Dynamic Modeling of Multizone, Multifeed High-Pressure LDPE Autoclaves

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ABSTRACT: A comprehensive mathematical model is developed to simulate the dynamic behavior of multizone, multifeed high-pressure ethylene polymerization autoclaves. To describe the complex flow patterns occurring in low-density polyethylene (LDPE) autoclaves, a user-specified multisegment, multirecycle model representation of the actual multizone reactor is established. A general reaction mechanism is employed to represent the kinetics of ethylene polymerization. Dynamic mass, molar species, and energy balances are derived to predict the polymerization rate, monomer conversion, molecular weight developments (e.g., M_n , M_w , long- and short-chain branching), and temperature profile with respect to time and spatial position in the reactor. Detailed results on the start-up and grade transition of a four-zone autoclave reactor are presented and the effects of the macromixing parameters (e.g., number of segments per reaction zone and the total and side external recycle ratios) on the dynamic behavior of the reactor are investigated. It is shown that the model macromixing parameters can significantly affect the initiator consumption rate in a reaction zone. The present model is capable of predicting accurately the dynamic behavior of LDPE autoclaves and, thus, can be employed in the design, optimization, and control of these reactors. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2327-2348, 1999

Key words: polymerization reactor modeling; high-pressure LDPE autoclaves; macromixing; molecular weight properties

INTRODUCTION

High-pressure ethylene polymerization is an industrial process of significant economic importance. Two reactor technologies, namely, tubular and autoclaves, are currently employed in the production of low-density polyethylene (LDPE). High-pressure LDPE reactors typically operate at high temperatures (150–330°C) and pressures (1200–3500 atm). Under these conditions, the reaction mixture behaves as a supercritical fluid. Temperatures above 330°C should be avoided because of possible ethylene decomposition.

An autoclave is a constantly mixed vessel made up of two or more reaction zones in series, separated by disks and stirred by a vertical stirrer shaft. Despite the large specific power input to the reacting system (20–100 kW/m³) effected by high agitation rates, the zones are not considered to be perfectly mixed due to the very fast reaction kinetics. The polymerization of ethylene in autoclaves is practically carried out in an adiabatic way. Cooling of the reaction mixture is effected by the introduction of cold monomers at several sidefeed points along the reactor. The reaction temperature in a zone is controlled by manipulating the corresponding initiator feed rate. It is important to point out that cautious reactor control is required because the reactor usually operates at an open-loop unstable steady state.

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The flow behavior in these reactors deviates significantly from ideal flow patterns (e.g., plug flow and perfectly mixed conditions), which makes the approximation of the flow behavior in the reactor necessary with more complicated mixing models. A number of macromixing models have been proposed in the literature (Donati et al.,¹ Singstad,² Chan et al.,³ Kwag and Choi⁴) to describe the nonideal flow patterns. Donati et al.¹ developed a multicomponent macromixing model for LDPE autoclaves based on fluid dynamic measurements made on a full-scale cold-flow industrial reactor. The tanks-in-series model with backflow has often been employed to approximate the flow patterns in LDPE autoclaves (Shastry et al.,⁵ Singstad²). According to this model, an internal backflow stream from a tank (or volume segment) to the previous tank of the reactor sequence is introduced to account for the nonideal macromixing flow in the autoclave. Chan et al.³ introduced a multisegment external recycle model to describe the nonideal flow behavior in LDPE autoclaves.

In the present study, a generalized compartment model with an external recycle was developed to account for the effect of macromixing on the polymerization kinetics (see Fig. 1). According to the proposed macromixing model, each reaction zone is divided into a sequence of perfectly mixed tanks, hereby to be called segments (see Fig. 1). The number of tanks as well as the size of tanks can vary for each zone. Note that the present model can handle any number of ethylene side streams introduced into specified zone segments. To account for possible backmixing of the reaction mixture, an external recycle stream from the first segment of a zone to all segments of the previous zone is introduced (see Fig. 1). By selecting the number and volumes of segments in a reaction zone and the external recycle parameters, β_i and γ_{ii} , the nonideal flow behavior in an autoclave can be approximated.

To model the molecular and compositional developments in an LDPE autoclave, a comprehensive kinetic mechanism describing the free-radical polymerization of ethylene is considered. Dynamic mass, molecular species, macromolecular properties, and energy balance equations are derived for each volume segment of the multizone autoclave reactor to simulate the transient reactor behavior. The method of moments based on the statistical representation of the number chain-length distribution is employed to reduce the infinite number of molecular species balances



Figure 1 The external recycle model.

into a low-order system of moment differential equations.

The present comprehensive model is capable of describing the complex macromixing phenomena occurring in an LDPE autoclave and quantifying the effects of process variables (e.g., ethylene feed rate, temperature, initiator concentration) and macromixing parameters (e.g., number of segments per zone and recycle parameters) on the ethylene conversion and molecular properties [e.g., number- and weight-average molecular weights, long-chain branching (LCB), and shortchain branching (SCB)] of the LDPE.

The article is organized as follows: In the second section, a generalized external recycle model is developed to approximate the complex flow patterns in industrial LDPE autoclaves. Simulation results are presented showing the effect of the various macromixing parameters on the residence time distribution (RTD). Subsequently, a detailed kinetic scheme is considered to account for all elementary reactions occurring in highpressure ethylene homopolymerization. Analytical expressions are derived for the net rates of production and consumption of the various macromolecular species. Following that, general dynamic mass, molar, and energy balances are derived to describe the time and spatial variation of ethylene conversion, temperature, and molecular properties in the reactor. In the final section, simulation results are presented showing the predictive capabilities of the model.

EXTERNAL RECYCLE MODEL

An autoclave is a constantly stirred vessel which operates under controlled temperature and pressure conditions. These reactors are long vessels with length-to-diameter ratios as high as 20 to 1. The reactor is usually subdivided into a number of reaction zones. Reaction conditions can be adjusted separately in each zone to produce polymers with the desired molecular properties.

A schematic diagram of a typical multizone, multifeed LDPE autoclave is shown in Figure 2. The reactor includes a number of monomer, initiator, and chain-transfer-agent (CTA) side-feed points. The inflow of the monomer and initiator at several points down the reactor provides satisfactory temperature control although the temperature may vary down the length of the reactor. The heat transfer through the wall is limited, thus the reactor operation is essentially adiabatic. Mixing is provided by an agitator running down the center of the vessel. Despite the very high power input per unit volume required to maintain good mixing conditions in each reaction zone, the flow patterns in the autoclave are far from ideal. Several investigators have shown that the degree of mixing affects the behavior of high-pressure LDPE autoclaves (Mercx et al.,⁶ Goto et al.,⁷ Georgakis and Marini,⁸ Villermaux et al.,⁹ Zwietering¹⁰). The main reason for the nonideal flow in LDPE autoclaves is the lack of homogeneity which is mainly due to the very fast reaction kinetics. It is important to point out that the characteristic reaction time constant associated with the initiator decomposition is of the order of 0.1 s.

Homogeneity of the reaction mixture is brought about by two different mixing mechanisms: (i) macroscopic, whereby mixing of different volume elements is induced by large-scale turbulent motions, and (ii) microscopic, which affects mixing on a molecular scale (e.g., molecular diffusion). For all practical reasons, macromixing



Figure 2 Schematic diagram of a four-zone LDPE autoclave.

can be associated with the RTD, whereas micromixing may be linked with the state of fluid aggregation. It was the objective of the present contribution to develop a general RTD model to characterize the nonideal flow behavior in LDPE autoclaves.

The RTD describes how much time different fluid elements have spent in the reactor and can be determined experimentally by injecting an inert chemical, called a tracer, into the reactor inlet and measuring the tracer concentration in the effluent stream as a function of time. The two most common methods of tracer injection are the *pulse input* and the *step input*.

In the pulse-input method, a known amount of tracer is suddenly injected into the feedstream entering the top of the reactor. The input tracer concentration, C_0 , is given by

$$C_0 = \frac{M}{QC(1, 1)} \,\delta(t) \tag{1}$$

where M denotes the total number of moles of injected material, $\delta(t)$ is the Dirac Delta function, and QC(1,1) is the feed volumetric flow rate, entering the first segment of the first zone. Note that M can be calculated in terms of the outlet concentration, C(t), as in eq. (2):

$$M = \int_0^\infty QC(N_e, L_e)C(t) dt$$
 (2)

where $QC(N_e, L_e)$ is the total volumetric flow rate at the reactor exit; N_e , the number of volume segments in the last zone; and L_e , the total number of zones.

The RTD function, E(t), expressed in reciprocal seconds, is given by the normalized outlet concentration according to eq. (3):

$$E(t) = C(t) \left/ \int_0^\infty C(t) \, dt \right. \tag{3}$$

Frequently, a dimensionless RTD function, $E(\Theta)$, is employed instead of the function E(t):

$$E(\Theta) = \tau E(t) \tag{4}$$

where τ denotes the reactor mean residence time and $\Theta = t/\tau$ is a dimensionless time.

Dynamic Molar Tracer Balances

Let us assume that the complex flow patterns in an a high-pressure LDPE autoclave can be approximated by the general compartment model shown in Figure 1. Accordingly, one can write the following dynamic tracer molar balance equations:

First segment in the first zone:

$$V(1, 1) \frac{dC_{1,1}}{dt} = QC(1, 1)C_0 + QSR(1, 2)C_{1,2} - Q(1, 1)C_{1,1}$$
(5)

First segment in zone "j":

$$V(1, j) \frac{dC_{1j}}{dt} = QSR(1, j+1)C_{1,j+1} + Q(N_{j-1}, j-1)C_{N_{j-1},j-1} - Q(1, j)C_{1,j} - QR(j)C_{1,j}$$
(6)

Any other segment "i" in zone "j":

$$V(i, j) \frac{dC_{i,j}}{dt} = QSR(i, j+1)C_{1,j+1} + Q(i-1, j)C_{i-1,j} - Q(i, j)C_{i,j} \quad (7)$$

where N_j , QC(i, j), Q(i, j), QSR(i, j + 1), and QR(j)denote the number of segments in the "j" zone, the volumetric feed flow rate into the "i" segment of zone "j," the total outlet volumetric rate from the "i" segment of zone "j," the inlet volumetric flow rate via the side recycle stream, and the total volumetric flow rate of the external recycle stream leaving the first segment of zone "j," respectively. V(i,j) is the volume of segment "i" in zone "j" and $C_{i,j}$ denotes the corresponding tracer concentration.

Using the appropriate form of molar balance eqs. (5)–(7) for each volume segment, a system of first-order differential equations can be obtained to describe the time variation of the tracer concentration in any segment in the reactor sequence. From the numerical integration of the resulting coupled molar balance equations, the tracer concentrations, $C_{i,j}$, in all segments of a given reactor configuration can be calculated. The outlet concentration, C(t), will be equal to the tracer concentration in the last segment of the last zone. Accordingly, the RTD function E(t) or $E(\Theta)$ can be calculated by means of eqs. (3) or (4).

To investigate the effect of the various macromixing model parameters on the RTD, the following dimensionless quantities are introduced—the ratio of the volumetric feed flow rate entering the "j" zone, QC(i,j), over the total outlet volumetric flow rate, $QC(N_e,L_e)$:

$$\alpha_{j} = \frac{QC(i,j)}{QC(N_{e},L_{e})} \tag{8}$$

and the ratio of the total volumetric flow rate of the external recycle stream leaving the first segment of zone "j," QR(j), over the total outlet volumetric flow rate from segment (1,j):

$$\beta_j = \frac{QR(j)}{Q(1,j) + QR(j)} \tag{9}$$

Note that the value of β_j for the first segment in the first zone will be equal to zero. Finally, the side recycle ratio, γ_{ij} , is defined as the ratio of the inlet volumetric recycle flow rate to the (i,j) seg-



Figure 3 Effect of the number of segments per zone on the RTD.

ment over the total outlet volumetric recycle flow rate from the first segment of zone "j + 1":

$$\gamma_{ij} = \frac{QSR(i, j+1)}{QR(j+1)} \tag{10}$$

Note that the value of γ_{ij} for all segments of the last zone will be zero.

Simulation Results

Computer simulations were carried out for typical reactor configurations in order to determine the effect of the various mixing parameters on the RTD. In all calculations, it was assumed that the reactor consisted of three zones and all segments (i,j) had the same volume. The RTD model parameters included the number of segments per zone (N_j) , the total recycle ratio of a zone, β_j , and the side recycle ratios, γ_{ij} .

Figures 3 and 4 illustrate the effect of the macromixing parameters (N_j, β_j) on the RTD. In particular, the effect of the number of segments per zone, N_j , on the calculated RTD is depicted in Figure 3 for $\beta_j = 0.2$ (j = 2,3), $\gamma_{ij} = 0.333$ $(i = 1, 2, \ldots, N_j)$, and $\alpha_1 = 1.0$. It can be seen that as the number of volume segments per zone increases the flow behavior of the reactor approaches that of a plug flow reactor. Figure 4 depicts the effect of the total recycle ratio, β_j , on the calculated RTDs for $N_j = 3$ (j

= 1, 2, 3, $\gamma_{ij} = 0.333$ ($i = 1, 2, ..., N_j$), and $\alpha_1 = 1.0$. It is apparent that as the total external recycle ratio increases the RTD of the autoclave approaches that of a perfectly mixed vessel. The effect of the side recycle ratios, γ_{ii} , on the calculated RTD presents a similar behavior. Notice that as the side recycle stream moves from the last volume segment to the first segment of a zone mixing increases and the reactor flow behavior approaches that of a perfectly mixed reactor. It is apparent from these results that the complex flow patterns observed in a nonideal LDPE autoclave can be approximated by the appropriate selection of the macromixing parameters (N_i) β_i, γ_{ii}). On the other hand, as will be seen in the fifth section, the choice of the mixing parameters can significantly affect the initiator consumption rate as well as the molecular weight properties of the LDPE.

KINETICS OF ETHYLENE POLYMERIZATION

At high pressures and temperatures, ethylene will undergo free-radical polymerization in the presence of an initiator (e.g., peroxide, oxygen). A general kinetic mechanism describing the free-radical polymerization of ethylene in a high-pressure reactor includes the following elementary reactions (Kiparissides et al.^{11–13}):



Figure 4 Effect of the total recycle ratio (β) on the RTD.

Initiation (by oxygen, peroxides, or azo compounds):

$$I_i \xrightarrow{k_{di}} 2R^{\bullet}; \quad i = 1, 2, \ldots, N_i$$

Chain initiation:

$$R^{\bullet} + M \xrightarrow{k_I} R_1$$

Propagation:

$$R_x + M \xrightarrow{k_p} R_{x+1}$$

Chain transfer to monomer:

$$R_x + M \xrightarrow{k_{tm}} D_x + R_1$$

Chain transfer to solvent (chain-transfer agent):

$$R_x + S \xrightarrow{k_{ts}} D_x + R_1$$

Chain transfer to polymer:

$$R_x + D_y \xrightarrow{k_{tp}} R_y + D_x$$

Termination by disproportionation:

$$R_x + R_y \xrightarrow{k_{td}} D_x + D_y$$

Termination by combination:

$$R_x + R_y \xrightarrow{k_{tc}} D_{x+y}$$

Intramolecular transfer (SCB):

$$R_x \xrightarrow{k_{bi}} R_x$$

 β -Scission of sec- and tert-radicals:

$$R_x + D_y \xrightarrow{k_\beta} D_x + R_z + D_{y^{-z}}^=$$

The subscript x denotes the number of ethylene units in a polymer chain. The above mechanism is sufficiently general and includes initiation and propagation reactions, termination by both combination and disproportionation, molecular weight control by transfer to the monomer and to CTA, LCB formation by transfer to the polymer, SCB formation by intramolecular transfer, and double-bond formation by β -scission of *tert*- and *sec*- radicals. The present kinetic mechanism does not account for possible depropagation reactions.

Homopolymerization Rate Functions

Let R(p) and D(p) be the concentrations of "live" polymer chains and "dead" polymer chains, respectively. Let r_R and r_D be the corresponding net rates of production of "live" polymer chains and "dead" polymer chains. Based on the above general kinetic mechanism, one can obtain the following expressions for r_R and r_D by combining the individual rates of generation and consumption of "live" and "dead" copolymer chains:

Net formation rate of "live" polymer chains:

$$r_{R_{x}} = \left\{ k_{I}[R^{\bullet}][M] + (k_{tm}[M] + k_{ts}[S]) \sum_{x=1}^{\infty} R(x) \right\}$$

$$\delta(x - 1) + k_{p}[R(x - 1) - R(x)][M]$$

$$- (k_{tm}[M] + k_{ts}[S])R(x) + k_{tp}[xD(x)] \left[\sum_{x=1}^{\infty} R(x)\right]$$

$$- k_{tp}R(x) \sum_{x=2}^{\infty} xD(x) - k_{tc}R(x) \sum_{x=1}^{\infty} R(x) - k_{td}R(x)$$

$$\times \sum_{x=1}^{\infty} R(x) - k_{\beta}R(x) \sum_{x=2}^{\infty} xD(x)$$

$$+ k_{\beta} \sum_{x=1}^{\infty} R(x) \sum_{y=x+1}^{\infty} D(y) \quad (11)$$

Net formation rate of "dead" polymer chains:

$$r_{D_x} = (k_{tm}[M] + k_{ts}[S])R(x) + k_{td}R(x)\sum_{x=1}^{\infty} R(x)$$
$$+ \frac{1}{2}k_{tc}\sum_{y=1}^{x-1} R(y)R(y-x) + k_{tp}R(x)\sum_{x=2}^{\infty} xD(x)$$

$$-k_{tp}xD(x)\sum_{x=1}^{\infty}R(x) + k_{\beta}R(x)\sum_{x=2}^{\infty}xD(x)$$
$$+k_{\beta}\left[\sum_{x=1}^{\infty}R(x)\right]\sum_{y=x+1}^{\infty}D(y)$$
$$-k_{\beta}xD(x)\sum_{x=1}^{\infty}R(x) \quad (12)$$

where $\delta(x)$ is the Kronecker's delta function [e.g., $\delta(x) = 1$ if x = 0 and $\delta(x) = 0$ if $x \neq 0$].

Based on the above definitions of rate functions and the fundamental reactor design equation (see following section), one can easily derive an infinite set of differential equations to describe the dynamic behavior (e.g., reactor start-up, grade transition) of an autoclave reactor. However, it is not practical to solve the resulting infinite system of molar balance differential equations. Instead, a lower-order system of differential equations is usually solved by using the method of moments. This method is based on the statistical representation of the molecular properties (e.g., M_n, M_w) through the use of the leading moments of the number chain-length distributions of "live" and "dead" macromolecules, defined as

$$\lambda_n = \sum_{x=1}^{\infty} x^n R(x) \tag{13}$$

$$\mu_n = \sum_{x=2}^{\infty} x^n D(x) \tag{14}$$

Accordingly, one can obtain the corresponding rate functions for the moments of the number chain-length distributions of "live" and "dead" polymer chains by multiplying each term of eqs. (11) and (12) by the term x^n and summing up the resulting expressions over the total variation of x. The final moment rate equations are (Kiparissides et al.¹¹):

$$r_{\lambda_{n}} = \sum_{i=1}^{n} 2f_{i}k_{di}[I_{i}] + k_{p} \left(\sum_{i=0}^{n} {n \choose i}\lambda_{i} - \lambda_{n}\right) [M]$$
$$- (k_{tm}[M] + k_{ts}[S])\lambda_{n} + k_{\beta}(\lambda_{0}\mu_{n+1} - \lambda_{n}\mu_{1})$$
$$- k_{tc}\lambda_{0}\lambda_{n} - k_{td}\lambda_{0}\lambda_{n} - k_{\beta}\lambda_{n}\mu_{1}$$
$$+ \frac{1}{n+1}k_{\beta}\lambda_{0}\mu_{n+1} \quad (15)$$

$$r_{\mu_{n}} = (k_{\rm tm}[M] + k_{\rm ts}[S])\lambda_{n} + k_{\rm td}\lambda_{0}\lambda_{n}$$

+ $\frac{1}{2}k_{\rm tc}\sum_{j=0}^{n} {n \choose j}\lambda_{j}\lambda_{n-j} + k_{\rm tp}(\lambda_{n}\mu_{1} - \lambda_{0}\mu_{n+1})$
+ $k_{\beta}\lambda_{n}\mu_{1} - k_{\beta}\lambda_{0}\mu_{n+1} + \frac{1}{n+1}k_{\beta}\lambda_{0}\mu_{n+1}$ (16)

It should be pointed out that when transfer to polymer reaction is included in the kinetic mechanism the *n*-order polymer moment equation will depend on the higher (n + 1)-order moment. To break down this moment dependence, several closure methods have been proposed in the litera-ture (Hulburt and Katz,¹⁴ Lee and Marano¹⁵). In the present study, the Hulburt and Katz¹⁴ approximation was employed. This technique assumes that the molecular weight distribution (MWD) can be represented by a truncated (after the first term) series of Laguerre polynomials by using a gamma distribution weighting function. Assuming that the first three terms of the Laguerre polynomials are sufficient for the representation of the molecular weight distribution, it can be shown that the third moment of the number chain-length distribution can be expressed as

$$\mu_3 = \frac{\mu_2}{\mu_1 \mu_0} \left(2\mu_2 \mu_0 - \mu_1^2 \right) \tag{17}$$

The other reaction rates of interest (e.g., initiator consumption rates and monomer consumption rate) are given by the following expressions:

Initiator consumption rates:

$$r_{Ii} = -k_{di}[I_i]; \quad i = 1, \dots, N_d$$
 (18)

Primary radical formation rate:

$$r_{R^{\bullet}} = 2f_i k_{di} [I_i] - k_I [R^{\bullet}] [M]$$
(19)

Monomer consumption rate:

$$r_M = -k_p[M]\lambda_0 \tag{20}$$

Solvent consumption rate:

$$r_S = -k_{\rm ts}[S]\lambda_0 \tag{21}$$

SCB formation rate:

$$r_{\rm SCB} = k_{\beta} \lambda_0 \tag{22}$$

LCB formation rate:

$$r_{\rm LCB} = k_{\rm tp} \lambda_0 \mu_1 \tag{23}$$

REACTOR DESIGN EQUATIONS

To derive the reactor-design equations, describing the dynamic operation of an LDPE autoclave, the following simplifying assumptions were made: (i) The mass accumulation in each volume segment is negligible within the integration interval $(t, t + \Delta t)$ (e.g., the density of the reaction mixture does not change significantly within the time interval Δt); (ii) the reaction mixture is treated as a one-phase system; (iii) heat effects due to chain initiation, termination, and transfer reactions are negligible; and (iv) the termination rate constant does not become diffusion-controlled (e.g., absence of gel effect). Based on the above assumptions, the pseudostate total mass balance for the (i,j) volume segment becomes (see Fig. 1):

$$Q(i - 1, j)\rho(i - 1, j) + QC(i, j)\rho_0$$

+ QCI(i, j)\rho_I(i, j)
+ QSR(i, j + 1)\rho(i, j + 1)
= Q(i, j)\rho(i, j) + QR(j)\rho(i, j) (24)

Similarly, the dynamic molar balance for the "X" species (e.g., initiator, ethylene, solvents, μ_n , λ_n , LCB, SCB) for the "*i*" volume segment of zone "*j*" is written:

$$V(i, j) \frac{d[X]_{i,j}}{dt} = Q(i - 1, j) [X]_{i-1,j} + QC(i, j) [X]_0$$
$$+ QSR(i, j + 1) [X]_{1,j+1} - Q(i, j)$$
$$[X]_{i,j} - QR(j) [X]_{i,j} - r_{X_{i,j}} V(i, j) \quad (25)$$

where the symbols $[X]_{i,j}$, $[X]_0$, and $r_{Xi,j}$ denote the concentration of "X" species in the (i,j) volume segment, the concentration of "X" in the feed stream, and the net rate of the consumption/production of "X," respectively. Note that for the initiator balances the ethylene feed flow rate, QC(i,j), is replaced by the initiator feed flow-rate

term QCI(i,j). Finally, the dynamic energy balance for the "*i*" volume segment of zone "*j*" takes the following form:

$$\begin{split} V(i, j) C_{p}(i, j) \rho(i, j) & \frac{dT_{i,j}}{dt} = \\ Q(i - 1, j) \Delta H_{i-1,j} \rho(i - 1, j) + QC(i, j) \Delta H_{0} \rho_{0} \\ &+ QSR(i, j + 1) \Delta H_{1,j+1} \rho(1, j + 1) \\ &+ QCI(i, j) \Delta H_{I} \rho_{I} - Q(i, j) \Delta H_{i,j} \rho(i, j) \\ &- QR(j) \Delta H_{i,j} \rho(i, j) - r_{X_{i,j}} V(i, j) [-\Delta H_{r}(i, j)] \end{split}$$
(26)

 $C_p(i_{\star}j), \rho(i_{\star}j), T(i_{\star}j), \Delta H_{i,j}, \Delta H_r(i_{\star}j), \Delta H_0$, and ρ_0 are the specific heat, density, temperature, specific enthalpy of the reaction mixture, heat of polymerization, specific enthalpy and density of the feed stream, respectively.

To obtain the dynamic molar balance equations for the four-zone autoclave, eq. (25) was applied for every species (e.g., $M, I_i, S, SCB, LCB, \lambda_0, \lambda_1$, μ_0, μ_1, μ_2 to each volume segment (i,j) of the selected reactor configuration (Fig. 1). In addition, the pseudostate total mass balance [e.g., eq. (24) and the energy balance (26) were written for each volume segment. To simplify the numerical calculations, the differential equations for the "live" moments were replaced by corresponding algebraic equations. The validity of the quasisteady-state approximation (QSSA) for the moments of "live" macroradicals was numerically assessed. It was found that the QSSA was valid provided that the lifetime of the "live" macroradicals was considerably shorter than the mean residence time of radicals in a volume segment. The molecular weight averages and the SCB and LCB per 1000 carbon atoms were accordingly calculated in terms of the moments of the NCLD of "dead" polymer chains:

Number-average molecular weight:

$$M_n = (\mu_1 / \mu_0) M W_e \tag{27}$$

where MW_e is the molecular weight of the ethylene;

Weight-average molecular weight:

$$M_w = (\mu_2/\mu_1)MW_e \tag{28}$$

Long-chain branches per 1000 carbon atoms:

LCB/1000
$$C = 500 \, [LCB]/\mu_1$$
 (29)

Short-chain branches per 1000 carbon atoms:

SCB/1000
$$C = 500[SCB]/\mu_1$$
 (30)

Finally, the cumulative ethylene conversion was calculated by the following equation:

$$\operatorname{Cum}(X) = \left\{ \sum_{j=1}^{N_f} QC(i,j) [M]_0 - QC(N_e, L_e) [M]_e \right\}$$
$$\left/ \sum_{j=1}^{N_f} QC(i,j) [M]_0 \quad (31)$$

where $QC(N_e, L_e)$ denotes the total outlet volumetric flow rate.

REACTOR SIMULATION RESULTS

To demonstrate the predictive capabilities of the present model, the dynamic behavior of a fourzone LDPE reactor was simulated. The nonideal flow behavior in the reactor was approximated by varying the macromixing parameters N_j , β_{j_i} and γ_{ii} . For the nominal case, it was assumed that each zone consisted of two equal-volume segments. Furthermore, it was assumed that 40% of the total monomer feed rate entered the first segment of the first zone, 30% entered the first segment of the second zone, and the remaining 30% of ethylene entered the first segment of the third zone. The initiator mixture was injected into the first segment of the first and third zones. The reactor was operated at a pressure of 1400 atm and the reactor mean residence time was equal to 26 s based on the total monomer volumetric flow rate. The values of the various kinetic constants, used in the present study, are reported in Table I. The rate constant for the initiator (DTBP) obeyed the following Arrhenius equation:

$$k_d = 3.06 \times 10^{12} \exp(-28400/RT)$$
 (32)

Finally, the thermophysical properties of the reaction mixture were calculated from correlations described in Kiparissides et al.¹¹

в	k_0	$\Delta E \ (\mathrm{J} \ \mathrm{mol}^{-1})$	$\Delta V (\mathrm{m^3 \ mol^{-1}})$
$k_{p}/k_{t}^{0.5}$	2500	31,642	$-26.2 imes10^{-6}$
k_{tm}^{p}/k_{n}	10^{-3}		_
$k_{\rm tr}/k_p$	5.9	21,168	$24.1 imes10^{-6}$
k_{tsi}/k_n	0.218	9629	$0.2 imes 10^{-6}$
k_{β}/k_{n}	0.463	16,775	_
k_b^P/k_p^P	8	10,500	$3.8 imes10^{-6}$

Table INumerical Values of the KineticConstant Ratios ε_i

 $\varepsilon = k_0 e^{-(\Delta E + P \Delta V)/RT}; \ k_p = 1.25 \times 10^8 \ \exp[(4061 - 0.24P)/T] \ lt/(mol^{-1} \ s^{-1}), \ P \ in \ atm.$

Results on the Reactor Start-up

As discussed in the Introduction, an LDPE autoclave typically operates at an unstable steady state. Therefore, to simulate the dynamic operation of the four-zone reactor, the temperatures of the reaction mixture at the last volume segment of the first and third zones had to be controlled at preselected set-point values. This was achieved by manipulating the corresponding initiator flow rate entering a zone with the aid of a discrete PID controller.

$$\Delta F_{In} = K_c \bigg[(e_n - e_{n-1}) + \frac{\Delta t}{\tau_I} e_n + \frac{\tau_D}{\Delta t} (e_n - 2e_{n-1} + e_{n-2}) \bigg]$$
(33)

where ΔF_{In} is the difference between the initiator flow rates at times t and $t - \Delta t$. e_n , e_{n-1} , and e_{n-2} represent the corresponding temperature errors $[T_m(n) - T_{sp}]$ at times t, $t - \Delta t$, and $t - 2\Delta T$. Finally, the symbols Δt , K_c , and τ_I denote the sampling period, gain, and integral time of the controller, respectively.

The reactor design equations, the controller eqs. (33), and the appropriate algebraic equations, describing the variation of the kinetic rate constants and thermophysical properties of the reaction mixture, were numerically solved using the Gear method. In total, 72 differential and 32 algebraic equations were written for the four-zone autoclave (nominal case). The initial reactor temperature at time (t = 0) was assumed to be 160°C. The temperature of the ethylene feed streams followed a stepwise decrease with time from 150 to 30°C (e.g., 150, 120, 90, 70, 60, 45, and 30°C) to progressively increase the ethylene conversion to its final value. From the numerical solution of the reactor model equations, the polymer weight fraction, the temperature, as well as all polymer molecular properties (e.g., M_n , M_w , LCB, SCB) were calculated as a function of time and position in the reactor. In what follows, the effect of the macromixing parameters (e.g., β_i , γ_{ii} , and N_i) on the reactor performance is discussed.

Figures 5–10 illustrate some representative results for the reactor start-up. The macromixing parameters were set equal to $\beta_2 = 0.7$, $\beta_3 = \beta_4$



Figure 5 Variation of the reaction temperature at the exit of each zone with time.



Figure 6 Steady-state spatial temperature profile in a four-zone autoclave.

= 0.5; $N_j = 2$, and $\gamma_{ij} = 0.5$. The value of the total recycle ratio entering the first zone (β_2) reflects the high degree of mixing at the top of the reactor. Figure 5 depicts the variation of temperature with respect to time at the exit of each zone.

Figure 6 shows the temperature profile along the reactor at the steady state. It should be noted that the reaction temperature was controlled at 240 and 260°C at the end of the first and third zones, respectively. The observed decrease of the tem-



Figure 7 Time variation of polymer weight fraction at the exit of each zone during reactor start-up.



Figure 8 Time variation of initiator flow rate into the first and third zones during reactor start-up.

perature at the beginning of the second and third zones is due to the introduction of fresh ethylene. The time variation of the cumulative polymer weight fraction at the end of each zone is shown in Figure 7. The observed stepwise increase of the polymer weight fraction is due to the corresponding stepwise decrease of the temperature of the ethylene feed streams from 150 to 30°C and the adiabatic operation of the reactor. Figure 8 shows the time variation of the initiator flow rates, in the first and third zones during the reactor startup. Notice that the required initiator flow rates,



Figure 9 Time variation of the number- and weight-average molecular weight at the exit of the reactor.



Figure 10 Time variation of LCB and SCB per 1000 C at the exit of the reactor.

to maintain the reaction temperature at the specified set-point values, increase with the monomer conversion (Fig. 7). It can also be seen that both manipulated variables initially oscillate but quickly reach their corresponding steady-state values after each step change in the temperature of the ethylene feed streams.

Figure 9 depicts the dynamic behavior of the number-average molecular weight (M_n) and weight-average molecular weight (M_w) at the end of the last zone. It should be noted that M_n decreases with time and attains its final value at about 1000 s after the reactor start-up. On the other hand, M_w increases with time until reaches its final steady-state value. Figure 10 shows the variation of the LCB and SCB with respect to time at the end of the last zone. The final steady-state values of the LCB and SCB at the reactor exit were 1.85 and 17.3 per 1000 carbon atoms, respectively.

Effect of the Macromixing Parameters

Figure 11 shows the effect of the total recycle ratio on the steady-state behavior of the four-zone LDPE autoclave. Notice that the total recycle parameter in the first zone was kept constant at $\beta_2 = 0.7$. The other two macromixing parameters were set equal to $N_j = 2$ and $\gamma_{ij} = 0.50$. It can be seen that an increase of the total recycle ratios β_3 and β_4 (e.g., increase of mixing) produces a more

uniform temperature profile because high recycle rates tend to smooth out the peaks in the temperature profile.

Although the temperature profile is affected by the mixing parameter β_i , in all cases studied, the ethylene conversion at the end of the multizone autoclave remains almost the same due to the tight control of the reaction temperature at the end of the first and third zones. However, it is important to observe the significant variation in the corresponding control variables (e.g., initiator flow rates) with respect to the total recycle ratio β_i (Fig. 12). As can be seen in Figure 12, the required initiator flow rate into the first zone at the steady-state reactor operation decreases as the recycle parameter β_i increases. A higher degree of mixing results in an overall increase of the reaction temperature (see Fig. 11), which, in turn, leads to a decrease of the specific initiator consumption rate (e.g., gram of initiator consumed per kilogram of PE produced), in agreement with the experimental observations of Luft et al.¹⁶ On the other hand, in the third zone, the specific initiator consumption rate exhibits a U-shape variation with respect to the design parameter β_i . This means that there will be an optimum value of β_i (optimal mixing configuration), minimizing the specific initiator consumption. A similar U-shape behavior of the specific initiator consumption with respect to the polymerization temperature



Figure 11 Effect of total recycle ratio (β) on the spatial temperature profile at the steady state.

was reported by several investigators (Luft et al.,¹⁶ Georgakis and Marini⁸). It has been shown both experimentally and theoretically that the specific initiator consumption rate initially decreases with the polymerization temperature up to a minimum value. However, a

further increase of temperature, beyond a characteristic value, T^* , results in an increase of the initiator consumption rate. This variable initiator consumption rate has been attributed to macro- and micromixing phenomena occurring in low-density high-pressure autoclaves.



Figure 12 Effect of total recycle ratio (β) on the steady-state initiator flow rates to the first and third zones.



Figure 13 Effect of total recycle ratio (β) on the steady-state polydispersity index.

The effect of β_j on the polydispersity index (PI) is depicted in Figure 13. Notice that as β_j increases both M_n and M_w decrease while LCB increases due to the higher polymerization temperatures. The observed decrease of PI is due to the more uniform temperature profile obtained with an increase of mixing. From these results, it becomes apparent that the macromixing parameter β_j does reflect the effect of mixing conditions on the key process variables (e.g., initiator consumption, temperature, and molecular properties of LDPE).

Thus, to simulate the operation of an industrial reactor, one has to solve a simple nonlinear parameter estimation problem. More specifically, assuming that the ethylene and initiator flow rates, the spatial temperature profile, and the molecular properties at the reactor exit are known, one can estimate the values of the macromixing parameter β_j so that the model predictions match the experimental measurements. It should be pointed out that the value of the micromixing parameter β_j reflects the local degree of mixing (e.g., high values indicate a high degree of mixing), which, in turn, can be related to the geometric characteristics (e.g., type of blades) of the agitation system.

The effect of the side recycle ratio, γ_{1j} , on the reactor temperature profile at the steady state was similar to the effect of the mixing parameter β_j . As the side recycle ratio to the first segment,

 γ_{1j} , changes from 0 to 1, mixing increases, which leads to a more uniform temperature profile along the reactor. However, in all cases studied, the polymer weight fraction was not significantly affected by the variation of γ_{ij} , which is consistent with the fact that the temperature profile in the reactor is tightly controlled and, thus, so is the polymerization rate.

Figure 14 illustrates the effect of the macromixing parameter γ_{ii} on the initiator flow rates into the first and third zones at the steady state. In all simulations, the values of the total recycle parameters were kept constant: $\beta_2 = 0.7$, $\beta_3 = \beta_4$ = 0.5. Each zone was divided into two equalvolume segments. It is interesting to notice that the variation of the initiator flow rates with respect to the macromixing parameter γ_{ii} follows a similar behavior to that reported for the parameter β_i in Figure 12, that is, better mixing in the first zone results in a decrease of the initiator flow rate, while an increase of the mixing in the third zone brings exactly the opposite result. By keeping in mind the U-shape variation of the specific initiator consumption with the polymerization temperature, the observed decrease in the first zone can be explained by the higher polymerization temperatures which lower the specific initiator consumption rate (e.g., the zone operates in the decreasing branch of the specific initiator consumption-temperature curve). On the other hand, the observed increase of the initiator flow rate



Figure 14 Effect of side recycle ratio (γ) on the steady-state initiator flow rates to the first and third zones.

into the third zone with γ_{ij} (e.g., increase of the specific initiator consumption with temperature) can be explained by the fact that the third zone operates at a temperature higher than T^* , the characteristic temperature corresponding to the minimum specific initiator consumption rate.

The effect of the number of volume segments per zone N_j on the initiator flow rate is shown in Figure 15. In these simulations, the values of the various macromixing parameters were set equal to $\beta_2 = 0.7$, $\beta_3 = \beta_4 = 0.5$; and $\gamma_{ij} = \gamma_{kj}$ for i,k= 1,2, ... N_j . The number of volume segments in



Figure 15 Effect of number of segments per zone (N) on the steady-state initiator flow rates to the first and third zones.



Figure 16 Effect of set-point changes of temperature controllers on the exit temperature in each zone. Set-point changes (first zone: $240 \rightarrow 250^{\circ}$ C; third zone: $260 \rightarrow 270^{\circ}$ C).

all zones was the same, that is, $N_1 = N_2 = N_3$ $= N_4$. As the number of segments in the first zone increases, the degree of mixing decreases (e.g., the flow behavior approaches that of a plug flow reactor) as well as the polymerization temperature, which leads to an initial increase of the initiator flow rate into the first zone. However, a further increase of the number of segments (e.g., $N_i = 4$) causes a decrease of the initiator flow rate. On the other hand, in the third zone, as the number of volume segments per zone increases, the initiator flow rate into the zone initially decreases to a minimum value, followed by a subsequent increase of the initiator flow rate for $N_i = 4$. The observed behavior of the initiator flow rate with respect to N_i is directly linked with the temperature changes caused by the variation of the macromixing parameter, N_i .

Results on Reactor Grade Transition

The dynamic behavior of the autoclave during a grade transition was investigated for three types of changes in operating conditions: (i) set-point changes of temperature, (ii) solvent concentration changes, and (iii) changes in the ethylene feed distribution. In all simulations, the macromixing parameters were kept constant (e.g., $\beta_2 = 0.7$, $\beta_3 = \beta_4 = 0.5$, $N_i = 2$, and $\gamma_{ij} = 0.5$). All step changes

in the operating conditions occurred at time 2000 s.

Figures 16–18 illustrate the dynamic behavior of the four-zone autoclave for a simultaneous change of the temperature set-points in the first and third zones from 240 to 250°C and from 260 to 270°C, respectively. Figure 16 shows the variation of the temperature with time in the four zones. The reactor reaches its new specified temperatures approximately 300 s after the introduction of set-point changes. The increase of temperature results in an increase of overall ethylene conversion from 18.6 to 19.3% (see Fig. 17) and a decrease of M_n and M_w from 20,270 to 19,660 and from 189,000 to 168,000, respectively.

Figure 19 shows the effect of a step-change decrease in the solvent concentration (e.g., from 5 to 1% wt) in all feed streams on the numberaverage and weight-average molecular weight. The decrease in solvent concentration resulted in an increase of both M_n and M_w .

Figures 20 and 21 illustrate the effect of an ethylene feed distribution change on the reactor operation. During this transition, the ethylene feed distribution changed from a 40%-30%-30% split (e.g., nominal case) to a 50%-30%-20% split, which means that more ethylene was fed to the top of the reactor. The dynamic behavior of the temperature in the four zones is shown in Figure



Figure 17 Effect of temperature set-point changes on the total ethylene conversion. Set-point changes as in Figure 16.

20. Notice that the temperatures in the first and third zones stay at the set-point values (e.g., 240 and 260°C) despite the change of ethylene feed distribution. On the other hand, the temperature

in the second zone increases from 245.5 to 248.9°C while the temperature in the last zone decreases from 264.5 to 262.9°C. To maintain the temperature in the first and third zones at the



Figure 18 Effect of temperature set-point changes on the number- and weightaverage molecular weights. Set-point changes as in Figure 16.



Figure 19 Effect of solvent concentration changes on the number- and weight-average molecular weights. Solvent concentration change (5% wt \rightarrow 1% wt).

specified set-point values, the initiator flow rates into the corresponding zones were varied as in Figure 21. The observed increase of the initiator flow rate into the first zone is explained by the higher ethylene feed rate (e.g., from 40 to 50%), while the observed decrease in the third zone is caused by the lower flow rate of the ethylene side stream into the third zone (e.g., from 30 to 20%).



Figure 20 Effect of ethylene feed distribution change on the temperature in each zone.



Figure 21 Effect of ethylene feed distribution change on the on the initator flow rates injected into the first and third zones.

It is interesting to notice that under the new ethylene feed distribution the overall conversion is slightly decreased from 18.6 to 18.4% while M_n and M_w vary from 20,270 to 20,220 and from 189,000 to 193,000, respectively. The small decrease in conversion is due to the increase of the ethylene feed rate to the first zone which operates at a lower temperature than that of the third zone.

MWD Calculations

The prediction of the complete MWD in LDPE reactors is of profound importance since the MWD controls the product quality and its optimal utilization. To our knowledge, there is only a limited number of publications dealing with the prediction of the joint bivariate molecular weight-LCB distribution (Mullikin and Mortimer,¹⁷ Feucht et al.,¹⁸ Lorenzini et al.¹⁹). Furthermore, there is no publication on the prediction of bimodal distibutions often observed in LDPE autoclaves.

Based on the originally proposed method of Teymour and Campbell,²⁰ Pladis and Kiparissides²¹ developed a new method for calculating the joint molecular weight–LCB distribution for highly branched polymers. According to this method, the total polymer chain population is separated into a number of classes, each one representing a population of polymer chains with similar molecular structure (e.g., linear chains and chains with one long-chain branch). Subsequently, one has to write the dynamic molar balance equations for the leading moments of "live" and "dead" polymer-chain distributions for each class of polymer chains as well as for the moments of the overall "live" and "dead" polymer-chain distributions. Using the calculated moments of each polymer class, the Wesslau distribution is employed to reconstruct the WCLD (Weight Chain Length Distribution) of each fraction of polymer chains:

$$W(x) = (2\pi x^2 \sigma^2)^{-1/2} \exp\left[-\frac{(\ln x - \ln x_m)^2}{2\sigma^2}\right] \quad (34)$$

where x denotes the degree of polymerization. The parameters of the two-variable distribution are calculated in terms of the leading moments of number chain-length distribution, that is:

$$x_m = (\mu_2/\mu_0)^{1/2}; \quad \exp(\sigma^2) = \mu_0\mu_2/\mu_1^2$$
 (35)

The overall WCLD is then calculated by the weighted sum of the WCLDs of all classes:



Figure 22 Calculated MWD at the end of a four-zone autoclave.

$$W_{\text{total}}(x) = \sum_{i=0}^{N_c} [W_i(x)\mu_1^i]/\mu_1$$
 (36)

It must be noted that depending on the total LCB content of the polymer a large number of classes (e.g., about 60 classes) may be needed for the accurate reconstruction of the MWD. Figure 22 shows the calculated MWD at the exit of the four-zone autoclave. The M_n , M_w , and PI of the reco-structed MWD are 24,500, 208,000, and 8.48, respectively, while the LCB content is 1.5 per 10^3 carbon atoms. It is important to notice that for the selected model parameters the predicted MWD shows a bimodal character which is typical of the LDPE produced in autoclaves.

CONCLUSIONS

The present study was concerned with the development of a detailed mathematical model to simulate the dynamic operation of LDPE autoclaves. A macromixing model was developed to describe the nonideal flow patterns in LDPE autoclaves. A general kinetic mechanism was used to represent the complex kinetics of high-pressure free-radical ethylene polymerization. To predict the molecular properties of the LDPE, the method of moments was employed. The present simulation results show that the degree of mixing in a reaction zone, manifested by the macromixing parameters (e.g., β_j , γ_{ij} , and N_j), can significantly affect the initiator consumption rate in a zone as well as the polymerization temperature profile and molecular properties of LDPE. As a result, knowledge of the actual values of the initiator flow rates, temperature profile, and final polymer molecular properties can lead to the identification of the mixing parameters in an autoclave. Thus, the proposed model can be effectively employed in the design, optimization, and control of the LDPE autoclaves. In this respect, a computer-aided simulation, control and design software package has been developed based on the present comprehensive mathematical model developments (Pertsinidis et al.²²).

NOMENCLATURE

C_p	heat capacity of reaction mixture		
C(t)	concentration of the tracer at time " t "		
	in the exit of the reactor		
$\operatorname{Cum}(X)$	monomer conversion		
e_i	temperature error in PID controller		
E(t)	residence-time distribution function		
f_i	initiator efficiency		
L_e	total number of reaction zones		
LCB	long-chain branching		
M_{e}	molecular weight of ethylene		
M_n	number-average molecular weight		
M_w	weight-average molecular weight		
N_e	number of segments in the last zone		
N_i	number of segments in zone j		
$r_{(X)_{i,i}}$	rate of X component or property in " i "		
*5.5	volume segment of zone "j"		
Q(i,j)	volumetric flow rate in the exit of seg-		
	ment " <i>i</i> " of zone " <i>i</i> "		

- QC(i,j) volumetric flow rate of feed or quenching stream into segment "i" of zone "j"
- QCI(i,j) volumetric flow rate of initiator feed into segment "i" of zone "j"
- QSR(i,j) volumetric flow rate of side recycle stream to "i" segment of zone "j"
- QR(j) total volumetric flow rate of recycle stream
- SCB short-chain branching
- T(i,j) temperature of reaction mixture in *i* segment of zone "*j*" T_0 feed temperature
- T_0 feed temperature V total volume of the reactor
- V(i,j) volume of segment "i" in zone "j"
- $[X]_{i,j}$ concentration of X component or property in "i" segment of zone "j"
- [X]₀ concentration of X component in feed or quenching stream

Greek Letter

- α_i zone volume ratio, V_i/V_{tot}
- $\vec{\beta}_i$ total recycle ratio to "j 1" zone
- γ_{ij} side recycle ratio to the "*i*" segment of zone "*j*"
- ΔE activation energy J mol⁻¹
- ΔH_I enthalpy of the initiator injection stream
- ΔH_r heat of reaction
- $\Delta H(i,j)$ enthalpy of reaction mixture in "i" segment of zone "j"
 - ΔH_0 enthalpy of feed stream
 - Δt sampling period (s)
 - ΔV activation volume, m³ mol⁻¹
 - ε_i ratio of kinetic constants
 - $\hat{\theta}$ dimensionless time
 - λ_n "*n*" moment of "live" NCLD, mol L⁻¹
 - $\mu_n^{"}$ "n" moment of "dead" NCLD, mol L⁻¹
 - $\rho(i,j)$ density of reaction mixture in "i" segment of zone "j"
 - ho_I density of the initiator injection stream
 - ρ_0 density of feed stream
 - au mean residence time
 - τ_I integral time of the PID controller (s)
 - au_D differential time of the PID controller (s)

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