# Parameter Estimation in a Simplified MWD Model for HDPE Produced by a Ziegler-Natta Catalyst

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A simplified steady-state model to predict MWDs of ethylene/butene and ethylene/hexene copolymers produced industrially using heterogeneous Z-N catalysts is developed. Estimability analysis is used to guide model simplification and to determine which parameters can be estimated using the available data. Scaling of response variables and parameters using information about their uncertainties ensures that appropriate results are obtained from the estimability analysis. Parameter estimates are obtained to provide good predictions of the measured MWDs. Although the parameter values obtained are specific to the Z-N catalyst of our industrial sponsor, the method should be useful for parameter estimation and model simplification in other catalytic polymerization systems.
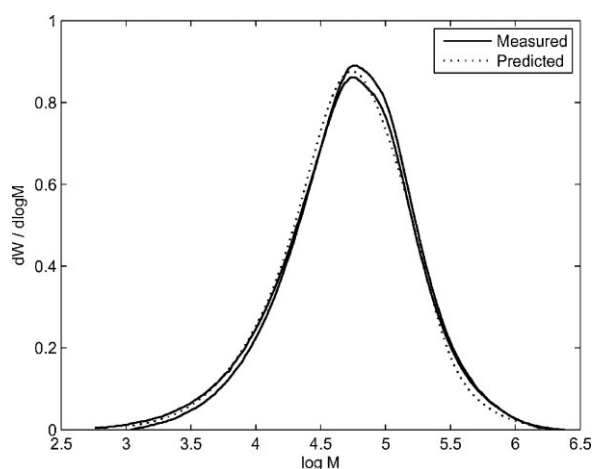
Introduction

Engineers want to predict end-use properties of polyolefins from reactor operating conditions so that they can optimize reactor operations and design new products. In our previous work,[1] we developed a simplified mathematical model to predict molecular weight distributions (MWDs) of ethylene/hexene copolymers, and used industrial data to obtain parameter estimates. This simplified model predicts MWD from reactor operating conditions (hydrogen concentration, ethylene partial pressure, hexene concentration) but does not account for temperature effects. In this work, we include temperature effects, and we extend the model to include both butene and hexene

comonomers. Many end-use properties of high-density polyethylene (HDPE), such as tensile strength, impact strength, melting point, and Young's modulus, are influenced by the MWD. The model proposed in this paper predicts MWD, and can be used in combination with other models[2] to predict end-use properties from reactor operating conditions.

The extended non-isothermal model has many more parameters than the original isothermal model,[1] and not all of these parameters can be readily estimated using the available industrial data set.[3] Estimability analysis[4–6] is used to determine which parameters can be estimated from the available data. The unestimable parameters are either left at their initial guesses, or are removed from the model by further simplification. In deciding which parameters can be estimated, the estimability analysis technique accounts for the model structure, for correlated effects of model parameters, and for the level of uncertainty in each of the initial parameter guesses. The

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algorithm produces a list of model parameters, ranked from most to least estimable. A revised version of the estimability algorithm, which was originally described by Yao et al.[6] and by Kou et al.,[4] is provided in the Appendix. Recently, Lund and Foss[7] presented a similar parameter-ranking technique that produces equivalent results to those from the method of Kou et al., using more computationally complex calculations.

This paper begins by describing the extension of the original isothermal copolymerization model to account for butene incorporation and for temperature effects. Next, the estimability ranking is determined. Some inestimable parameters are removed from the model by assuming similar reaction rates (and similar activation energies) at different types of catalyst sites. The parameter estimation approach is described and the results are assessed for physical consistency. The final parameter estimates obtained are physically reasonable and will provide a useful starting point for designing new experiments to further improve parameter estimates and model predictions.

Model Extension

The extended simplified model, which accounts for temperature effects and for incorporation of both butene and hexene comonomers, is shown in Table 1.

As shown in Figure 1, Equation (1.1) uses the sum of five Flory distributions to predict points on the MWD curve obtained using steady-state reactor operating conditions.[3] m_j is the mass fraction of copolymer produced at the jth type of active site, τ_j is the ratio of the rate of chain-stopping to chain-propagating events at the jth type of active site, and r is the chain length. The expression for τ_j in Equation (1.2) is different from that in the original simplified model because it includes Arrhenius expressions to account for the temperature dependence of reaction rates. $k_{tj_0}^{\mathrm{H}}$ is the rate constant for chain transfer to hydrogen at the reference temperature, T_0, and $k_{pj_0}^{\mathrm{E}}$ is the rate constant for propagation with ethylene at the same reference temperature. Note that chain propagation with butene and hexene are ignored in Equation (1.2). This is a reasonable assumption for HDPE copolymers, because the mole fraction of butene or hexene incorporated is small. k_{tj}^{β} and k_{tj}^{I} are rate constants for β-hydride elimination and for chain transfer to impurities, respectively. Note that no temperature effects are included in the second term of Equation (1.2). The concentration of impurities in the reactor is unknown, so the overall coefficient involving k_{tj}^{β} and k_{tj}^{I} is lumped into a single parameter for estimation. Also note that chain transfer to comonomers is neglected in Equation (1.2) because these reactions are negligible compared to other chain-stopping reactions.[1,8]

Equation (1.3) shows that the mass fraction of copolymer produced at site j can be determined from a numerator term, N_j, divided by the sum of the numerators for all sites. The expression for N_1 in Equation (1.4) was derived in an analogous fashion to the expression for N_1 in our earlier isothermal hexene copolymerization model.[1] Activation energies appear in this extended model to account for temperature effects, and additional additive terms account for butene incorporation. Equation (1.4) contains the chain-transfer-to-hydrogen rate constant, $k_{tj_0}^{\mathrm{H}}$, because we assume that sites are temporarily dormant after chain transfer to hydrogen,[1,8] as shown in the mechanism in Table 2. Dormant sites are reinitiated by reactions with ethylene, butene, and hexene. Kissin[8] found that reinitiation reactions with comonomers are important at the low-molecular-weight sites, but not at the high-molecular-weight sites. Because of Kissin's findings, it is assumed that low-molecular-weight sites (sites 1 and 2) undergo reinitiation reactions with ethylene and comonomers, and that high-molecular-weight sites (sites 3 to 5) only reinitiate with ethylene.[1] Expressions for numerators N_2–N_5 in Equation (1.5)–(1.8) are similar to Equation (1.4) for N_1. Note that site 2 was used as a reference site in the derivation of these expressions[1] and that β_j, which appears in Equation (1.4) and (1.6)–(1.8), is the ratio of the number of catalyst sites of type j (growing chains plus dormant sites) to catalyst sites of type 2. Since site 2 is the reference site, $\beta_2 = 1$.

Since the kinetic rate constants in the model always appear as ratios, it is impossible to estimate the individual rate constants independently. The model has been reparameterized, as shown in Table 3, to show the lumped parameters that we attempt to estimate. Definitions of these lumped parameters are provided in Table 4. Parameters K_{1j} and K_4 defined in Equation (3.1) and (3.2) influence τ_j, whereas the α parameters in Table 4 are used to predict mass fractions, m_j. The ε parameters account for temperature effects.

Deconvolution analysis[3] of the industrial MWD data revealed that sites 1 and 2 (the low-molecular-weight sites) tend to respond in a similar manner to changes in the reactor operating conditions, and that sites 3–5 (the high-molecular-weight sites) also tend to respond together. This behavior indicates that there may be only two chemically distinct types of active sites on the Ziegler-Natta (Z-N) catalyst and that broadening of the MWD may be due to catalyst-support interactions. Therefore, as shown in Table 4, some parameter values are shared between similar sites to reduce the number of parameters that appear in the model. For example, α_{1j}, the ratio of the propagation rate constant for ethylene to the reinitiation rate constant for ethylene, is assumed to be common to sites 1 and 2 (the low-molecular-weight sites) and a

separate common value is used for the three high-molecular-weight sites (see Equation 4.3 and 4.4).

Based on the work of Kissin,[8] our previous deconvolution analysis,[3] and experience with estimating parameters in the original isothermal model,[1] further simplifying assumptions were made to reduce the number of new parameters included in the extended non-isothermal model shown in Table 3:

Since τ values do not appear to change with temperature in the absence of hydrogen,[8] we assume that K_4 is not temperature dependent.

α_1, the ratio of the rate constant for propagation with ethylene to the rate constant for reinitiation with ethylene, was assumed to be temperature independent, because this ratio was not very influential in the earlier isothermal model.

Table 1. Kinetic model equations for predicting MWD.

$$\frac{dW}{d\log_{10} Mw} = m_1\left[r^2\ln(10)\tau_1^2\exp(-\tau_1 r)\right] + m_2\left[r^2\ln(10)\tau_2^2\exp(-\tau_2 r)\right] \tag{1.1}$$
$$+ m_3\left[r^2\ln(10)\tau_3^2\exp(-\tau_3 r)\right] + m_4\left[r^2\ln(10)\tau_4^2\exp(-\tau_4 r)\right]$$
$$+ m_5\left[r^2\ln(10)\tau_5^2\exp(-\tau_5 r)\right]$$

$$\tau_j = \frac{k_{tj0}^H\exp\left(\frac{-E_{tj}^H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}{k_{pj0}^E\exp\left(\frac{-E_{pj}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[H_2]}{[C_2]} + \frac{\left(k_{tj}^\beta + k_{tj}^I[I]\right)}{k_{pj}^E}\frac{1}{[C_2]} \tag{1.2}$$

$$m_j = \frac{N_j}{\sum\limits_{j=1}^{5} N_j} \tag{1.3}$$

$$N_1 = \left(\frac{k_{p1_0}^E\exp\left(\frac{-E_{p1}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_1}{k_{p2_0}^E\exp\left(\frac{-E_{p2}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)} + \frac{k_{p1_0}^{But}\exp\left(\frac{-E_{p1}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_1}{k_{p2_0}^E\exp\left(\frac{-E_{p2}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_4]}{[C_2]} + \frac{k_{p1_0}^{Hex}\exp\left(\frac{-E_{p1}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_1}{k_{p2_0}^E\exp\left(\frac{-E_{p2}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_6]}{[C_2]}\right) \tag{1.4}$$
$$\left(1 + \frac{k_{t2_0}^H\exp\left(\frac{-E_{t2}^H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{i2_0}^E\exp\left(\frac{-E_{ij}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2] + k_{i2_0}^{But}\exp\left(\frac{-E_{i2}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + k_{i2_0}^{Hex}\exp\left(\frac{-E_{i2}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=3,4,5}\left(1 + \frac{k_{tj_0}^H\exp\left(\frac{-E_{tj}^H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^E\exp\left(\frac{-E_{ij}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]}\right)$$

$$N_2 = \left(1 + \frac{k_{p2_0}^{But}\exp\left(\frac{-E_{p2}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}{k_{p2_0}^E\exp\left(\frac{-E_{p2}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_4]}{[C_2]} + \frac{k_{p2_0}^{Hex}\exp\left(\frac{-E_{p2}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}{k_{p2_0}^E\exp\left(\frac{-E_{p2}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_6]}{[C_2]}\right) \tag{1.5}$$
$$\left(1 + \frac{k_{t1_0}^H\exp\left(\frac{-E_{t1}^H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{i1_0}^E\exp\left(\frac{-E_{i1}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2] + k_{i1_0}^{But}\exp\left(\frac{-E_{i1}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + k_{i1_0}^{Hex}\exp\left(\frac{-E_{i1}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=3,4,5}\left(1 + \frac{k_{tj_0}^H\exp\left(\frac{-E_{tj}^H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^E\exp\left(\frac{-E_{ij}^E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]}\right)$$

Table 1. Continued

$$
N_3 = \left(\frac{k_{p3_0}^{E} \exp\left(\frac{-E_{p3}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_3}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)} + \frac{k_{p3_0}^{But}\exp\left(\frac{-E_{p3}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_3}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_4]}{[C_2]} + \frac{k_{p3_0}^{Hex}\exp\left(\frac{-E_{p3}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_3}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_6]}{[C_2]} \right) \tag{1.6}
$$

$$
\prod_{j=1,2}\left(1+\frac{k_{tj_0}^{H}\exp\left(\frac{-E_{tj}^{H}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^{E}\exp\left(\frac{-E_{ij}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]+k_{ij_0}^{But}\exp\left(\frac{-E_{ij}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4]+k_{ij_0}^{Hex}\exp\left(\frac{-E_{ij}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)
$$

$$
\prod_{j=4,5}\left(1+\frac{k_{tj_0}^{H}\exp\left(\frac{-E_{tj}^{H}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^{E}\exp\left(\frac{-E_{ij}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]}\right)
$$

$$
N_4 = \left(\frac{k_{p4_0}^{E} \exp\left(\frac{-E_{p4}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_4}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)} + \frac{k_{p4_0}^{But}\exp\left(\frac{-E_{p4}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_4}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_4]}{[C_2]} + \frac{k_{p4_0}^{Hex}\exp\left(\frac{-E_{p4}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_4}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_6]}{[C_2]} \right) \tag{1.7}
$$

$$
\prod_{j=1,2}\left(1+\frac{k_{tj_0}^{H}\exp\left(\frac{-E_{tj}^{H}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^{E}\exp\left(\frac{-E_{ij}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]+k_{ij_0}^{But}\exp\left(\frac{-E_{ij}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4]+k_{ij_0}^{Hex}\exp\left(\frac{-E_{ij}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)
$$

$$
\prod_{j=3,5}\left(1+\frac{k_{tj_0}^{H}\exp\left(\frac{-E_{tj}^{H}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^{E}\exp\left(\frac{-E_{ij}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]}\right)
$$

$$
N_5 = \left(\frac{k_{p5_0}^{E} \exp\left(\frac{-E_{p5}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_5}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)} + \frac{k_{p5_0}^{But}\exp\left(\frac{-E_{p5}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_5}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_4]}{[C_2]} + \frac{k_{p5_0}^{Hex}\exp\left(\frac{-E_{p5}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\beta_5}{k_{p2_0}^{E}\exp\left(\frac{-E_{p2}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}\frac{[C_6]}{[C_2]} \right) \tag{1.8}
$$

$$
\prod_{j=1,2}\left(1+\frac{k_{tj_0}^{H}\exp\left(\frac{-E_{tj}^{H}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^{E}\exp\left(\frac{-E_{ij}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]+k_{ij_0}^{But}\exp\left(\frac{-E_{ij}^{But}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4]+k_{ij_0}^{Hex}\exp\left(\frac{-E_{ij}^{Hex}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)
$$

$$
\prod_{j=3,4}\left(1+\frac{k_{tj_0}^{H}\exp\left(\frac{-E_{tj}^{H}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[H_2]}{k_{ij_0}^{E}\exp\left(\frac{-E_{ij}^{E}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_2]}\right)
$$

As shown in Table 5, initial guesses for parameters involving hexene and ethylene were obtained from the isothermal model.[1] Parameters involving butene were given the same initial guesses as the corresponding hexene parameters. Initial values for the Arrhenius-type parameters were calculated from deconvolution results presented by Kissin.[8]

The initial parameter values in Table 5 can be used to predict comonomer incorporation (i.e., using Equation 3.9a–3.10b in Table 3). Several simplifying assumptions were made in the development of these equations, so that the approximate level of comonomer incorporation could be predicted without including additional parameters in the model. The most problematic assumption required is
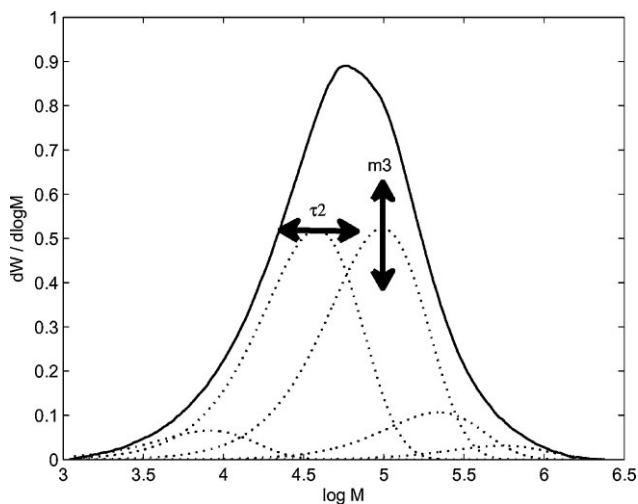
Figure 1. The predicted MWD is the sum of the five component Flory distributions.

that the rate of propagation is not influenced significantly by the terminal group (ethylene, butene, or hexene) on the growing polymer chain.[1] The industrial data set[3] used for fitting the model parameters contains overall comonomer incorporation measurements and measured MWD curves. If detailed comonomer composition distribution or sequence length information were also available, then a more complex copolymerization model that properly accounts for reactivity ratios at the various type of sites could have been estimated. Nevertheless, the main objective of the current research is to develop a simplified

model to predict the MWD curve from reactor operating conditions. Equation (3.10) is included in the model to ensure that the parameter values in the MWD model are consistent with observed overall levels of comonomer incorporation.

Estimability Analysis

The model parameters were ranked from most estimable to least estimable using the estimability ranking technique described in the Appendix. This parameter ranking technique uses a sensitivity matrix whose elements, $\partial y_i / \partial \theta_k$, are partial derivatives of each predicted model response, y_i, with respect to each of the parameters of interest, θ_k. The y_i values for each experimental run consist of 100 equally spaced points (on the log scale) from the predicted MWD curve and a single comonomer incorporation (in mass fraction) value. Proper scaling of each element of the sensitivity matrix is required to ensure that the elements are dimensionally consistent and that some parameters or predicted responses do not dominate the ranking due to their large numerical values. To address this concern, Kou et al.[4] used initial guesses for parameters, and typical values for predicted responses as scaling factors. The proposed algorithm in the Appendix uses an improved method for scaling that provides the modeler with an opportunity to include additional knowledge. As shown in the Appendix, each element of the sensitivity matrix is scaled using the uncertainty in the initial value for the corresponding parameter, $s_{\theta k}$, and the uncertainty

Table 2. Reaction mechanism for ethylene α-olefin terpolymerization (note that this simplified mechanism does not account for the influence of the terminal monomer on reaction rates).

Propagation with ethylene	$Y_{j,n} + C_2 \xrightarrow{k_{pj}^E} Y_{j,n+1}$
Propagation with comonomer (butene)	$Y_{j,n} + C_4 \xrightarrow{k_{pj}^{But}} Y_{j,n+1}$
Propagation with comonomer (hexene)	$Y_{j,n} + C_6 \xrightarrow{k_{pj}^{Hex}} Y_{j,n+1}$
Chain transfer to hydrogen	$Y_{j,n} + H_2 \xrightarrow{k_{tj}^H} Y_{jD}$
Chain transfer to cocatalyst and other impurities	$Y_{j,n} + I \xrightarrow{k_{tj}^I} Y_{j,1}$
Spontaneous chain transfer (β-hydride elimination)	$Y_{j,n} \xrightarrow{k_{tj}^{\beta}} Y_{j,1}$
Reinitiation with ethylene	$Y_{jD} + C_2 \xrightarrow{k_{ij}^E} Y_{j,1}$
Reinitiation with butene	$Y_{jD} + C_4 \xrightarrow{k_{ij}^{But}} Y_{j,1}$
Reinitiation with hexene	$Y_{jD} + C_6 \xrightarrow{k_{ij}^{Hex}} Y_{j,1}$

Table 3. Reparameterized model equations to predict MWD and comonomer incorporation.

$$\frac{dW}{d\log_{10} Mw} = m_1\left[r^2 \ln(10)\tau_1^2 \exp(-\tau_1 r)\right] + m_2\left[r^2 \ln(10)\tau_2^2 \exp(-\tau_2 r)\right] \tag{3.1}$$
$$+ m_3\left[r^2 \ln(10)\tau_3^2 \exp(-\tau_3 r)\right] + m_4\left[r^2 \ln(10)\tau_4^2 \exp(-\tau_4 r)\right]$$
$$+ m_5\left[r^2 \ln(10)\tau_5^2 \exp(-\tau_5 r)\right]$$

$$\tau_j = K_{1j} \exp\left(\varepsilon_{K1j}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2]} + K_4 \frac{1}{[\text{C}_2]} \tag{3.2}$$

$$m_j = \frac{N_j}{\sum\limits_{j=1}^{5} N_j} \tag{3.3}$$

$$N_1 = \left(\alpha_{21}\exp\left(\varepsilon_{\alpha21}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3\text{Blow}}\exp\left(\varepsilon_{\alpha3\text{Blow}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_4]}{[\text{C}_2]} + \alpha_{3\text{Hlow}}\exp\left(\varepsilon_{\alpha3\text{Hlow}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_6]}{[\text{C}_2]}\right) \tag{3.4}$$
$$\left(1 + \alpha_{1\text{low}}K_{12}\exp\left(\varepsilon_{K12}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4B}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4H}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_6]}\right)$$
$$\prod_{j=3,4,5}\left(1 + \alpha_{1\text{high}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2]}\right)$$

$$N_2 = \left(1 + \alpha_{3\text{Blow}}\exp\left(\varepsilon_{\alpha3\text{Blow}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_4]}{[\text{C}_2]} + \alpha_{3\text{Hlow}}\exp\left(\varepsilon_{\alpha3\text{Hlow}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_6]}{[\text{C}_2]}\right) \tag{3.5}$$
$$\left(1 + \alpha_{1\text{low}}K_{11}\exp\left(\varepsilon_{K11}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4B}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4H}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_6]}\right)$$
$$\prod_{j=3,4,5}\left(1 + \alpha_{1\text{high}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2]}\right)$$

$$N_3 = \left(\alpha_{23}\exp\left(\varepsilon_{\alpha23}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3\text{Bhigh}}\exp\left(\varepsilon_{\alpha3\text{Bhigh}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_4]}{[\text{C}_2]} + \alpha_{3\text{Hhigh}}\exp\left(\varepsilon_{\alpha3\text{Hhigh}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_6]}{[\text{C}_2]}\right) \tag{3.6}$$
$$\prod_{j=1,2}\left(1 + \alpha_{1\text{low}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4B}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4H}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_6]}\right)$$
$$\prod_{j=4,5}\left(1 + \alpha_{1\text{high}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2]}\right)$$

$$N_4 = \left(\alpha_{24}\exp\left(\varepsilon_{\alpha23}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3\text{Bhigh}}\exp\left(\varepsilon_{\alpha3\text{Bhigh}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_4]}{[\text{C}_2]} + \alpha_{3\text{Hhigh}}\exp\left(\varepsilon_{\alpha3\text{Hhigh}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_6]}{[\text{C}_2]}\right) \tag{3.7}$$
$$\prod_{j=1,2}\left(1 + \alpha_{1\text{low}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4B}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4H}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_6]}\right)$$
$$\prod_{j=3,5}\left(1 + \alpha_{1\text{high}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2]}\right)$$

$$N_5 = \left(\alpha_{25}\exp\left(\varepsilon_{\alpha25}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3\text{Bhigh}}\exp\left(\varepsilon_{\alpha3\text{Bhigh}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_4]}{[\text{C}_2]} + \alpha_{3\text{Hhigh}}\exp\left(\varepsilon_{\alpha3\text{Hhigh}}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{C}_6]}{[\text{C}_2]}\right) \tag{3.8}$$
$$\prod_{j=1,2}\left(1 + \alpha_{1\text{low}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4B}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4H}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[\text{C}_6]}\right)$$
$$\prod_{j=3,4}\left(1 + \alpha_{1\text{high}}K_{1j}\exp\left(\varepsilon_{K1j}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[\text{H}_2]}{[\text{C}_2]}\right)$$

Table 3. Continued

$$f_{Bj} = \cfrac{1}{1 + \cfrac{\alpha_{2j} \exp\left(\varepsilon_{\alpha 2j}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)}{\alpha_{3Bj} \exp\left(\varepsilon_{\alpha 3Bj}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \cfrac{1}{\frac{[C_4]}{[C_2]}}} \qquad (3.9a)$$

$$f_{Hj} = \cfrac{1}{1 + \cfrac{\alpha_{2j} \exp\left(\varepsilon_{\alpha 2j}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)}{\alpha_{3Hj} \exp\left(\varepsilon_{\alpha 3Hj}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \cfrac{1}{\frac{[C_6]}{[C_2]}}} \qquad (3.9b)$$

$$m_B = \sum_{j=1-5} m_j \left(\frac{3f_{Bj}}{1 + 2f_{Bj}}\right) \qquad (3.10a)$$

$$m_H = \sum_{j=1-5} m_j \left(\frac{3f_{Hj}}{1 + 2f_{Hj}}\right) \qquad (3.10b)$$

Table 4. Lumped parameter definitions.

$$K_{1j} = \frac{k_{tj_0}^H}{k_{pj_0}^E} \qquad (4.1)$$

$$K_{4j} = \frac{\left(k_{tj}^\beta + k_{tj}^I [I]\right)}{k_{pj}^E} \qquad (4.2)$$

$$\alpha_{1low} = \alpha_{11} = \alpha_{12} = \frac{k_{p1_0}^E}{k_{i1_0}^E} = \frac{k_{p2_0}^E}{k_{i2_0}^E} \qquad (4.3)$$

$$\alpha_{1high} = \alpha_{13} = \alpha_{14} = \alpha_{15} = \frac{k_{p3_0}^E}{k_{i3_0}^E} = \frac{k_{p4_0}^E}{k_{i4_0}^E} = \frac{k_{p5_0}^E}{k_{i5_0}^E} \qquad (4.4)$$

$$\alpha_{2j} = \frac{k_{pj_0}^E \beta_j}{k_{p2_0}^E} \qquad (4.5)$$

$$\alpha_{3Blow} = \alpha_{3B1} = \alpha_{3B2} = \frac{k_{p1_0}^{But} \beta_1}{k_{p2_0}^E} = \frac{k_{p2_0}^{But}}{k_{p2_0}^E} \qquad (4.6)$$

$$\alpha_{3Bhigh} = \alpha_{3B3} = \alpha_{3B4} = \alpha_{3B5} \frac{k_{p3_0}^{But} \beta_3}{k_{p2_0}^E} = \frac{k_{p4_0}^{But} \beta_4}{k_{p2_0}^E} = \frac{k_{p5_0}^{But} \beta_5}{k_{p2_0}^E} \qquad (4.7)$$

$$\alpha_{3Hlow} = \alpha_{3H1} = \alpha_{3H2} = \frac{k_{p1_0}^{Hex} \beta_1}{k_{p2_0}^E} = \frac{k_{p2_0}^{Hex}}{k_{p2_0}^E} \qquad (4.8)$$

$$\alpha_{3Hhigh} = \alpha_{3H3} = \alpha_{3H4} = \alpha_{3H5} = \frac{k_{p3_0}^{Hex} \beta_3}{k_{p2_0}^E} = \frac{k_{p4_0}^{Hex} \beta_4}{k_{p2_0}^E} = \frac{k_{p5_0}^{Hex} \beta_5}{k_{p2_0}^E} \qquad (4.9)$$

$$\alpha_{4B} = \frac{k_{i1_0}^{But}}{k_{i1_0}^E} = \frac{k_{i2_0}^{But}}{k_{i2_0}^E} \qquad (4.10)$$

$$\alpha_{4H} = \frac{k_{i1_0}^{Hex}}{k_{i1_0}^E} = \frac{k_{i2_0}^{Hex}}{k_{i2_0}^E} \qquad (4.11)$$

$$\varepsilon_{Kj} = \frac{E_{pj}^E - E_{tj}^H}{R} \qquad (4.12)$$

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Table 4. Continued

$$\varepsilon_{\alpha 2j} = \frac{E_{p2}^{E} - E_{pj}^{E}}{R} \tag{4.13}$$

$$\varepsilon_{\alpha 3Blow} = \varepsilon_{\alpha 3B1} = \varepsilon_{\alpha 3B2} = \frac{E_{p2}^{E} - E_{p1}^{But}}{R} = \frac{E_{p2}^{E} - E_{p2}^{But}}{R} \tag{4.14}$$

$$\varepsilon_{\alpha 3Bhigh} = \varepsilon_{\alpha 3B3} = \varepsilon_{\alpha 3B4} = \varepsilon_{\alpha 3B5} = \frac{E_{p2}^{E} - E_{p3}^{But}}{R} = \frac{E_{p2}^{E} - E_{p4}^{But}}{R} = \frac{E_{p2}^{E} - E_{p5}^{But}}{R} \tag{4.15}$$

$$\varepsilon_{\alpha 3Hlow} = \varepsilon_{\alpha 3H1} = \varepsilon_{\alpha 3H2} = \frac{E_{p2}^{E} - E_{p1}^{Hex}}{R} = \frac{E_{p2}^{E} - E_{p2}^{Hex}}{R} \tag{4.16}$$

$$\varepsilon_{\alpha 3Hhigh} = \varepsilon_{\alpha 3H3} = \varepsilon_{\alpha 3H4} = \varepsilon_{\alpha 3H5} = \frac{E_{p2}^{E} - E_{p3}^{Hex}}{R} = \frac{E_{p2}^{E} - E_{p4}^{Hex}}{R} = \frac{E_{p2}^{E} - E_{p5}^{Hex}}{R} \tag{4.17}$$

$$\varepsilon_{\alpha 4B} = \frac{E_{i1}^{E} - E_{i1}^{But}}{R} = \frac{E_{i2}^{E} - E_{i2}^{But}}{R} \tag{4.18}$$

$$\varepsilon_{\alpha 4H} = \frac{E_{i1}^{E} - E_{i1}^{Hex}}{R} = \frac{E_{i2}^{E} - E_{i2}^{Hex}}{R} \tag{4.19}$$

Table 5. Initial guesses, uncertainties and estimability ranking of the parameters in the model in Table 3.

Parameter	Initial value	Scaling value	Rank
K_{11}	0.0149	6.209×10^{-3}	27
K_{12}	0.0030	9.0×10^{-4}	25
K_{13}	0.0012	5.57×10^{-4}	17
K_{14}	0.0003	5.39×10^{-4}	23
K_{15}	0	8.8781×10^{-3}	3
i_4	9.4×10^{-4}	1.3055×10^{-4}	18
α_{1low}	1 325.8	1 893.7	4
α_{1high}	3 222.2	5 048.4	5
α_{21}	0.4755	0.2074	21
α_{23}	1.9492	1.0260	14
α_{24}	0.3370	0.2042	9
α_{25}	0.0579	0.0656	11
α_{3Blow}	0.4370	0.5	19
α_{3Bhigh}	1.73×10^{-9}	0.5	7
α_{3Hlow}	0.4370	0.5	22
α_{3Hhigh}	1.73×10^{-9}	0.5	8
α_{4B}	0.0491	51.3868	1
α_{4H}	0.0491	51.3868	2
ε_{K11}	$-2\,828.7$	$-1\,414.4$	15
ε_{K12}	$-1\,603$	-801.5	10
ε_{K13}	$-2\,613.9$	$-1\,307$	6
ε_{K14}	$-3\,652$	$-1\,826$	20
ε_{K15}	$-3\,652$	$-1\,826$	33

Table 5. Continued

Parameter	Initial value	Scaling value	Rank
$\varepsilon_{\alpha 21}$	−3 974	−1 987.2	16
$\varepsilon_{\alpha 23}$	1 439	719.4	24
$\varepsilon_{\alpha 24}$	6 983	3 491.4	12
$\varepsilon_{\alpha 25}$	10 758	5 379	13
$\varepsilon_{\alpha 3Blow}$	−3 974.4	−3 974.4	26
$\varepsilon_{\alpha 3Bhigh}$	6 982.8	6 982.8	31
$\varepsilon_{\alpha 3Hlow}$	−3 974.4	−3 974.4	28
$\varepsilon_{\alpha 3Hhigh}$	6 982.8	6 982.8	32
$\varepsilon_{\alpha 4B}$	0	1 504.2	29
$\varepsilon_{\alpha 4H}$	0	1 504.2	30

in the corresponding measured response, s_{yi}. An appropriate value for $s_{\theta k}$ reflects how far the modeler is willing to allow the particular parameter to move away from its initial guess, and s_{yi} reflects the modeler's knowledge about the reproducibility of measurements for the different responses. Using the proposed scaling, the limited information in the data is used to estimate influential parameters whose values are not well known. Less-influential parameters and parameters whose initial values are more certain rank lower on the list. Parameters that rank near the bottom of the list may be kept at their initial values, if there is insufficient information to estimate all of the parameters.

In the current work, a value of $s_{yi} = 0.0154$ is used for MWD responses, and $s_{yi} = 0.0143$ was used for comonomer incorporation responses. These scaling values were determined from pooled variance estimates determined from three pairs of replicate experiments (see Figure 5a–c). Scaling factors $s_{\theta k}$ and the corresponding initial guesses for all of the parameters are shown in Table 5. Note that some of the initial parameter values in Table 5 are parameter estimates obtained using the isothermal model.[1] For these parameters, the corresponding $s_{\theta k}$ values are the standard deviations of the parameter estimates from the isothermal model estimation. For other parameters that do not appear in the isothermal model, $s_{\theta k}$ values were selected based on how far we anticipated that the parameter could move away from the initial guess before its value might become physically unreasonable. For example, the initial value of $\varepsilon_{K11} = -2\,828.7$ in Table 5 was calculated using data from a different Z-N catalyst obtained at several temperatures.[8] A value of $s_{\theta k}$, which is half of this initial guess, was selected to reflect our expectation that the final estimate for ε_{K11} could be quite different from −2 828.7 but should be similar in size. The objective function for parameter estimation for the non-

isothermal models also uses the s_{yi} values to weight the molecular weight and comonomer incorporation terms:

$$J = \sum \left(\frac{y_{MWD} - \hat{y}_{MWD}}{s_{yMWD}} \right)^2 + \sum \left(\frac{y_{CI} - \hat{y}_{CI}}{s_{yCI}} \right)^2 \quad (1)$$

The estimability algorithm was able to rank the parameters in Table 5 from most estimable to least estimable. However, singularity problems were encountered when ranking the final two parameters. This result suggests that, at very most, 32 parameters could be simultaneously estimated using the available MWD and composition data, because estimating all 33 parameters would lead to severe numerical conditioning problems. The parameter estimability rankings are shown in the final column of Table 5. A low rank number indicates a parameter that should be easy to estimate because of the large amount of information in the available data (compared to the uncertainty, $s_{\theta k}$). A high rank number indicates a parameter that cannot be readily estimated due to a lack of parameter influence on the predicted responses or due to correlation with the effects of parameters that appear earlier in the ranked list.

Parameter Estimation

The estimability analysis indicates that at most 32 parameters could be estimated without encountering severe numerical difficulties during parameter estimation. However, better model predictions may be obtained if fewer parameters are estimated. As a result, it is important to determine how many parameters should be estimated from the ranked list. Kou et al.[4] suggested using a pre-specified cut-off value for the magnitude of columns in the

residual sensitivity matrix. When the magnitudes of the residuals became smaller than this cut-off value, Kou et al. stopped the ranking procedure and the parameters that had been ranked were then estimated. Unfortunately, it is difficult to choose an appropriate cut-off value, making the number of estimated parameters somewhat arbitrary. An improved method for determining how many parameters to estimate is used in this article.

When too many parameters are estimated using limited data, the high levels of uncertainty associated with the parameter estimates result in large variances for the model predictions.[9,10] When only a subset of the model parameters is estimated (while keeping the other parameters at their initial guesses), model predictions and parameter estimates are biased due to the incorrect values of the fixed parameters.[9] This bias decreases when additional parameters are estimated. The optimal number of parameters to estimate balances the trade-off between variance and bias to produce model predictions with the lowest mean-squared prediction error.[10] A straightforward way to examine this trade-off is to use cross-validation,[11] as described below. Cross-validation tests the predictive ability of a model by removing data from the available data set. Model parameters are then estimated and used to predict the removed data.

Cross-validation was performed by selecting four key runs from the complete set of the 31 experimental runs. These four runs correspond to very different points in the operating space. Two runs used butene comonomer and two used hexene. The four points covered a range of temperatures and hydrogen-to-ethylene ratios. Various numbers of parameters from the ranked list were then estimated four times. Each time, data from one of the selected experiments were left out, and the remaining 30 runs were used to estimate the parameters. The estimated parameters were then used to predict the responses for their corresponding left-out run. This procedure was repeated for each of the four runs selected. The weighted sum of squared residuals (see Equation 1) was then calculated and added together for the four left-out runs (using the corresponding sets of parameter values). This cross-validation procedure was performed for different numbers of parameters being estimated, and the resulting values of this cross-validation objective function are plotted in Figure 2 versus the number of parameters that were estimated from the ranked list. A low value of the objective function indicates good predictive ability of the model and the parameters. One benefit of the cross-validation approach is that it provides a measure of how well the model can predict data that were not used for estimation. Cross-validation also provides information about the sensitivity of parameter values to particular experimental data points. Note that four key runs were chosen for cross-validation, rather than using all 31 runs,
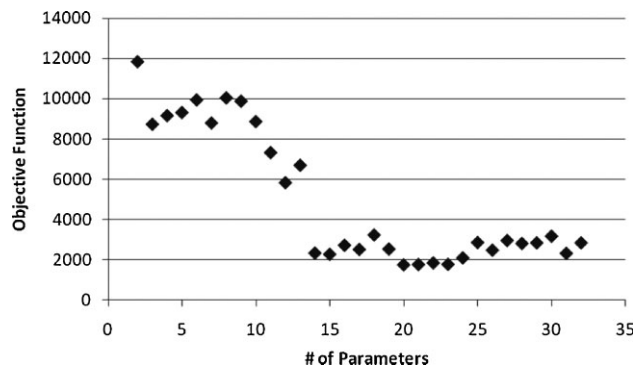

Figure 2. Influence of number of parameters estimated in the model in Table 3 on the cross-validation objective function.

because of the heavy computational load required to estimate the parameters.

The predictive ability of the model tended to improve as more parameters were estimated, up to approximately 14 parameters. Estimating additional parameters either had very little influence on the quality of the model predictions or resulted in worse predictions. The 14 highest-ranked parameters were then reestimated using all 31 runs in the data set, and are reported in Table 6.

The lower-ranked parameters that were not estimated tend to be activation energy parameters. The temperature effects in many kinetic rate constants may not be influential enough over the range of temperatures studied

Table 6. Parameter estimates for the 14 most-estimable parameters from the model in Table 3. Parameter estimates that are statistically different from zero at the 95% confidence level are shown in bold. Approximate 95% confidence intervals, based on linearization, were used to determine whether parameters are significant.

Rank	Parameter	Estimate
1	α_{4B}	**7.3420**
2	α_{4H}	**26.9599**
3	K_{15}	2.2222×10^{-14}
4	α_{1low}	**2 667.2**
5	α_{1high}	**544.7**
6	ε_{K13}	**−2 924.1**
7	α_{3Bhigh}	2.2246×10^{-14}
8	α_{3Hhigh}	2.2205×10^{-14}
9	α_{24}	**0.0942**
10	ε_{K12}	**−2 308.8**
11	α_{25}	**0.0159**
12	$\varepsilon_{\alpha24}$	**2 348.6**
13	$\varepsilon_{\alpha25}$	1 108.3
14	α_{23}	**0.3708**

Table 7. Reparameterized equations for computing MWD. This model was developed after making simplifying assumptions to reduce the number of unknown parameters to 25.

$$\frac{dW}{d\log_{10} Mw} = m_1\left[r^2 \ln(10)\tau_1^2 \exp(-\tau_1 r)\right] + m_2\left[r^2 \ln(10)\tau_2^2 \exp(-\tau_2 r)\right]$$
$$+m_3\left[r^2 \ln(10)\tau_3^2 \exp(-\tau_3 r)\right] + m_4\left[r^2 \ln(10)\tau_4^2 \exp(-\tau_4 r)\right]$$
$$+m_5\left[r^2 \ln(10)\tau_5^2 \exp(-\tau_5 r)\right]$$

(7.1)

$$\tau_j = K_{1j}\exp\left(\varepsilon_{K1low}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]} + K_4\frac{1}{[C_2]} \quad \text{for } j=1,2 \text{ OR}$$

$$\tau_j = K_{1j}\exp\left(\varepsilon_{K1high}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]} + K_4\frac{1}{[C_2]} \quad \text{for } j=3,4,5$$

(7.2)

$$m_j = \frac{N_j}{\sum\limits_{j=1}^{5} N_j}$$

(7.3)

$$N_1 = \left(\alpha_{21}\exp\left(\varepsilon_{\alpha21}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3Blow}\exp\left(\varepsilon_{\alpha3Blow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[C_4]}{[C_2]} + \alpha_{3Hlow}\exp\left(\varepsilon_{\alpha3Hlow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[C_6]}{[C_2]}\right)$$
$$\left(1 + \alpha_{1low}K_{12}\exp\left(\varepsilon_{Klow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=3,4,5}\left(1 + \alpha_{1high}K_{1j}\exp\left(\varepsilon_{Khigh}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]}\right)$$

(7.4)

$$N_2 = \left(1 + \alpha_{3Blow}\exp\left(\varepsilon_{\alpha3Blow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[C_4]}{[C_2]} + \alpha_{3Hlow}\exp\left(\varepsilon_{\alpha3Hlow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[C_6]}{[C_2]}\right)$$
$$\left(1 + \alpha_{1low}K_{11}\exp\left(\varepsilon_{Klow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=3,4,5}\left(1 + \alpha_{1high}K_{1j}\exp\left(\varepsilon_{Khigh}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]}\right)$$

(7.5)

$$N_3 = \left(\alpha_{23}\exp\left(\varepsilon_{\alpha2high}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3Bhigh}\frac{[C_4]}{[C_2]} + \alpha_{3Hhigh}\frac{[C_6]}{[C_2]}\right)$$
$$\prod_{j=1,2}\left(1 + \alpha_{1low}K_{1j}\exp\left(\varepsilon_{Klow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=4,5}\left(1 + \alpha_{1high}K_{1j}\exp\left(\varepsilon_{Khigh}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]}\right)$$

(7.6)

$$N_4 = \left(\alpha_{24}\exp\left(\varepsilon_{\alpha2high}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3Bhigh}\frac{[C_4]}{[C_2]} + \alpha_{3Hhigh}\frac{[C_6]}{[C_2]}\right)$$
$$\prod_{j=1,2}\left(1 + \alpha_{1low}K_{1j}\exp\left(\varepsilon_{Klow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=3,5}\left(1 + \alpha_{1high}K_{1j}\exp\left(\varepsilon_{Khigh}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]}\right)$$

(7.7)

$$N_5 = \left(\alpha_{25}\exp\left(\varepsilon_{\alpha2high}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) + \alpha_{3Bhigh}\frac{[C_4]}{[C_2]} + \alpha_{3Hhigh}\frac{[C_6]}{[C_2]}\right)$$
$$\prod_{j=1,2}\left(1 + \alpha_{1low}K_{1j}\exp\left(\varepsilon_{Klow}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2] + \alpha_{4B}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_4] + \alpha_{4H}\exp\left(\varepsilon_{\alpha4}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)[C_6]}\right)$$
$$\prod_{j=3,4}\left(1 + \alpha_{1high}K_{1j}\exp\left(\varepsilon_{Khigh}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)\frac{[H_2]}{[C_2]}\right)$$

(7.8)

(80–115 °C) to allow the estimation of separate activation energy parameters for individual types of active sites. To make the best possible use of the data, another round of model simplification was used. To further reduce the number of parameters in the model, it was assumed that sites 1 and 2 have common activation energy parameters, and that sites 3–5 share a different set of common values. We also assumed that, since there is little propagation with comonomers at the high-molecular-weight sites, it is reasonable to ignore the associated temperature effects (no activation energy parameter associated with α_{3Bhigh} and α_{3Hhigh}). These simplifications reduced the number of model parameters from 33 to 25. The reparameterized model equations are shown in Table 7.

With the model further simplified, a second round of estimability analysis was performed. The estimability rankings, along with the initial parameter estimates and the scaling values, are shown in Table 8. This time, the estimability algorithm was able to rank all 25 model parameters.

With the new estimability rankings in place, a new cross-validation plot (similar to Figure 2) was generated and is shown in Figure 3. This time, the objective function decreases until 16 parameters have been estimated. The MWD fits for the four runs used in cross-validation are shown in Figure 4a–d, and the parameter estimates are shown in Table 9. The MWD model is able to match all four MWD curves very well. There is little difference between the final model predictions and the predictions obtained using the cross-validation parameters, indicating that the model has good predictive capability for the four selected runs. The data set used for parameter estimation contains data from experimental runs that were replicated at three different sets of operating conditions. Model predictions and experimental data for these runs are shown in Figure 5a–c. The small deviations between the model predictions and the data are similar in size to the deviations between the measured MWD curves.

Figure 6 shows the behavior of the overall objective function for parameter estimation as additional para-

Table 8. Estimability rankings for the simplified 25-parameter model that appears in Table 7.

| Parameter	Initial value	Scaling value	Rank
K_{11}	0.0149	6.209×10^{-3}	21
K_{12}	0.0030	9.0×10^{-4}	23
K_{13}	0.0012	5.57×10^{-4}	13
K_{14}	0.0003	5.39×10^{-4}	19
K_{15}	0	8.8781×10^{-3}	3
K_4	9.4×10^{-4}	1.3055×10^{-4}	15
α_{1low}	1 325.8	1 893.7	4
α_{1high}	3 222.2	5 048.4	5
α_{21}	0.4755	0.2074	18
α_{23}	1.9492	1.0260	12
α_{24}	0.3370	0.2042	10
α_{25}	0.0579	0.0656	11
α_{3Blow}	0.4370	0.5	17
α_{3Bhigh}	1.73×10^{-9}	0.5	6
α_{3Hlow}	0.4370	0.5	20
α_{3Hhigh}	1.73×10^{-9}	0.5	8
α_{4B}	0.0491	51.3868	1
α_{4H}	0.0491	51.3868	2
ε_{Klow}	$-2\,308.8$	-801.5	16
ε_{Khigh}	$-2\,924.1$	$-1\,307$	7
$\varepsilon_{\alpha21}$	$-3\,974$	$-1\,987.2$	14
$\varepsilon_{\alpha2high}$	2 348.6	3 491.4	9
$\varepsilon_{\alpha3Blow}$	$-3\,974.4$	$-3\,874.4$	22
$\varepsilon_{\alpha3Hlow}$	$-3\,974.4$	$-3\,974.4$	24
$\varepsilon_{\alpha4}$	0	1 504.2	25
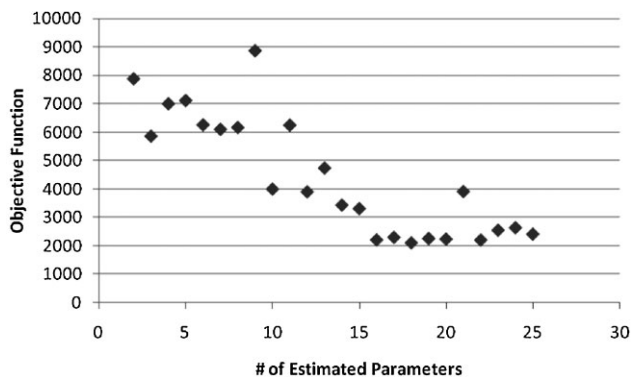
Figure 3. Influence of number of parameters estimated in the model in Table 7 on the cross-validation objective function.

meters are estimated from the complete set of 31 runs. This figure confirms that the fit to the data cannot be improved significantly by estimating more than 16 parameters. The parameter estimates in Table 9 are consistent with the initial guesses and the scaling values from Table 8, indicating that none of the parameter estimates is physically or statistically unrealistic.

Unfortunately, comonomer incorporation is not as well predicted as the MWDs (see Figure 7). This is because the single comonomer incorporation data point from each run does not have much weight (compared to the 100 MWD points for each run) in the parameter-estimation objective function. The results in Figure 5 and 7 may correspond to a local optimum in the parameter estimation surface. To fix

Table 9. Parameter estimates of the 16 most-estimable parameters in the 25-parameter model. Parameter estimates that are statistically different from zero at the 95% confidence interval are shown in bold. Approximate 95% confidence intervals, based on linearization, were used to determine whether parameters are significant.

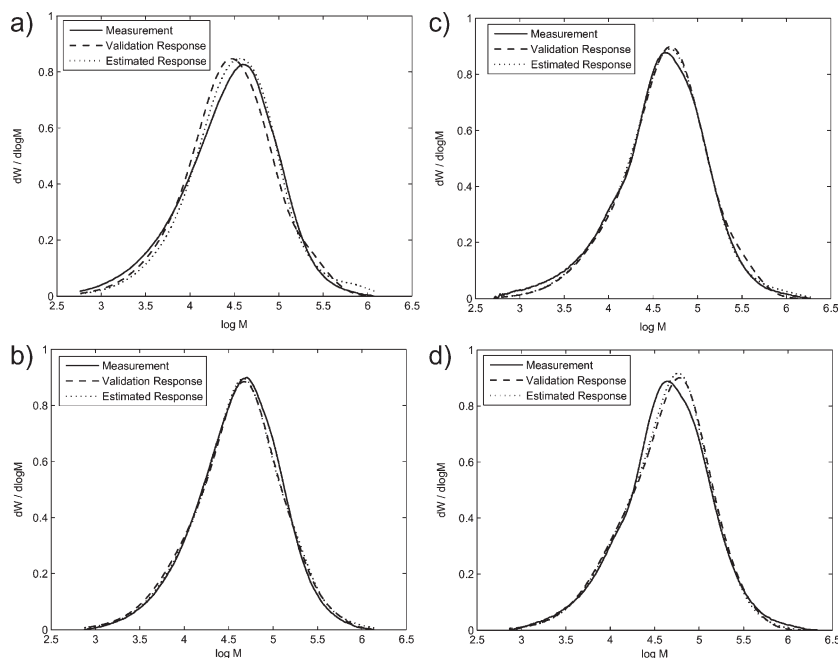| Rank	Parameter	Estimate
1	α_{4B}	**6.7180**
2	α_{4H}	**23.4994**
3	K_{15}	3.7257×10^{-7}
4	α_{1low}	**2 423.9**
5	α_{1high}	**426.1679**
6	α_{3Bhigh}	4.2991×10^{-13}
7	ε_{Khigh}	**−3 582.1**
8	α_{3Hhigh}	8.2273×10^{-13}
9	$\varepsilon_{\alpha2high}$	566.7239
10	α_{24}	**0.0623**
11	α_{25}	**0.0171**
12	α_{23}	**0.3434**
13	K_{13}	**0.0010**
14	$\varepsilon_{\alpha21}$	**−3 385.1**
15	K_4	**8.1760×10^{-4}**
16	ε_{Klow}	**−2 387.0**

Figure 4. Predictions of MWD for runs used for cross-validation. The solid line is the measured MWD, the dotted line is the fit with all runs included in the parameter estimation, and the dashed line is the prediction with this run left out of the parameter estimation. (a) Butene at 90 °C, (b) hexene at 80 °C, (c) butene at 110 °C, (d) hexene at 100 °C.
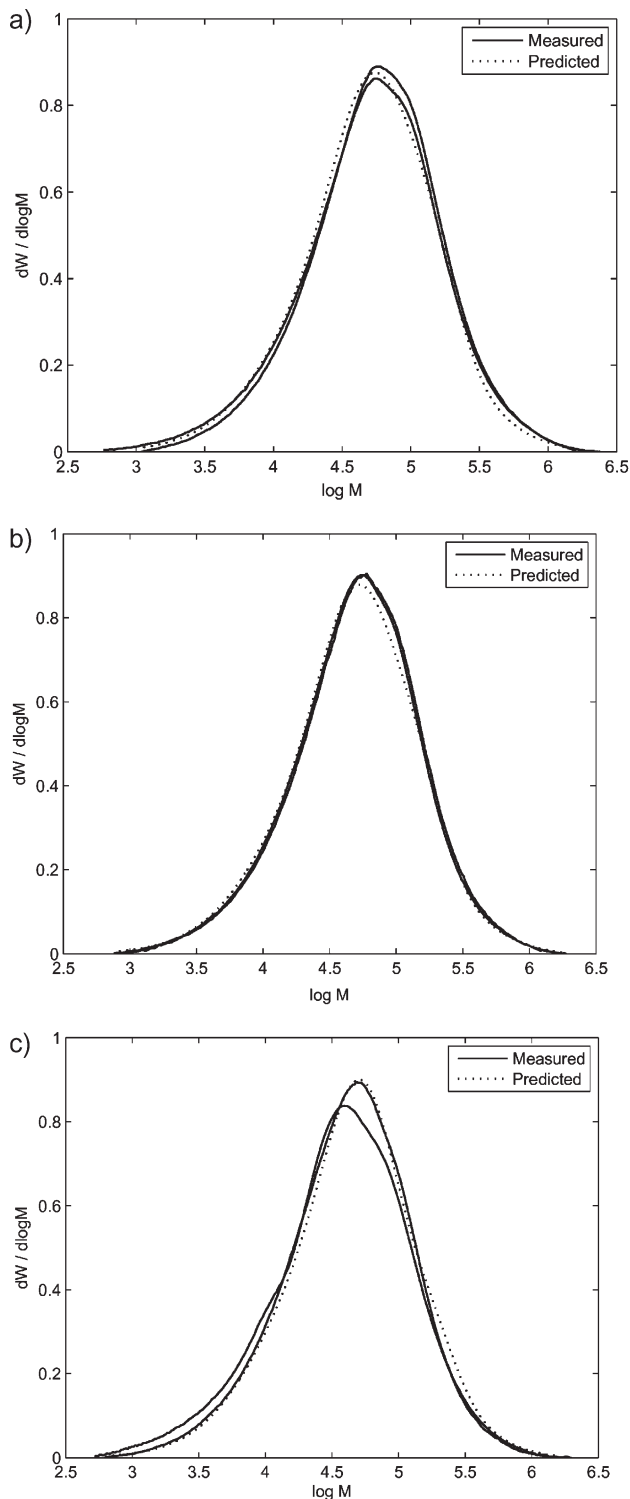
Figure 5. Predictions of three pairs of replicate runs. Runs (a) and (b) were conducted with hexene at 90 °C and run (c) was conducted with hexene at 80 °C. Predictions were made using the model in Table 7 and the parameter estimates in Table 8 and 9.
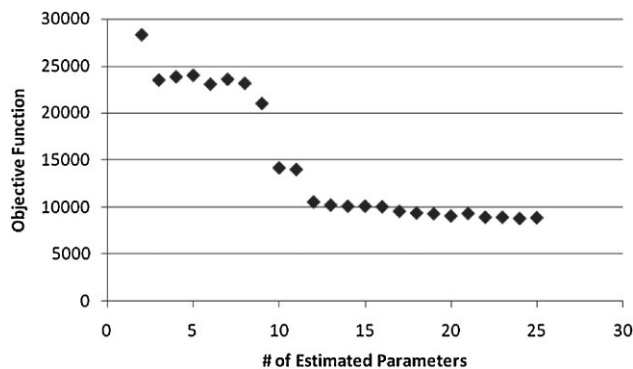

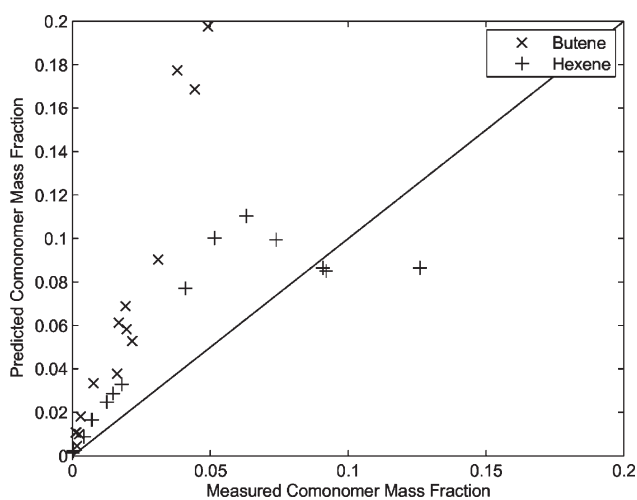Figure 6. Parameter estimation objective function decreases as more parameters are added.

Figure 7. Comparison of predicted and measured comonomer incorporation using parameter values in Table 8 and 9.
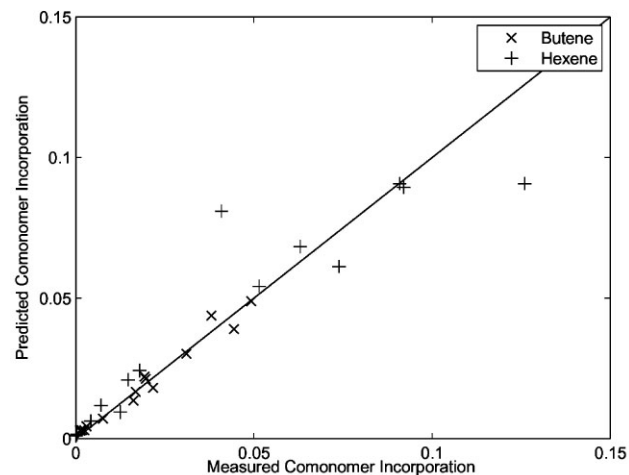

Figure 8. Comparison of predicted and measured comonomer incorporation using the final parameter values in Table 10.

this problem, another round of estimability analysis and parameter estimation was needed. In the first step, only the comonomer incorporation data were included and no MWD information was used in the estimability ranking or parameter estimation. Using the comonomer incorporation sensitivity coefficients, the eight most estimable parameters related directly to comonomer incorporation predictions were determined (i.e., α_{3Bhigh}, α_{3Hhigh}, α_{4B}, α_{4H}, $\varepsilon_{\alpha 3Blow}$, $\varepsilon_{\alpha 3Hlow}$, α_{3Blow}, α_{3Hlow}). These eight parameters were reestimated starting from the values in Table 8 and 9 to obtain an improved fit of the comonomer incorporation data. Next, the 16 parameters in Table 9 were reestimated to fit both the MWD and comonomer data, using the new values of the eight comonomer parameters as starting values (and fixed values). Parameters were successively reestimated until further improvements in the objective function and comonomer incorporation fit were not observed. The new parameter values drastically improved

the comonomer incorporation fit, as can be seen in Figure 8, with a small improvement in the MWD fits, as well (not shown). The complete set of final parameter estimates is provided in Table 10. The overall objective function, in Equation (1) was reduced from 10 070 to 9 457 when the parameters in Table 10 were used instead of those in Table 8 and 9.

Conclusion

A simplified model has been developed to predict MWDs from ethylene/hexene and ethylene/butene copolymerization using a Z-N catalyst. Estimability analysis and cross-validation were shown to be useful tools for deciding which parameters should be estimated using limited industrial data, and for guiding decisions about model simplification. Twenty of 25 parameters were estimated in the simplified model, which provides good predictions of MWD curves and comonomer incorporation. The small mismatch between model predictions and experimental MWD results are similar in magnitude to deviations between MWD curves from replicate experimental runs. The parameter estimates from this study will be useful for designing experiments aimed at further model improvement, and the parameter estimation and model simplification strategy can be applied to other catalytic polymerization models.

Table 10. Final parameter values. The twenty bold values correspond to parameters that were estimated using the experimental data.

Parameter	Estimate
K_{11}	0.0149
K_{12}	0.0030
K_{13}	**0.0011**
K_{14}	0.0003
K_{15}	$\mathbf{4.0 \times 10^{-13}}$
K_4	$\mathbf{7.9 \times 10^{-4}}$
α_{1low}	**2 431.6**
α_{1high}	**390.7**
α_{21}	0.4755
α_{23}	**0.3419**
α_{24}	**0.0671**
α_{25}	**0.0154**
α_{3Blow}	**0.0378**
α_{3Bhigh}	**0.0154**
α_{3Hlow}	**0.3065**
α_{3Hhigh}	$\mathbf{4.44 \times 10^{-9}}$
α_{4B}	**10.63**
α_{4H}	**28.84**
ε_{Klow}	**−3 095**
ε_{Khigh}	**−4 070**
$\varepsilon_{\alpha 21}$	**−2 476**
$\varepsilon_{\alpha 2high}$	**−259.5**
$\varepsilon_{\alpha 3Blow}$	**−4 377**
$\varepsilon_{\alpha 3Hlow}$	**495.6**
$\varepsilon_{\alpha 4}$	0

Nomenclature

$[H_2]$	gas phase hydrogen concentration (bar)
$[C_2]$	gas phase ethylene concentration (bar)
$[C_6]$	gas phase hexene concentration (bar)
$[I]$	gas phase impurities concentration (bar)
α_{1low}	lumped parameter, ratio relating chain transfer to hydrogen to reinitiation with ethylene at sites 1 and 2
α_{1high}	lumped parameter, ratio relating chain transfer to hydrogen to reinitiation with ethylene at sites 3–5
α_{2j}	lumped parameter, ratio relating propagation with ethylene at site j to propagation with ethylene at site 2
α_{3Blow}	lumped parameter, ratio relating propagation with butene at sites 1 and 2 to propagation with ethylene at site 2
α_{3Bhigh}	lumped parameter, ratio relating propagation with butene at sites 3–5 to propagation with ethylene at site 2
α_{3Hlow}	lumped parameter, ratio relating propagation with hexene at sites 1 and 2 to propagation with ethylene at site 2

α_{3Hhigh}	lumped parameter, ratio relating propagation with hexene at sites 3–5 to propagation with ethylene at site 2
α_{4B}	lumped parameter, ratio relating reinitiation with butene to reinitiation with ethylene at sites 1 and 2
α_{4H}	lumped parameter, ratio relating reinitiation with hexene to reinitiation with ethylene at sites 1 and 2
β_j	ratio of potential sites of type j to potential sites of type 2
ε_{Kj}	lumped parameter, activation energies relating propagation with ethylene to chain transfer to hydrogen at site j (K)
$\varepsilon_{\alpha2j}$	lumped parameter, activation energies relating propagation with ethylene at site j to propagation with ethylene site 2 (K)
$\varepsilon_{\alpha3Blow}$	lumped parameter, activation energies relating propagation with butene at sites 1 and 2 to propagation with ethylene site 2 (K)
$\varepsilon_{\alpha3Bhigh}$	lumped parameter, activation energies relating propagation with butene at sites 3–5 to propagation with ethylene site 2 (K)
$\varepsilon_{\alpha3Hlow}$	lumped parameter, activation energies relating propagation with hexene at sites 1 and 2 to propagation with ethylene site 2 (K)
$\varepsilon_{\alpha3Hhigh}$	lumped parameter, activation energies relating propagation with hexene at sites 3–5 to propagation with ethylene site 2 (K)
$\varepsilon_{\alpha4B}$	lumped parameter, activation energies relating reinitiation with ethylene to reinitiation with butene at sites 1 and 2 (K)
$\varepsilon\alpha_{4B}$	lumped parameter, activation energies relating reinitiation with ethylene to reinitiation with hexene at sites 1 and 2 (K)
E_{tj}^{H}	activation energy for chain transfer to hydrogen at site j (J·mol^{-1})
E_{pj}^{E}	activation energy for propagation with ethylene at site j (J·mol^{-1})
E_{pj}^{But}	activation energy for propagation with butene at site j (J·mol^{-1})
E_{pj}^{Hex}	activation energy for propagation with hexene at site j (J·mol^{-1})
E_{ij}^{E}	activation energy for reinitiation with ethylene at site j (J·mol^{-1})
E_{ij}^{But}	activation energy for reinitiation with butene at site j (J·mol^{-1})
E_{ij}^{Hex}	activation energy for reinitiation with hexene at site j (J·mol^{-1})
f_{Bj}	butene mole fraction incorporated by site j
f_{Hj}	hexene mole fraction incorporated by site j
J	objective function value
K_{1j}	lumped parameter, ratio relating chain transfer to hydrogen to propagation with ethylene at site j

K_4	lumped parameter, ratio relating spontaneous chain transfer and chain transfer to impurities to propagation with ethylene at all sites (bars)
k_{ij0}^{E}	pre-exponential kinetic rate constant for reinitiation with ethylene at site j (bars^{-1}·s^{-1})
k_{ij0}^{But}	pre-exponential kinetic rate constant for reinitiation with butene at site j (bars^{-1}·s^{-1})
k_{ij0}^{Hex}	pre-exponential kinetic rate constant for reinitiation with hexene at site j (bars^{-1}·s^{-1})
k_{pj0}^{E}	pre-exponential kinetic rate constant for propagation with ethylene at site j (bars^{-1}·s^{-1})
k_{pj0}^{But}	pre-exponential kinetic rate constant for propagation with butene at site j (bars^{-1}·s^{-1})
k_{pj0}^{Hex}	pre-exponential kinetic rate constant for propagation with hexene at site j (bars^{-1}·s^{-1})
k_{tj0}^{H}	pre-exponential kinetic rate constant for chain transfer to hydrogen at site j bars^{-1}·s^{-1}
k_{tj}^{β}	kinetic rate constant for spontaneous chain transfer at site j (s^{-1})
k_{tj}^{I}	kinetic rate constant for chain transfer to impurities at site j (bars^{-1}·s^{-1})
m_j	mass fraction of polymer produced at site j
m_B	mass fraction of butene incorporation
m_H	mass fraction of hexene incorporation
N_j	mass fraction model numerator for site j
R	gas constant (J·mol^{-1}·K^{-1})
r	chain length
$s_{\theta k}$	parameter uncertainty in estimability analysis scaling
s_{yi}	response uncertainty in estimability analysis scaling
τ_j	inverse number-average molecular weight of site j
θ_k	parameter k in estimability analysis
T	reactor temperature (K)
T_0	reference temperature, $T_0 = 363.15$ K (K)
y_i	response i in estimability analysis
$Y_{j,n}$	growing polymer chain of length n at site of type j
Y_{jD}	temporarily dormant site of type j
Z	sensitivity matrix in estimability analysis
$\hat{Z}_K$	least-squares prediction of Z in estimability analysis iteration K

Appendix: Estimability Analysis Algorithm for Parameter Ranking

Estimability analysis is a tool for determining which parameters should be estimated when complex models contain too many parameters to be estimated using the available data. The estimability analysis algorithm used in this research is a simple and convenient tool, which was first proposed by Yao et al.[6] and then further developed by

Kou et al.[4,5] who studied olefin polymerization models with large numbers of parameters. Alternative tools, such as the approach of Li et al.,[12] are less convenient to use. Li's method uses two separate measures, one that tests for parameter influence (magnitude of sensitivity coefficients) and a second that tests for linear independence. There is no easy way to combine the results from the two measures to decide which parameters should be estimated using the available data. Recently, Lund and Foss[7] proposed a method that produces identical results to the method of Kou et al., but Lund's method is more computationally complex. Chu and Hahn[13] have also suggested using an orthogonalization method to determine which parameters cannot be estimated together. Unfortunately, their method for parameter ranking uses a computationally intensive genetic algorithm to select parameters that should be estimated, using information from their orthogonalization results.

Estimability analysis uses sensitivity coefficients, which are the first-order partial derivatives of the response variables, y_i, with respect to the parameters, θ_k. A sensitivity matrix is constructed using these parametric sensitivity coefficients. Each column in the matrix contains partial derivatives with respect to a particular parameter, and each row corresponds to partial derivatives for a specific predicted response:

$$Z = \begin{bmatrix} \frac{\partial y_1}{\partial \theta_1} & \cdots & \frac{\partial y_1}{\partial \theta_k} \\ \vdots & \ddots & \vdots \\ \frac{\partial y_i}{\partial \theta_1} & \cdots & \frac{\partial y_i}{\partial \theta_k} \end{bmatrix}$$

The number of columns in Z is equal to the number of parameters in the model and the number of rows is equal to the total number of response values that will be used for parameter estimation. For example, the model in Table 3 has 33 unknown parameters and the data set available to estimate these parameters contains 31 MWD curves (with 100 points each) and 31 comonomer incorporation measurements. The resulting sensitivity matrix has dimensions of 3 131 by 33. The sensitivity coefficients in Z should be properly scaled so that they are dimensionally consistent and can be meaningfully compared. To accomplish this objective, we propose that each coefficient should be multiplied by the uncertainty in the corresponding initial parameter guess, $s_{\theta k}$, and divided by the uncertainty in the particular measured response, s_{yi}, resulting in scaled sensitivity coefficients of the form:

$$\frac{\partial y_i}{\partial \theta_k} \frac{s_{\theta k}}{s_{yi}}$$

The relative influence of the various parameters can be found by examining the magnitudes of the entries in the columns of the sensitivity matrix. Parameters with large influence will correspond to columns with large (positive or negative) scaled sensitivity coefficients. To rank the parameters from most to least estimable, the following algorithm, which takes into account both the influence of the parameters and the correlations between their effects, is used:

1. Calculate the magnitude (sum of squares) of each column of the scaled sensitivity matrix, Z. Although analytical derivatives are used in the current research project, numerical derivatives could also be used.
2. Select the column with the largest magnitude. This column corresponds to the most estimable parameter.
3. Put the selected column into matrix X_K. When the first parameter is selected, $K = 1$, and the matrix will contain only one column. When subsequent parameters are selected, the X_K matrix will contain K columns.
4. Calculate $\hat{Z}_K$, the least-squares prediction of the scaled sensitivity matrix, using the information in X_K

$$\hat{Z}_K = X_K (X_K^T X_K)^{-1} X_K^T Z$$

5. Calculate the residual matrix R_K

$$R_K = Z - \hat{Z}_K$$

6. Calculate the magnitude of each column of R_K. The column with the largest magnitude corresponds to the next most estimable parameter.
7. Select the corresponding column in Z and augment the matrix X_K by including the new column. This augmented matrix is X_{K+1}.
8. Advance the iteration counter by 1 and repeat steps 4–7 until either all the parameters are ranked or singularity problems are encountered when inverting $X_K^T X_K$.

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