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Simulation of Free Radical High-Pressure Copolymerization in a Multi-Zone Autoclave Reactor: Compartment Model Investigation

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Summary: A compartment model is used to describe the complex flow of a high-pressure ethylene copolymerization process in an industrial multi-feed multi-zone autoclave reactor at steady state operation conditions. To capture the imperfect mixing effects due to fresh initiator injection, each zone is considered as a set of three interconnected well mixed CSTRs with recycle streams. Volumes of the reactors and the recycle flow are adjusted to get the best fit with results of steady state well mixed analysis for each zone. Once the temperature and conversion as state variables in each reaction volume are known, the properties of polymer produced in each zone and those of final polymer can be determined. Using a realistic set of kinetic mechanisms, temperature, monomer conversion, molecular weights and short and long chain branching frequencies in each zone and at the exit point of the reactor are estimated. Some of the model results are compared with experimental data obtained for an industrial reactor.

Keyword: autoclave; compartment model; kinetics; radical polymerization; simulation

Introduction

Low density polyethylene and copolymers are thermoplastics which are used in a large variety of applications. Generally they are produced in either autoclave or tubular reactors operating at high temperatures (150-300°C) and pressure (1200-3500 atm). Under these conditions, the reaction mixture behaves as a supercritical fluid. Autoclave reactors, with a length to diameter ratio of 4-20, typically operate at lower temperature and pressure than do tubular reactors and behave more like a continuous stirred tank reactor, resulting in a broad molecular weight distribution. Mixing is provided by a shaft running down the center of the vessel with several impeller blades of different types. The reactor is usually subdivided into a number of reaction zones. Heat transfer through the walls is limited, so that the reactor is essentially adiabatic and cooling is provided by the inflow of cold monomer. The inflow of initiator and monomer at several points down the

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reactor vessel provides control of the temperature which may vary down the length of the reactor. This control is used to produce polymer with the desired molecular properties (breadth of molecular weight distribution, branching level,...). There are several complications which make the modeling of autoclave type reactors highly challenging, namely; non-ideal mixing, the presence of unstable steady states, the possible existence of reactions in two phases and the possibility of gel formation due to cross-linking reactions. In order to develop a comprehensive model capable of predicting the actual plant operating conditions as well as the polymer properties, one must address all of these items without making the model too complex to be readily solved. Figure 1 shows a schematic diagram of a typical multi-zone, multi-feed LDPE (Low Density PolyEthylene) autoclave reactor.

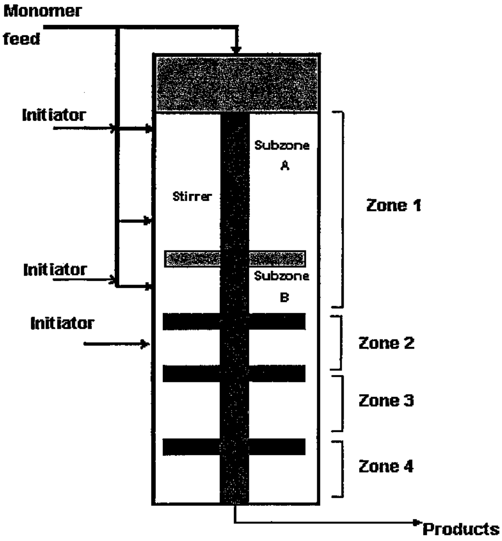

Figure 1. Schematic of a multi-zone multi-feed Autoclave Reactor.

Despite the very high power input per unit volume required to maintain good mixing conditions in each reaction zone, the flow behavior in these reactors deviates significantly from ideality (e.g., plug flow and perfectly mixed conditions), which requires the adoption of more complex mixing models to approximate the reaction system. The mixing pattern in an autoclave type reactor tends to be of a recirculating nature. The effect of mixing on reactor performance is very important, especially since an imperfectly mixed vessel requires more initiator per unit of polymer produced than does a more perfectly mixed vessel under the same conditions[1].

In a typical autoclave reactor at high pressure and temperature operating conditions, the initiator half-life time is on the order of seconds (or less) while reactor residence time is usually 30-60 s. Under these conditions, the initiator half-life may be shorter than the mixing time and initiator concentration is not uniform throughout the reactor. The initiator tends to decompose near the feed points, and not in the bulk of the reactor, thus not promoting as much polymerization as if the initiator was uniformly distributed throughout the reaction mixture. The CFD (Computational Fluid Dynamics) models[2,3] clearly show that the feed plume is not well mixed on the macroscale.

Even for perfectly mixed systems, free-radical initiators are not 100% effective in creating new polymer chains. An *effective* or *apparent* initiator efficiency factor is introduced to account for this loss of primary radicals, which is accentuated by poor mixing of fresh initiator into the vessel. In high-pressure ethylene polymerization processes, it is observed that initiator consumption rate is a nonlinear function of reaction temperature. At low reaction temperatures the initiator consumption rate decreases with increasing reaction temperature; however, as the reaction temperature is further increased, the initiator consumption rate increases. This phenomenon has been observed even in a small laboratory scale reactor where a homogeneous mixture of initiators and monomers is injected in a single feed stream to the reactor[4]. To mitigate the decline in initiator efficiency, LDPE producers usually feed two or more initiators so that as the temperature increases and the first initiator become ineffective, additional higher-temperature initiators begin to generate free radicals. This practice allow reasonable production rates over a wider range of operating temperatures but can have a negative influence on reactor stability[7].

Nonlinear initiator demand with temperature has been modeled both as an empirical microscale initiator efficiency effect[5,6] and through imperfect macroscale mixing (further discussion below). In our previous publication[16] we employed the first approach to represent the behavior of a multizone autoclave system, modifying the apparent initiator efficiency of each zone to match industrial data. In this work we explore application of a compartment (mixing) model to represent the system. Both approaches rely on parameters whose values must be determined by comparison with experimental data on initiator demand[7].

A number of macromixing models have been proposed in the literature[6,9,13] to describe the nonideal flow patterns. Typically, these models represent the reactor as several compartments with defined connectivity and recycle, with each compartment having well-defined micromixing characteristics (usually perfectly mixed). Macromixing patterns inside the reactor are captured by convective material transport between different compartments. These models have been used to study imperfect mixing in continuous LDPE autoclave reactor[8,9] and a semibatch reactor[10]. They have also been used to study the influence of mixing on reactor stability[11] and interaction of mixing and gelation[12].

Donati et. al.[13,14] developed a model for LDPE autoclaves based on fluid dynamic measurements made on a full-scale cold-flow industrial reactor with a single impeller. The flow in this vessel tended to be downward near the wall, with backflow in the center. They modeled this flow pattern as two annuli divided into several CSTRs with axial flow and radial mixing between the two annuli. The regions near the impeller and the bottom of the tank were modeled as CSTRs with no radial gradients.

Georgakis and Marini[1] proposed a simpler model to represent imperfect mixing in a large scale autoclave reactor. In their effort, a single autoclave reactor is divided into three hypothetical CSTR compartments in series with different volumes. The first two CSTRs account for a very small fraction of the total reactor volume, representing the inlet plume where the injected initiator is not fully mixed with the rest of the reacting fluid. The third CSTR accounts for the remaining reactor volume where most of polymerization reaction takes place. The action of impeller in the zone gives origin to a certain recirculating flow rate between the three volumes. The recirculating flow rate is generally much higher than the feed flow rate. To account for backmixing of the reaction mixture, recycle streams from the main reaction volume to the two small reaction volumes are considered. The division of the real reactor volume into three reaction compartments is based on the measurement of the initiator injection velocity through a nozzle in the reactor and has an effect of lowering the overall initiator efficiency (or increasing initiator consumption). The volume of two segregated compartments and the mixing parameters were determined using the size of a nozzle and the total flow rate of monomer and initiator solution through the nozzle. In their modeling work, the volume fraction of the segregated volume was about 3-5% of the total reactor (or zone) volume. It has been observed that when the volume fraction of the segregated fluid element was about 2-10% of the total reactor volume, the predictions of the perfectly mixed and compartment models were almost identical. Even as the volume of the segregated fluid elements was increased from 2 to 10% of the total reactor volume, specific initiator consumption rate only increased slightly[1,15].

The mixing models can be extended to represent an autoclave reactor with multiple side injections of monomer and initiator feeds, as discussed by Chan et. al.[9] The autoclave reactor is described as a series of several primary volume elements that consist of a CSTR segment and a plug flow segment. Each plug flow segment is again divided into a finite number of smaller CSTRs for computational purposes. In each volume element, there is an internal recycle flow. Quite obviously, the volume ratio of the CSTR component in each primary volume element to the total reactor volume and the number of plug flow segments in the primary volume element are two of the most important mixing parameters in their model. Parametric sensitivity analysis was carried out using the model to explore the effect of nonideal mixing on the reactor performance. When a multicompartmented autoclave reactor is used for polymerization, the variation in the initiator efficiency factor can significantly affect the temperature in the second or the third reaction zone.

In this work a compartment model is used to investigate and simulate the high-temperature free radical homo- and copolymerization of ethylene and vinyl acetate in an industrial high-pressure autoclave reactor. Each zone in a multi-zone autoclave reactor is considered as a set of three CSTRs with specified volumes and recycle ratio. The final polymer properties are provided by determining the process performance variables in each compartment and the whole system of CSTRs.

Mixing model

A compartment model used for modeling of polymerization multi-zone autoclave reactor in this study is shown in Figure 2. Each zone of the reactor is divided into three CSTRs in series, with a certain flowrate or recycle stream between them. Thus cell $j+1$ is considered as a set of three CSTRs with volumes V_1, V_2, and V_3. Flow from the previous zone is assumed to feed directly into the main compartment (V_3), while fresh monomer and initiator feed enters through compartment 1 of the zone. To standardize model formulation, both flows are expressed as a ratio to the mass flow of the inlet stream at the very top of the autoclave reactor, denoted as F. Thus the generalized equations are based on the top feed, not total monomer flow rate, as a reference flow rate. βF represents the ethylene, comonomer, unreacted initiator, radicals and polymer from the previous reaction zone in a multi-zone autoclave reactor (cell j), or pure monomer flow used to cool the motor at the top of the first zone. γF and I_f represent, respectively, the fresh monomer and initiator feed to the zone. f_1 and f_2 are recycle streams going to the first and the second compartments from V_3. Their ratio is assumed to be the same as the volume ratio of the first compartment to that of the second to reflect the volume difference between two small mixing zones. φ represents any process variable: temperature, monomer conversion, initiator concentration, moments of live and dead polymer chains, and short and long chain branch values, and subscript 1,2,3 and j represents the values of state variables in and at the exit point of volume reaction with corresponding subscripts.

By use of this nomenclature, each zone or subzone in the multisection autoclave can be modeled. This mixing model is similar to the one proposed by Marini and Georgakis[8], extended to a multizone system. In the model it is assumed that: mixing in each reaction volume is complete so that the values of state variables at the exit point are the same as those in reaction cell; the properties and states of the reaction mixture are additive; no heat transfers out from the reactor wall; and the reaction in each cell is adiabatic.

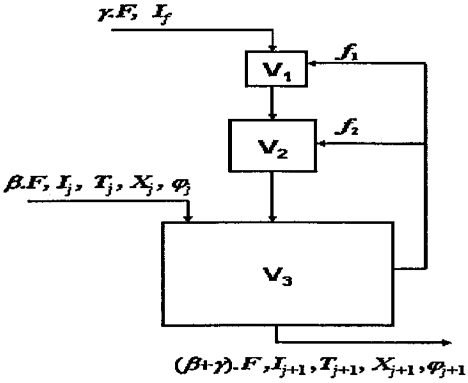

Figure 2. Compartments model configuration.

With reference to Figure 2, the monomer and initiator mass balance and the energy balance equations for each compartment at steady state conditions are:

$$\frac{\gamma F}{\rho_f V_1}\varphi_f - \frac{\gamma F + f_1}{\rho_1 V_1}\varphi_1 + \frac{f_1}{\rho_3 V_1}\varphi_3 + R_{\varphi_1} = 0 \tag{1}$$

$$\frac{\gamma F + f_1}{\rho_1 V_2}\varphi_1 - \frac{\gamma F + f_1 + f_2}{\rho_2 V_2}\varphi_2 + \frac{f_2}{\rho_3 V_2}\varphi_3 + R_{\varphi_2} = 0 \tag{2}$$

$$\frac{\gamma F + f_1 + f_2}{\rho_2 V_3}\varphi_2 - \frac{(\beta+\gamma)F + f_1 + f_2}{\rho_3 V_3}\varphi_3 + \frac{\beta F}{\rho_j V_3}\varphi_3 + R_{\varphi_3} = 0 \tag{3}$$

where φ and R_φ are the concentration and rate of production or consumption (with minus sign) of any species in the reaction mixture: monomer conversion (X), initiator concentration (I), polymer chain moments (λ_{10}, λ_1, λ_2, μ_0, μ_1, μ_2, and also branching properties) and convective energy term ($\int C_p dT$). Each subscript in the above equations shows the value of the parameter or variable at the operating conditions in the corresponding compartment. The total recycle ratio, the most important mixing or recycle parameter is defined by:

$$f_r = \frac{f_1 + f_2}{(\beta+\gamma)F + f_1 + f_2} \tag{4}$$

The numerical values of all parameters and physical properties, the copolymerization kinetic mechanisms, and the expressions for rate of production or consumption of any species are taken from our previous well-mixed zone model[16] of this system; moment closure details are given in the same reference. The resulting balance equations, a set of nonlinear coupled algebraic equations, are solved using MATLAB software whose solution gives the profile or changes in monomer and initiator concentration, temperature, live and dead polymer chain moments and branching frequencies of polymer chains. The base parameters for the compartments mixing model are presented in Table 1, although f_1 was varied for some simulations.

Table 1. Mixing model parameters used for simulation of multi-feed multi-zone autoclave reactor.

Compartments volume:	$V_2=2V_1$; $V_1+V_2=5\%(V_1+V_2+V_3)$
Recycle streams:	$f_1=4.8(\beta+\gamma)F$ [a] ; $f_2=2f_1$

[a] Corresponds to value of $f_r=0.86$[17]

Results and Discussion

The compartment model consisting of three well-mixed CSTR was modified to simulate the imperfect mixing effects of cold fresh initiator injection in a multi-zone multi-feed high-pressure autoclave reactor for production of LDPE and ethylene/vinyl acetate copolymers. Tuned using experimental plant data and a full set of kinetic mechanism and coefficients[16] with reasonable values for mixing parameters, solution of the set of equations gives the values of operation and state variables and also polymer properties for each compartment and at the exit point of the reactor. The effect of recycle ratio is also considered, concentrating on the behavior in the top zone of the reactor system. Figure 3 shows the calculated temperatures in V_1 and V_2 (representing the inlet plume) as the value of recycle ratio changes at different specified values of the zone (V_3) temperature. Because V_3 consists of about 95% of reaction volume, its temperature, which can be determined experimentally, controls the exit temperature of the plume. For $f_r>1$ the temperature in V_2 does not deviate significantly from V_3 temperature, with the temperature in V_1 slightly lower. Increasing the recycle ratio causes the temperatures in the first and second compartments to increase due to entering convective energy; i.e. approaching CSTR behavior in the zone.

Figure 4 shows the concentration of initiator in the first and the second compartments for the same set of simulations. At any exit temperature, as the recycle ratio increases (mixing improves), the concentration of initiator in the plume decreases due to the higher influx of fluid with low initiator level from V_3. The corresponding higher temperatures of V_1 and V_2 (Figure 3) also lead to a more uniform radical concentration and reaction rate in the three zones, and a more homogeneous well-mixed mixture. Due to the higher rates of recycle to the second compartment compared to the first, the initiator level (and temperature) reaches a "well-mixed" value at lower values of the total recycle rate.

Figure 5 shows the polydispersity index (PDI) of polymer at the zone exit for the same set of LDPE simulations. As the recycle ratio increases the PDI increases, as previously documented by Zhang and Ray[17]. In a well-mixed system (high recycle ratio), the more uniform polymer concentration leads to increased branching and thus polydispersity. At low recycle ratios, the polymer generated in the plume has lower branching levels due to the lower temperatures and polymer concentrations in the V_1 and V_2 compartments. Thus it is seen that mixing can have significant effects on the polymer structure.

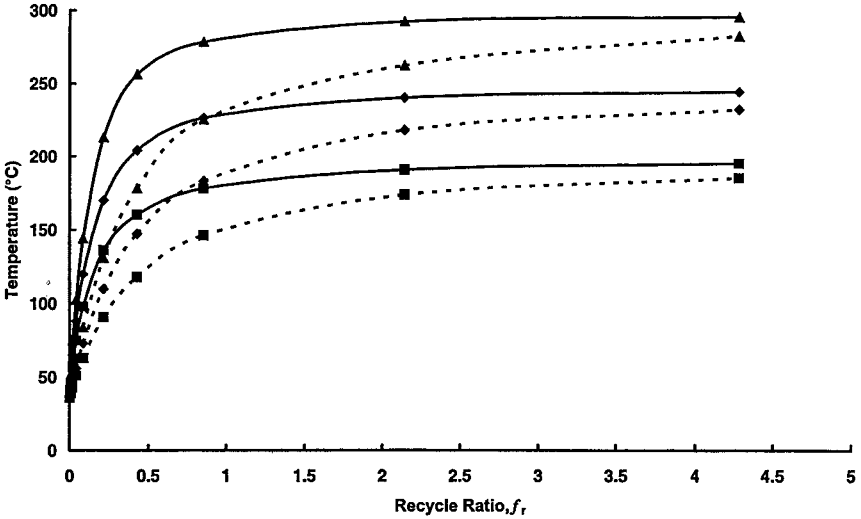

Figure 3. Temperatures in V_1 (---) and V_2 (—) calculated for three different zone (V_3) temperatures: ▲T_3=300°C; ◆T_3=250°C; ■T_3=200°C. Simulation parameters: T_f=35°C; $\beta=\gamma=1$; $V_2=2V_1$ and $f_2=2f_1$.

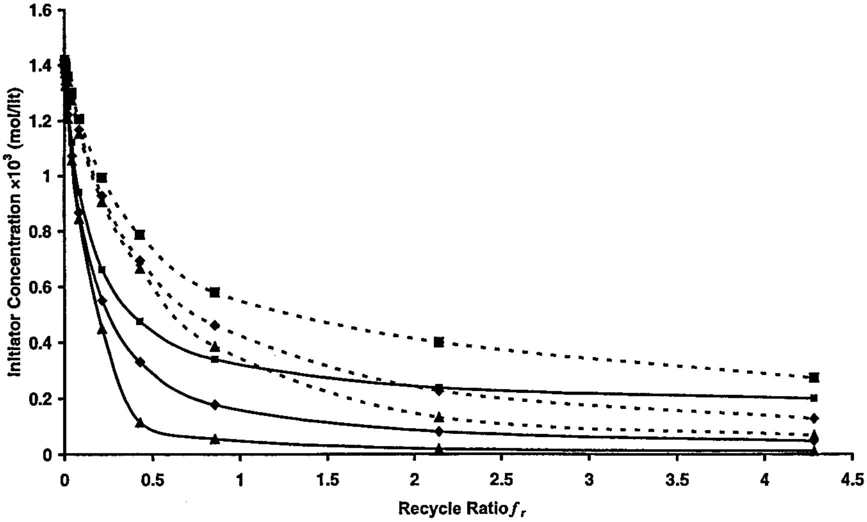

Figure 4. Initiator concentrations in V_1 (---) and V_2 (—) calculated for three different zone (V_3) temperatures: ▲T_3=300°C; ◆T_3=250°C; ■T_3=200°C. Simulation parameters: T_f=35°C; $\beta=\gamma=1$; $V_2=2V_1$ and $f_2=2f_1$.

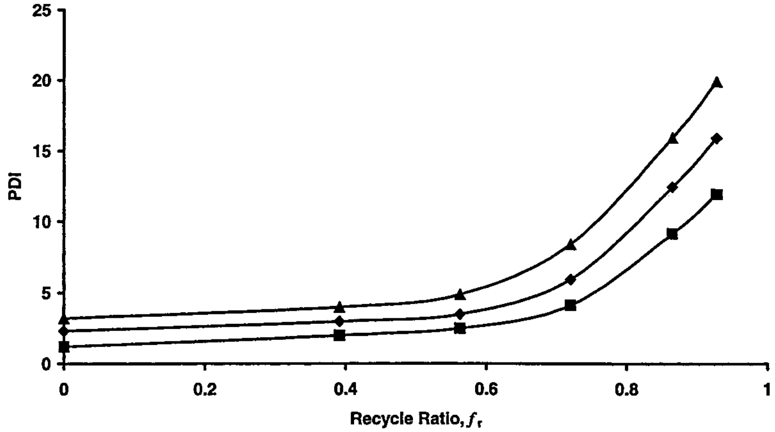

Figure 5. Polydispersity index calculated as a function of recycle ratio for three different zone temperatures: ▲T_3=300°C; ♦T_3=250°C; ■T_3=200°C. Ethylene homopolymerization with: T_f=35°C; β=γ=1; V_2=2V_1 and f_2=2f_1.

After examining the effect of mixing on the polymerization behavior in a single zone, we now turn back to the full multi-zone multi-feed model. For the next set of simulations, the recycle ratio is kept fixed at f_r=0.86, a value selected based upon geometrical flow representation[8] and system response analysis[17]. With the specific values for compartment model parameters (Table 1), the model is used to determine molecular weight and PDI of polymer produced in a three zone autoclave system and the results are compared with those provided by a perfect mixing model. In this set of simulations, the temperature of the first zone is systematically varied (by changing the effective initiator efficiency), with the temperatures of the subsequent zones calculated according to mass and energy balances using the initiator efficiencies determined in our previous work[16]. Table 2 shows the flow parameters and relative zone volumes for the multi-zone system.

Table 2. Compartment model flow parameters and operation conditions for homo- and copolymerization in a three-zone autoclave.

Property		Zone 1	Zone 2	Zone 3
β		1	2	2
γ		1	0	0
Volume (%)		57	19	24
Zone temperature at operating conditions (°C)	Homopolymerization	240	265	290
	Copolymerization	143	199	214
Initiator Feed (ppm)	Homopolymerization	375	7.5	6.6
	Copolymerization	70	40	0

It was shown in our previous work[16] that it is necessary to tune the model MW-controlling kinetic coefficients (transfer to monomer, transfer to polymer and β-scission) from their base literature values in order to get a reasonable match with industrial experimental data. Figures 6 and 7 show the number average degree of polymerization (X_n) and PDI results for polymers produced in a three-zone high pressure autoclave reactor using both the perfectly mixed and compartment models for the same set of kinetic coefficients[16]. The average chain lengths of polymer (Fig. 6) are calculated to be almost identical for the perfect-mixing and compartment models. In the compartment model about 95% of the polymerization reaction takes place in the main reaction volume (the third compartment, V_3) and radical and polymer concentrations are almost identical in both models. Figure 7 shows that the compartment model predicts slightly higher values of PDI than the perfect mixing model. This confirms that the backmixing flows increase the rate of transfer to polymer and higher values of PDI are attained.

Figure 8 shows the capability of using the compartment model for investigating both homopolymerization and copolymerization recipes in the multi-zone autoclave system, with operating conditions summarized in Table 2. The mixing model predicts a lower value of branching level for copolymerization processes, as was also shown for the perfectly mixed model[16].

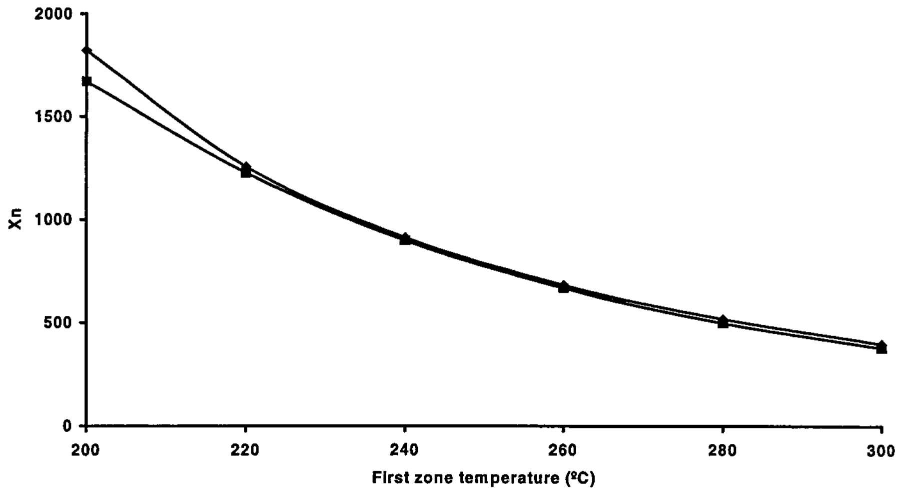

Figure 6. Number average degree of polymerization for ethylene homopolymer produced in a three zone autoclave calculated using ♦ Compartment model; ■ Perfectly mixed model. T_f=35°C; flow parameter values (β and γ) from Tab. 2; compartment model parameters from Tab. 1.

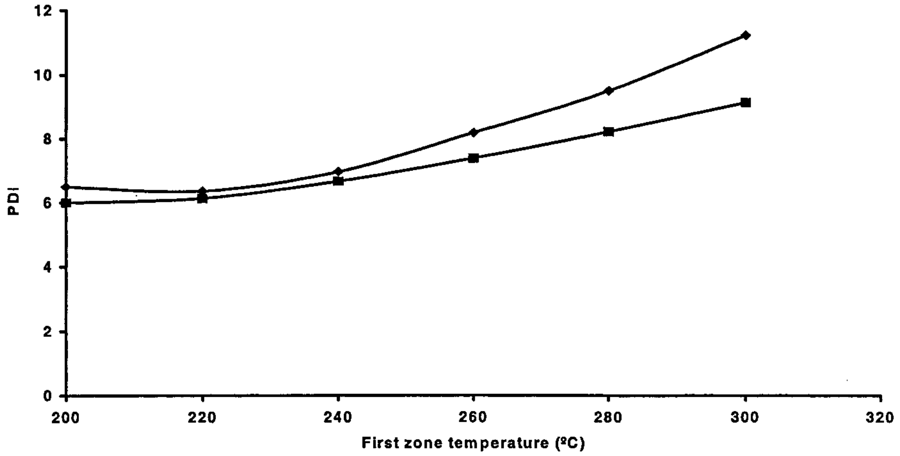

Figure 7. Polydispersity Index for polymer produced in a three zone autoclave. Symbols and model parameters as for Figure 6.

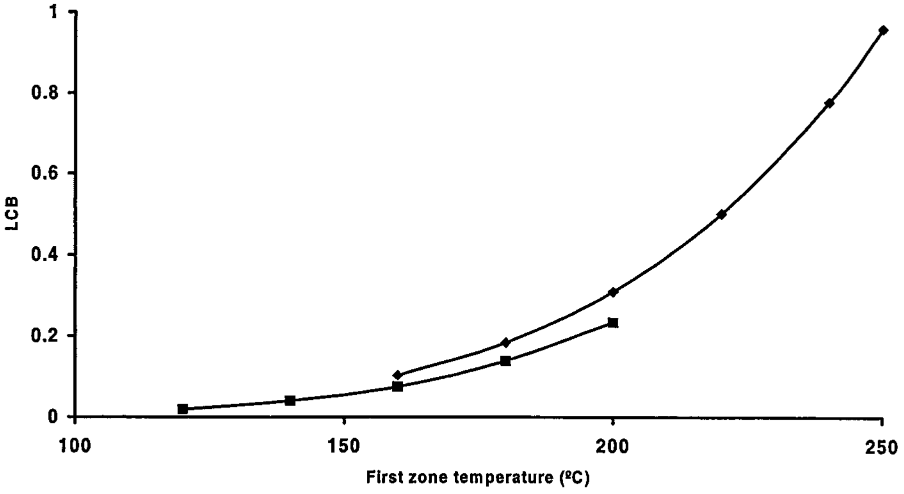

Figure 8. Long chain branching levels (per 1000 backbone C-atoms) calculated for: ■ ethylene homopolymer; ♦ ethylene / vinyl acetate copolymer produced in a three-zone autoclave reactor. T_f=35°C; all parameters and conditions as listed in Tables 1 and 2.

Conclusions

The compartment model provides a more reasonable framework for studying imperfect mixing effects in a high-pressure multi-zone autoclave reactor. The injection plume has lower temperatures and higher initiator levels than the bulk of each zone, affecting observed initiator consumption. Mixing has a small but appreciable effect on polymer characteristics, most notably polydispersity. This model will be further used to better understand the industrial autoclave system from which the experimental data were obtained.

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