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Steady State Simulation of Ethylene Polymerization Using Multiple-Site Coordination Catalysts

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Summary: Simulation models are important tools for the development and optimization of polymerization processes because they can describe catalyst performance and polymer properties as a function of polymerization kinetics and process conditions. As the polyolefin industry moves towards the production of resins with more complex microstructures, these models become essential for process understanding and product design. A simulation model has been developed for the polymerization of ethylene in a process with *n* reactors working in series. The model can predict raw material conversions and product properties like the molecular weight distribution (MWD) coupled with short chain branching distribution (SCBD), melt index, density and fluff morphology. Model parameters have been obtained from laboratory data. The model predictions are in good agreement with experimental results.

Keywords: coordination catalysts; polyethylene; process simulation; product simulation

Introduction

The polyolefin industry is becoming more competitive day to day. This competitiveness demands the frequent optimization and development of catalysts, processes and products. Moreover, since polymerization reactor capacities keep increasing, production engineers need tools for precise control of plant performance in order to decrease off-spec production. Simulation models allow research engineers and scientists to achieve these goals more quickly and efficiently.

In this work, a model for the simulation of steady-state polyethylene production with coordination catalysts in a process with n reactors working in series has been developed. Each one of the reactors can polymerize ethylene under different process conditions, resulting in monomodal polyethylene resins if $n = 1$ and multimodal resins if $n > 1$. Multimodal resins can have excellent mechanical properties and procesability. These polymerizations need very stable catalysts due to their long reactor residence times and good response to chain transfer agents and comonomer incorporation. The resulting polymer microstructure is complex and can be affected by many process variables, increasing the degrees of freedom for plant and product quality control. Product morphology is also an important variable, because it can cause bottlenecks in process units donwstream of the reactor and cut down plant output. A reliable mathematical model that accounts for all these effects, such as the one proposed herein, is essential for the complete understanding of these multi-reactor processes.

Model Development

Our simulation model is divided into two main parts, one focusing on the process and the other describing product properties. The latter can also be subdivided into polymer microstructure and polymer morphology models.

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The process simulation part describes the plant mass balances in the polymerization reactors, flash units and heat exchangers. Mass balance components comprise ethylene, hydrogen, α-olefin comonomers and the diluent. Reaction rate constants for ethylene, hydrogen and comonomers have been obtained from laboratory data, allowing us to calculate reaction rates with the following general equation,

$$R_{P,i} = k_{P,i} \times [Cat] \times [X_i] \qquad (1)$$

where $[X_i]$ represents the concentration of ethylene, comonomer or hydrogen, $[Cat]$ is catalyst concentration, and $k_{p,i}$ is the experimental rate constant for reactant of type i.

The catalyst concentration in the reactor is calculated from a first order deactivation model. The kinetic constant for the deactivacion step has been calculated from laboratory data, using typical procedures.

The summation of all reaction rates corresponds to the polymer production rate,

$$R_P = R_{C2} + R_{Com} + R_{H2} \qquad (2)$$

where R_{C2}, R_{Com}, R_{H2} are the rate of ethylene, comonomer and hydrogen consumption, respectively.

Once the reaction rate is known, the mass balances can be solved to calculate ethylene, comonomer and hydrogen conversions, polymer production rate, catalyst productivity, reactors residence time, inlet flow rates of raw materials, reflux flow rate, and the concentrations of reactants in the liquid and gas phases of the reactor.

Several optimization algorithms have been included in the model, allowing the user to set values for control process variables. The model set point variables can be hydrogen/ethylene molar ratio, comonomer/ethylene molar ratio, slurry concentration, polymer weight percentage made in each reactor, and fresh diluent flow percentage with respect to recovery diluent flow feed to the reactors. The user can choose the value for any of theses variables and the program will automatically calculate the manipulated variable values which gives the desired set conditions.

Hydrogen is the most commonly used chain transfer agent in polyethylene production, while α-olefins are employed as comonomers to control the SCBD in the polymer chain. The concentrations of these components with respect to ethylene, along with polymerization temperature, are the process variables that control polymer structure for a given catalyst. These values are calculated in the mass balance part of the model and used to predict polymer properties.

In the product quality simulation modules, the main goal is to predict the MWD coupled with the SCBD of the polymer (MWD-SCBD). The MWD-SCBD defines many mechanical and rheological properties of the polymer. Besides, it is important to know the polymer melt index and density, because these are usual plant quality control variables. In addition, the fluff morphology must also be predicted. The fluff morphology is defined by the polymer particle size distribution (PSD) and average particle size, important features for the optimum behaviour of the reactor downstream units.

There are several simulation techniques to obtain the molecular weight distribution of a polyolefin, like Monte-Carlo[1] and Galerkin methods,[2] and also instantaneous distributions with uncertain distributions[3] instead of the Flory distribution used in this work. Monte-Carlo is a very powerful tool that gives us detailed information of the polymer microstructure, but needs higher computation effort and validation of the results of the statistical model. On the other hand, the method of instantaneous distributions can simulate the MWD of polyolefins made by coordination catalysts with little computation effort. The effect of particle heat and mass transfer on polymerization kinetic and polymer properties has also been studied in the literature.[4] Concentration gradients, if they exists, can broaden the MWD of polyolefins made with heterogeneous catalysts, but not to the extent of the broad MWD of polyolefins observed in practice. Particle mass and heat transfer effects have been neglected in the present model.

In the present work, to simulate the MWD, the model uses the multiple-active site concept and a typical chain transfer model.[5–8] The catalyst is assumed to have a finite number of active site types; usually the minimun number of active site types that permits an adequate description of the experimental MWD. Each active site type produces polymer with MWD that follows Flory's most probable distribution,

$$w_{(j)}(\log r) = 2.3026\left(\frac{r}{r_{n_{(j)}}}\right)^2 \exp\left(-\frac{r}{r_{n_{(j)}}}\right) \quad (3)$$

where r is chain length and r_n is the average chain length. The subscipt j denotes the active site type.

The deconvolution of experimental MWDs is used to estimate the transfer parameters for the MWD according to the equation,

$$\frac{1}{r_{n_{(j)}}} = \frac{k_{\beta(j)} + k_{A(j)}A + k_{M(j)}M + k_{H(j)}H_2}{k_{p(j)}M} \quad (4)$$

where k_b, k_A, k_M, k_H are the rate constants of β-hydrogen elimination, and transfer to aluminium, monomer and hydrogen, respectively.

From the MWD curves of the products made in each reactor, the molecular weight averages M_n, M_w, and M_z, as well as polidispersity can be calculated. Similar averages for polymers made in two or more reactors can be calculated using the weight fractions of polymer made in each reactor:

$$M_n = \frac{1}{\sum_{i=1}^{N_r} \frac{\varphi^{(i)}}{M_n^{(i)}}} \quad (5)$$

$$M_w = \sum_{i=1}^{N_r} \varphi^{(i)} M_w^{(i)} \quad (6)$$

$$M_z = \sum_{i=1}^{N_r} \varphi^{(i)} M_w^{(i)} M_z^{(i)} \bigg/ \sum_{i=1}^{N_r} \varphi^{(i)} M_w^{(i)} \quad (7)$$

where N_r is the number of reactors and φ is the weight fraction of polymer made in each reactor. The subscript i indicates the reactor in the series.

The short chain branching distribution along the polymer chain length is calculated using the active site concept with homogeneous comonomer incorporation.[9] GPC-FTIR analyses [10] have been used to get the experimental MWD-SCBD using a deconvolution procedure to give SCB level for each active site type as a function of process conditions. GPC-FTIR combines a fast analysis procedure with detailed information about the polymer microstructure. Other techniques to compute the chemical composition distributions involves TREF or Crystaf analysis[11] and TREF-GPC.[12–13] The first option gives less information because does not link MWD with CCD, while the second produces a better description of polymer microstructure.

Melt index is calculated with a power model that uses polymer M_w as input variable.[14–16] The melt index of multimodal products can be obtained using a typical mixing rule with polymer weight fraction and individual melt indexes for the polymer produced in each reactor as inputs.

The polymer density is calculated using the following equation,

$$\rho_{(i)} = A + B \cdot \ln MI_{2.16,(i)} - C \cdot \left(\frac{[C]}{[M]}\right)_{(i)}^{D} \quad (8)$$

where $\rho_{(i)}$ is the density of polyethylene made in each reactor, $MI_{2.16}$ is the melt index with a load of 2.16 kg,[17] $[C]/[M]$ is comonomer to monomer ratio in each reactor, and A, B, C and D are empirical model parameters.

As in the previous case, the density of multimodal products is calculated from an inverse mixing rule, with individual polymer weight fractions and densities as inputs.

Finally, a morphology model has been included in the simulation package.[18] The main variables for this model are catalyst particle size distribution, catalyst productivity, reactors residence time distributions and reactor configuration. Except for the first input, all of the other variables are calculated in the reaction simulation.

The morphology model predicts the polymer particle size distribution and the average particle size. Mechanical effects inside the reactor such as particle erosion and friction, and growing polymer particle fracture and agglomeration have not been included in the model.

Simulation Results: Polymer Microstructure

Figure 1 and 2 show a comparison of experimental data and model prediction for the MWD-SCBD of two samples produced at different process conditions.

These graphical representations show a good agreement between model prediction and experimental results for both MWD and SCBD, giving a detailed picture of the microstructure of these resins.

Figure 3 to 5 compare experimental data to model predictions for polymer melt index, density, and average comonomer incorporation, respectively.

Again, model predictions are in good agreement with experimental results for all polymer properties evaluated.

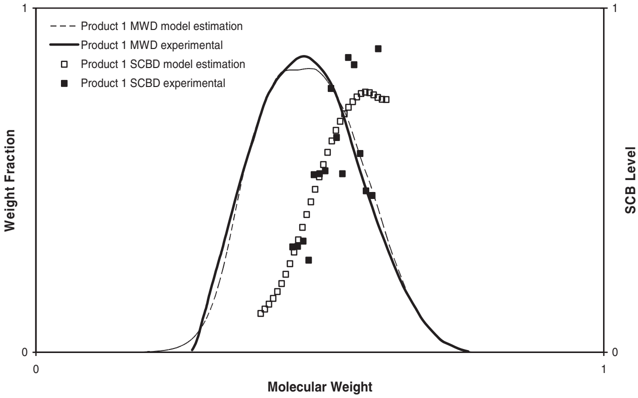

Figure 1.
Molecular weight and short chain branch distributions of Product 1.

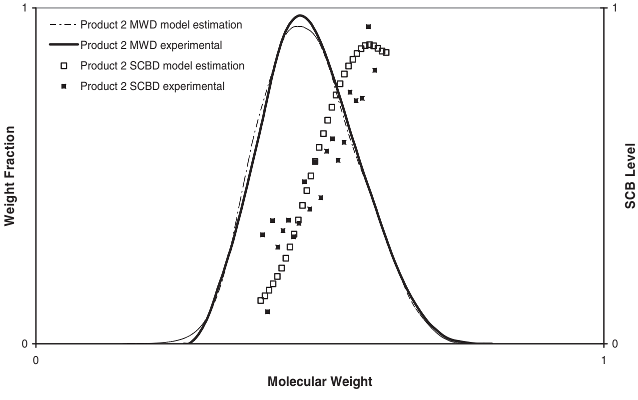

Figure 2.
Molecular weight and short chain branch distributions of Product 2.

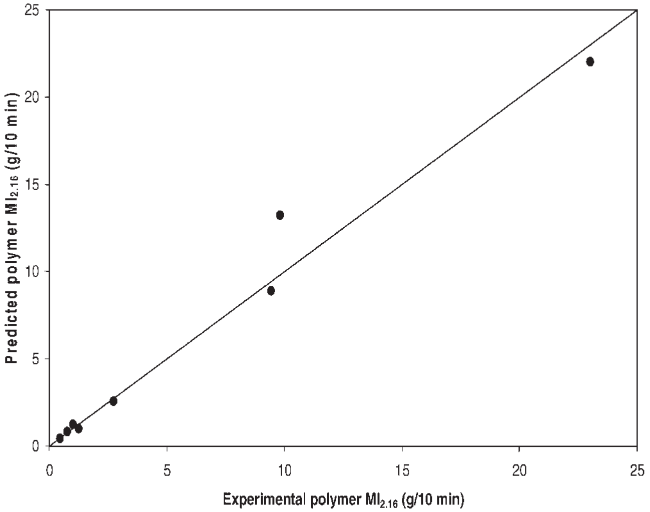

Figure 3.
Comparison of experimental data and model predictions for polymer melt index.

Conclusions

A simulation model for the polymerization of ethylene with multiple-site coordination catalysts at steady state in a process with n reactors operating in series has been developed.

The simulation package includes a process mass balance solver and a product property estimation module. The process simulation module calculates polymer production, catalyst productivity and process stream flows. The product property module predicts the molecular weight distribution and short chain branching distribution, melt index, density, comonomer average incorporation and fluff morphology for polymer produced in each reactor.

The predictions for molecular weight distribution and short chain branching

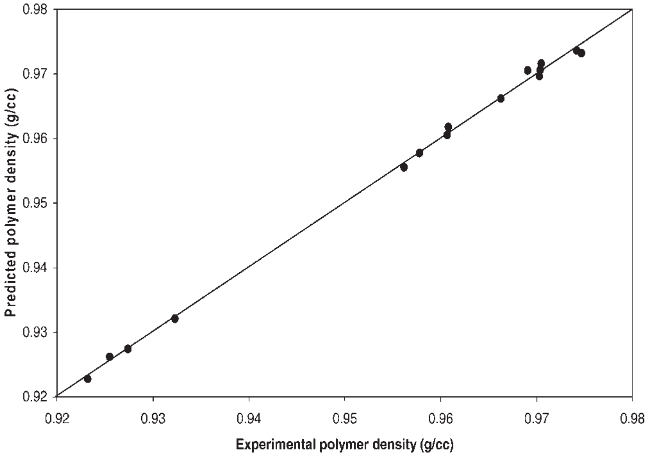

Figure 4.
Comparisons of experimental data and model predictions for polymer density.

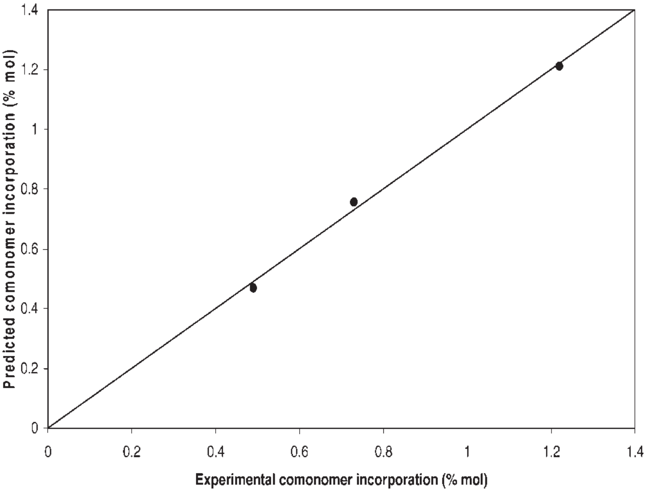

Figure 5.
Comparison of experimental data and model predictions for average comonomer incorporation in the polymer.

distribution, melt index, density and average comonomer incorporation are in good agreement with experimental results. The particle size distribution model has also been implemented in the simulation package and is currently under experimental validation.

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