M_1 \) as ethylene and \( M_2 \) as vinyl acetate.

The reaction rate, \( r \), in the dynamic component balance equation can then be calculated. The components considered in Eqn. (1) include: two monomers, initiator, modifier, solvent, inert, and also free-radicals and polymer. For examples, the reaction rates for free-radicals and polymer are calculated as below:

\[ r_{f_1} = 2k_{f1}[I][M][R_i(x)][\delta_{0}], r_{f_2} = 2k_{f2}[I][M][R_i(x)][\delta_{0}] \]

\[ r_{p_1} = k_{p1}[M][R_i(x)][\delta_{0}], r_{p_2} = k_{p2}[M][R_i(x)][\delta_{0}] \quad (7) \]

where \([Ra]\) is the overall free-radical concentration, \( \delta \) is the Kronecker’s Delta, and double sum is for the summation of all chain length and all number of long chain branches. The reaction rate constants are expressed in Arrhenius form as:

\[ k = A_0 e^{-(Ea + PVa) / RT} \quad (9) \]

In order to calculate the number average of molecular weights and the weight average of molecular weights of this system, the moment equations are utilized in this paper. The following double moments for the radical and polymer distributions are defined as in the following Eqns. (10) and (11).

\[ \lambda_{m,n} = \sum_{i=1}^{\infty} \sum_{x=0}^{\infty} x^m R_i(x) \quad (10) \]

\[ \mu_{m,n} = \sum_{i=1}^{\infty} \sum_{x=0}^{\infty} x^m P_i(x) \quad (11) \]

where the first index corresponds to the branch distribution while the second one corresponds to the length distribution. In Eqn. (10), \( \lambda_{0,0} \) is actually the overall free-radical concentration, \([Ra]\). Applying quasi steady state assumption (QSSA), the moments of radical, \( \lambda_{m,n} \), can be calculated. For example,

\[ \lambda_{0,0} = \left( \frac{2k_{f1}[I]}{K_{ic} + K_{id}} \right)^{0.5} \quad (12) \]

All dynamic moment balance for the polymer, \( \mu_{m,n} \), can also be developed from Eqns. (1), (8), and (11).

With the moments of radical and polymer, the number average of molecular weights (\( \overline{M_n} \)) and the weight average of molecular weights (\( \overline{M_w} \)) can be expressed as:

\[ \overline{M_n} = \frac{\mu_{0,1} + \lambda_{0,1}}{\mu_{0,0} + \lambda_{0,0}} \overline{M_{mon}} \quad (13) \]

\[ \overline{M_w} = \frac{\mu_{0,2} + \lambda_{0,2}}{\mu_{0,1} + \lambda_{0,1}} \overline{M_{mon}} \quad (14) \]

where \( \overline{M_{mon}} \) is the average molecular weight of the monomers as:

\[ \overline{M_{mon}} = \frac{[M_1]M_{W1} + [M_2]M_{W2}}{[M_1] + [M_2]} \quad (15) \]

The number-average long-chain branching frequency for every one thousand carbon atom can be expressed as:

\[ LCB = 500 \frac{\mu_{1,0} + \lambda_{1,0}}{\mu_{0,1} + \lambda_{0,1}} \quad (16) \]

The melt index from plant data can be calculated according to an empirical correlation in McAuley, et al. (1990) as:

\[ \text{Melt Index} = \left( \frac{\overline{M_n}}{111525} \right)^{-3.47} \quad (17) \]
The comonomer wt. % in the polymer \( (CW) \) can be calculated as:

\[
CW = \frac{r_{M_2} \times MW_2}{r_{M_1} \times MW_1 + r_{M_2} \times MW_2} \times 100(\%)
\]  

(18)

3. SIMULATION RESULTS

The industrial plant that we work with has a proprietary steady-state model to predict their plant output conditions. We acquired their input data which needed to feed into their model and then using our model for the output prediction. The following Figure 3 contains some component concentrations for comparison purpose. The component concentrations include: \([I]\) for initiator; \([M1]\) for ethylene; \([M2]\) for vinyl acetate; \([T]\) for chain modifier; \([N]\) for inert; and \([S]\) for solvent. From this figure, one would observe that our model predicted reasonably well in comparison with the proprietary plant steady-state model.

![Figure 3. Comparison with proprietary plant model for a product grade.](image)

Industrial operating condition data of seven product grades with melt indexes ranging from ones to over four hundred will be used as fitted data to obtain the key kinetic parameters in the model. The plant output information includes the production rate (kg/hr), melt index, and comonomer wt. %. The plant outputs for the seven grades are listed in Table 1.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Production Rate (kg/hr)</th>
<th>MI</th>
<th>Comonomer wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1905</td>
<td>1.52</td>
<td>21.81</td>
</tr>
<tr>
<td>2</td>
<td>1432</td>
<td>2.49</td>
<td>23.17</td>
</tr>
<tr>
<td>3</td>
<td>1716</td>
<td>21.65</td>
<td>18.6</td>
</tr>
<tr>
<td>4</td>
<td>2016</td>
<td>89.21</td>
<td>8.51</td>
</tr>
<tr>
<td>5</td>
<td>1959</td>
<td>87.8</td>
<td>9.44</td>
</tr>
<tr>
<td>6</td>
<td>1715</td>
<td>166.47</td>
<td>19.19</td>
</tr>
<tr>
<td>7</td>
<td>1763</td>
<td>417.35</td>
<td>19.27</td>
</tr>
</tbody>
</table>

Table 1. Plant outputs for seven grades

From the sensitivity analysis of the kinetic parameters, the following Table 2 indicates the most influential elementary reactions for the three plant output variables. In this table, propagation reaction and termination by disproportionation reactions are most important for the production rate prediction. Thus, these kinetic parameters are adjusted first to fit the plant production rate. Sum of squared prediction error is used for the minimization search. Table 2 also indicates that propagation, chain transfer to modifier, and \(\beta\)-scission of terminal radical reactions are most important for the melt index prediction. Thus, the kinetic parameters for the chain transfer to modifier, and \(\beta\)-scission of terminal radicals reactions are adjusted further for the melt index prediction.

<table>
<thead>
<tr>
<th>Plant output data</th>
<th>Most influential elementary reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Rate</td>
<td>Propagation, termination by disproportionation</td>
</tr>
<tr>
<td>Melt Index</td>
<td>Propagation, chain transfer to modifier, (\beta)-scission of terminal radicals</td>
</tr>
<tr>
<td>Comonomer wt. %</td>
<td>Propagation</td>
</tr>
</tbody>
</table>

Table 2. Most influential elementary reactions

Finally, a combined objective function is used to obtain the above kinetic parameters again with values obtained from the last two optimization searches as initial guess for the final combined optimization. The combined objective function is defined as:

\[
\text{Objective} = \text{Sum of squared prediction errors} + \text{Combined objective function}
\]
The results from the optimization search required two kinetic parameter sets to properly fit the wide range of plant data. One kinetic parameter set is used for the lower melt index operating conditions (Grades 1, 2, and 3). The other kinetic parameter set is used for the higher melt index operating conditions (Grades 4, 5, 6, and 7). The fitted results can be seen in the following Figures 4 and 5. Notice that all plant outputs are predicted very closely to the plant date. This indicated that this dynamic model is quite reliable for later study to find optimum operating condition moves during grade transitions.

\[
\min_{\Delta x_{k}, \Delta x_{c}} \text{OF} = \sum_{i=1}^{n} \left[ \left( \frac{PR_{\text{plant}} - PR_{\text{predicted}}}{PR_{\text{plant}}} \right)^{2} + \left( \frac{MI_{\text{plant}} - MI_{\text{predicted}}}{MI_{\text{plant}}} \right)^{2} + \left( \frac{CW_{\text{plant}} - CW_{\text{predicted}}}{CW_{\text{plant}}} \right)^{2} \right]
\]

(19)

4. CONCLUSIONS

In this paper, rigorous dynamic model of an industrial autoclave reactor for the production of ethylene-vinyl acetate copolymer has been established. This reactor model includes detailed polymerization reaction mechanism and also dynamic component balance and energy balance. In order to calculate the number average of molecular weights and the weight average of molecular weights of this system, the moment equations are also utilized in this paper. Industrial operating condition data of seven product grades with melt index ranging from ones to over four hundred has been used to obtain the key kinetic parameters in the model. The predicted outputs of melt index, comonomer wt. % in polymer, and polymer production rate are compared closely to the plant data. Two sets of model parameters are used to fit these wide ranges of operating conditions. This dynamic model can be used in a later study to optimize operating condition moves during grade transitions and also for developing plantwide control strategy of the overall copolymerisation process.

ACKNOWLEDGEMENT

This work is supported by National Science Council of the R. O. C. under grant no. NSC-92-2214-E-011-008

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