# Effects of Imperfect Mixing on Low-Density Polyethylene Reactor Dynamics

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*Earlier work considered the effect of feed conditions and controller configuration on the runaway behavior of LDPE autoclave reactors assuming a perfectly mixed reactor. This study provides additional insight on the dynamics of such reactors by using an imperfectly mixed reactor model and bifurcation analysis to show the changes in the stability region when there is imperfect macroscale mixing. The presence of imperfect mixing substantially increases the range of stable operation of the reactor and makes the process much easier to control than for a perfectly mixed reactor. The results of model analysis and simulations are used to identify some of the conditions that lead to unstable reactor behavior and to suggest ways to avoid reactor runaway or reactor extinction during grade transitions and other process operation disturbances.*

## Introduction

Adiabatic autoclave reactors used for the production of low density polyethylene (LDPE) are known to have serious runaway problems because of the onset of ethylene decomposition reactions (cf. Zhang et al., 1996). In addition, it is well known that because of the rapid reaction and short reactor residence times, there is inadequate macroscale mixing of the feedstream. The characteristic times for initiator decomposition are larger than those for macroscale mixing only at very low temperatures; at the typical operating temperatures for LDPE reactors, however, the initiator half-life is shorter than the mixing times and adequate macroscale mixing becomes an important issue (van der Molen and van Heerden, 1970). Engineering efforts are often made to improve the mixing in order to make the polymer properties more uniform. It has also been suggested that imperfect micromixing may lead to local hot spots that can deflagrate into thermal runaway of the entire reactor (such as Smit, 1992). To better understand the effects of imperfect mixing on reactor behavior and product properties, both compartment models (such as Marini and Georgakis, 1984a,b,c; Ochs et al., 1996) and computational fluid mechanics (CFD) models have been employed. The CFD models (such as Read et al., 1997; Tosun and Bakker, 1997) clearly show that the feed plume is not well mixed on the macroscale and also that "dead zones" can appear with some reactor and agitator designs. However, no one has used these models to study the stability and dynamic behavior of these reactors. In this work, as an approximation to the true macroscale mixing situation, compartment models have been employed because they have been shown effective in representing initiator consumption curves. Here a three compartment model (Figure 1) will be used to investigate the dynamics and stability of an LDPE autoclave reactor when ethylene decomposition kinetics are included in the model. In earlier work from this group (Zhang et al., 1996), the stability and runaway behavior of a perfectly mixed reactor was studied. There it was seen that the stable region of reactor operation was very small for perfectly mixed reactors. There have been comments (Marini and Georgakis, 1984a; Smit, 1996) that imperfect mixing may actually enhance the stability of LDPE autoclaves. In this article we shall investigate this question and show that an optimum amount of imperfect mixing greatly enlarges the region of stable reactor operation and can be a great help in preventing reactor runaway or reactor extinction episodes.

## Reactor Model

The most abundant information available from commercial LDPE autoclaves regarding imperfect mixing is the effect of temperature on specific initiator consumption. Using the compartment model shown in Figure 1, predicted curves of initiator consumption per unit mass of product as reactor temperature is varied are shown in Figure 2. As indicated in

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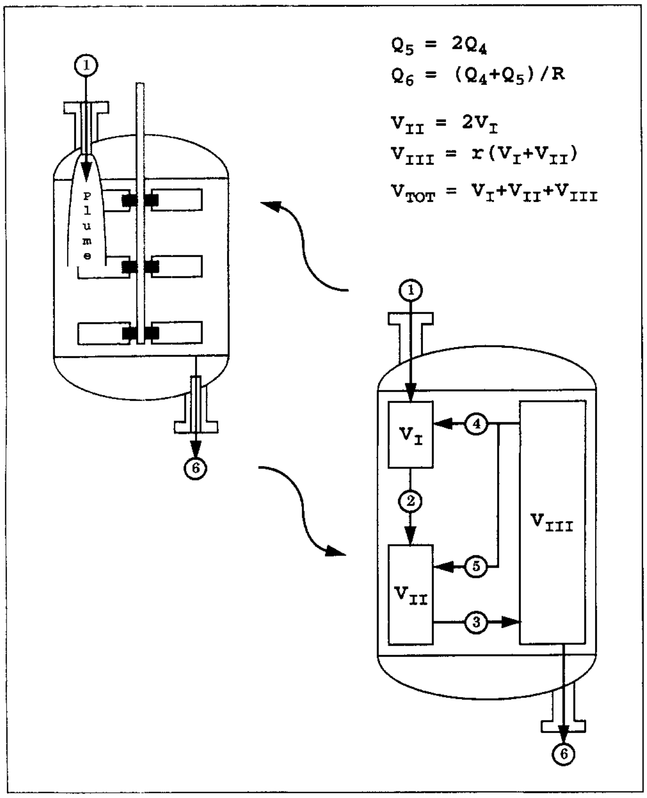

**Figure 1. Configuration of LDPE autoclave reactor model.**

Two small mixing zones in series represent the plume.

Figure 1, the parameter $R$ represents the average number of times material cycles through the feed plume before exiting the reactor. Thus, larger values of $R$ indicate higher degrees of macroscale mixing. Note that for each value of the recycle ratio $R$ there is a temperature for which the initiator consumption goes through a minimum and then increases; this increase is more dramatic at lower values of $R$, which correspond to reduced macroscale mixing. The curve for $R = 500$ shows only a slight increase in initiator consumption at higher temperatures and almost coincides with the monotonic decrease in initiator consumption predicted by the perfect mixing model. In practice, experimentally observed values of specific initiator consumption follow curves similar to those shown in Figure 2 for values of $R \sim 10$–$20$. 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 becomes ineffective, additional higher-temperature initiators begin to generate free radicals. This practice allows reasonable production rates over a wider range of operating temperatures but, as we show in this article, also has a negative influence on reactor stability.

Some workers (Goto et al., 1981; Kwag and Choi, 1994a,b) have modeled these initiator consumption curves as an empirical microscale initiator efficiency effect while others (Marini and Georgakis, 1984a; Ochs et al., 1996 and the present work) can reproduce these through imperfect macroscale mixing effects. When the model that uses an empirical microscale initiator efficiency is compared to the compartmental model, one can see that both models rely on parameters whose values must be determined by comparison with experimental data on initiator efficiency. However, CFD calculations (Read et al., 1997; Tosun and Bakker, 1997) have been used successfully to predict the effect of temperature on specific initiator consumption. These calculations show that under some industrial conditions, serious macroscale imperfect mixing exists. Unfortunately, CFD calculations are more demanding and time consuming than compartment models. Thus, once the existence of serious macroscale mixing problems is established by CFD or other analysis, compartment models are better suited for exploring broadly the

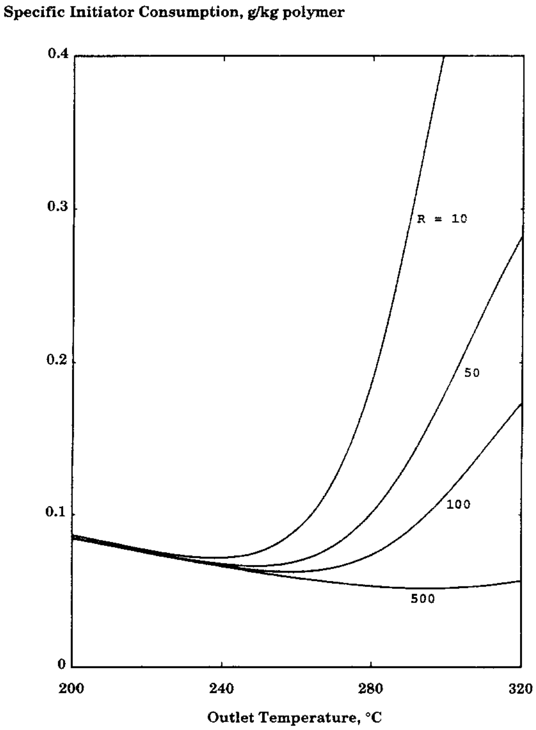

**Figure 2. Effect of operating temperature on initiator consumption per unit mass of polymer produced at high values of recycle ratio.**

**Table 1. Polymerization and Decomposition Kinetics**

| Name | Reaction |
|---|---|
| | *Polymerization* |
| Standard Initiation | $I \rightarrow 2R\cdot \quad R\cdot \rightarrow P_1$ |
| Special Initiation | $C + M \rightarrow P_1$ |
| Forward and Reverse Propagation | $P_n + M \leftrightarrow P_{n+1}$ |
| Termination by Coupling | $P_n + P_m \rightarrow D_{n+m}$ |
| Termination by Disproportionation | $P_n + P_m \rightarrow D_n + D_m$ |
| Termination by Inhibition | $P_n + X \rightarrow D_n$ |
| Spontaneous Termination | $P_n \rightarrow D_n$ |
| | *Decomposition* |
| Initiation | $2C_2H_4 \rightarrow C_2H_3\cdot + C_2H_5\cdot$ |
| Propagation | $C_2H_5\cdot \leftrightarrow C_2H_4 + H\cdot$ |
| Propagation | $C_2H_5\cdot + C_2H_4 \rightarrow C_2H_6 + C_2H_3.$ |
| Propagation | $H\cdot + C_2H_4 \rightarrow H_2 + C_2H_3\cdot$ |
| Propagation | $C_2H_3\cdot \rightarrow C + CH_3\cdot$ |
| Propagation | $CH_3\cdot + C_2H_4 \rightarrow CH_4 + C_2H_3\cdot$ |
| Termination | $2CH_3\cdot \rightarrow C_2H_6$ |
| Termination | $CH_3\cdot + C_2H_3\cdot \rightarrow C_2H_2 + CH_4$ |
| Termination | $2C_2H_3\cdot \rightarrow C_2H_2 + C_2H_4$ |

**Table 2. Base Simulation Parameters**

| Variable | Notation* | Value |
|---|---|---|
| Recycle stream to outlet stream flow rate | $R=(Q_4+Q_5)/Q_6$ | 10.0 |
| Ratio of plume feed flow rates | $R_P=Q_5/Q_4$ | 2.0 |
| Reaction volume to feed plume volume | $r=V_{III}/(V_I+V_{II})$ | 7.0 |
| Ratio of plume volumes | $r_P=V_{II}/V_I$ | 2.0 |
| Overall reactor residence time, s | $\tau=V_{TOT}/Q_1$ | 75.0 |
| Feed temperature, °C | $T_F$ | 120.0 |
| Feed concentration of initiator,** ppm | $W_{IF}$ | 7.5 |
| Feed concentration of reactive impurity,†, ppm | $W_{AF}$ | 0.0 |

*See Figure 1 for details on the notation used.
**The initiator is di-tert-butyl-peroxide (DTBP).
†The reactive impurity is acetylene.

process implications. Suggested process modifications should be finally checked by careful CFD calculations.

Both the imperfect mixing model for LDPE autoclave reactors and the kinetic scheme for simultaneous polymerization and decomposition have been described in detail before (Ochs et al., 1996; Zhang et al., 1996). Only their relevant aspects will be discussed now; the corresponding kinetic model is listed in Table 1. Let us consider the compartment model shown in Figure 1 where we assume that each of the compartments representing various regions in a reactor, from injection to outlet regions, are well-mixed CSTRs. The simulations were performed using the POLYRED package, the software for POLYmerization REactor Design developed at the University of Wisconsin Polymerization Reaction Engineering Laboratory (UWPREL).

Using POLYRED, it is possible to configure a flowsheet containing three well-mixed reactors connected as shown in Figure 1. The results appearing in the remaining figures were obtained by using ISAAC, the Interactive Stability and Continuation Analysis Driver (Hyanek et al., 1995; Zhang et al., 1996) that is also part of POLYRED. This algorithm carries out continuation analysis and determines the stability character of the flowsheet. Unless stated otherwise, the results described in the next section have been generated by configurations derived from the base case shown in Table 2. The base case uses operating conditions that are typical of industrial reactors, and parameters that are similar to those used in previous applications of the compartmental model (Marini and Georgakis, 1984a; Ochs et al., 1996).

## Results

Typical continuation and stability diagrams for the perfect mixing model of simultaneous polymerization and decompo-

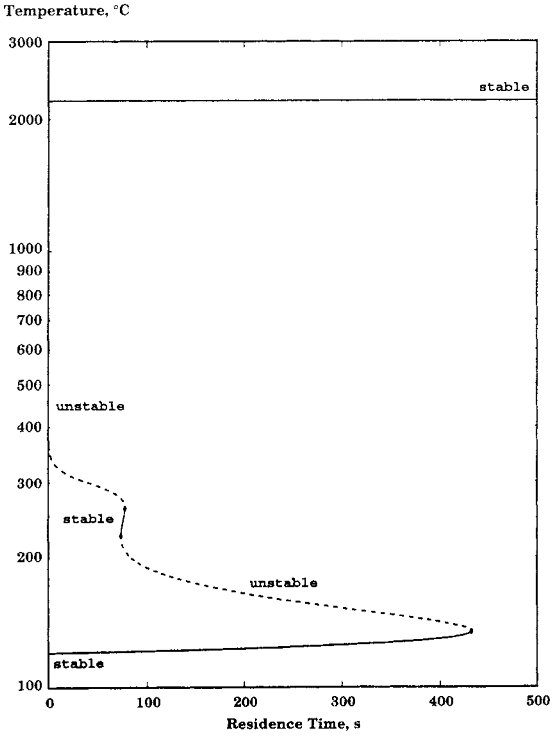

**Figure 3a. Continuation and stability diagram for the perfect mixing model.**

Effect of residence time on outlet temperature.

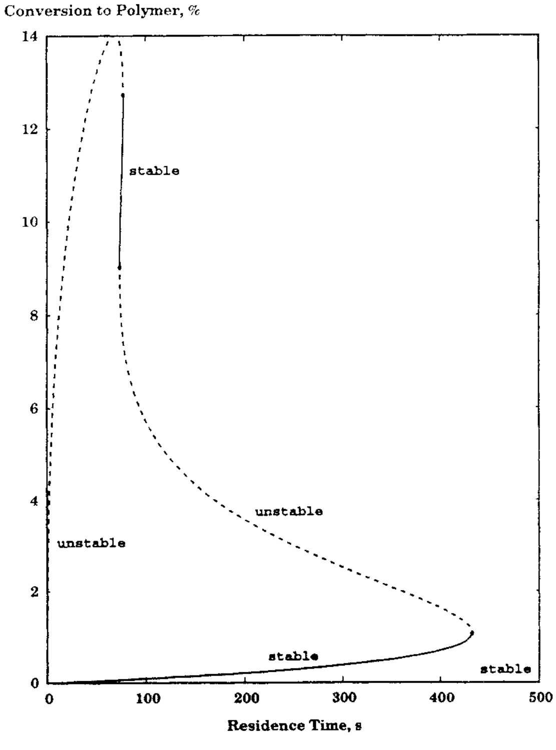

**Figure 3b. Continuation and stability diagram for the perfect mixing model.**

Effect of residence time on monomer conversion to polymer.

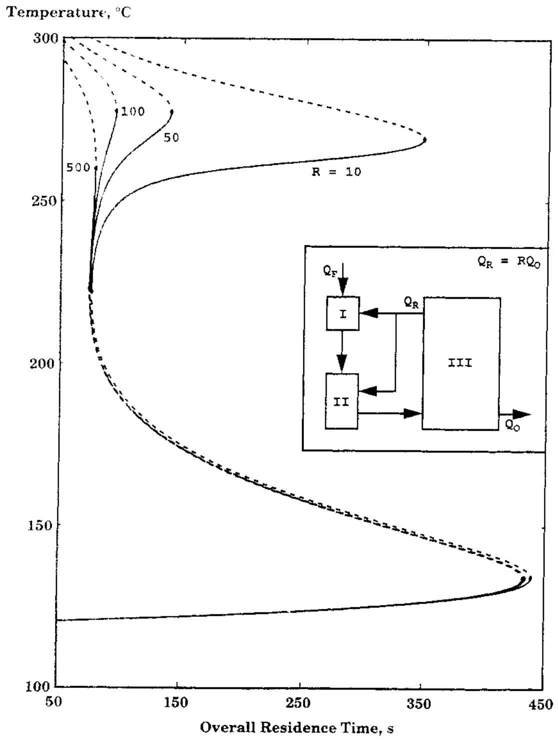

Figure 4a. Effect of residence time on outlet temperature at high values of recycle ratio *R* for the imperfect mixing model.

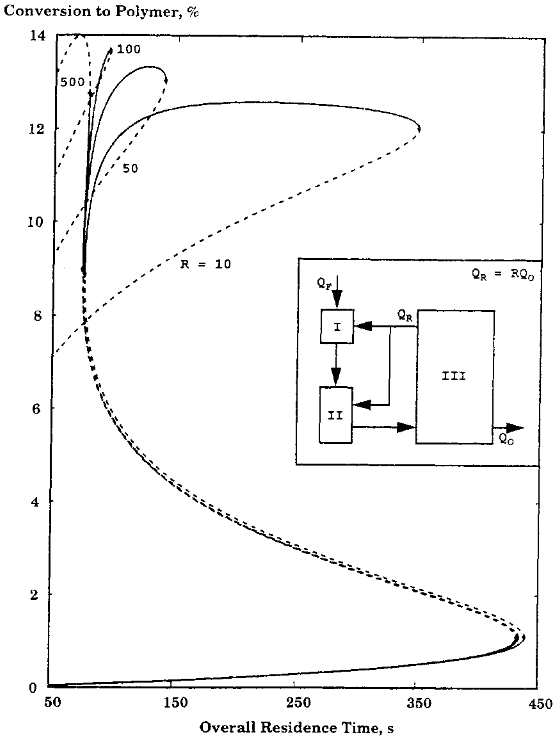

Figure 4b. Effect of residence time on monomer conversion to polymer at high values of recycle ratio *R* for the imperfect mixing model.

sition in LDPE autoclave reactors are shown in Figures 3a and 3b, where residence time has been selected as the continuation parameter. The overall residence time is defined in this case as the ratio of total reactor volume to inlet volumetric flow rate.

In autoclave reactors, a feedback loop is typically used to control the operating temperature by adjusting the amount of initiator in the feed. Unless otherwise indicated, the steady-state simulations discussed here correspond to the open-loop behavior of an autoclave reactor with fixed initiator feed concentration. The open-loop behavior is most important, because the feedback controller may not be fast enough or have sufficient span of control to rescue reactor runaway or extinction situations.

On either of the curves of Figures 3a and 3b, three stable and two unstable branches appear, represented by solid and dashed lines, respectively. The lowest stable branch corresponds to monomer conversion values below 1%, while the lowest unstable branch corresponds to conversion values between 1 and 9%. The next stable branch is the normal operating branch and covers conversions in the range from 9 to 13%. The highest unstable branch is characterized by increasing consumption of monomer by decomposition reactions; it is along this branch that conversion to polymer reaches a peak and drops to zero as the decomposition products become more and more abundant. This unstable branch represents the transition to a final stable branch that appears at much higher temperatures and corresponds to complete reactor runaway (Zhang et al., 1996). Thus, depending on the residence time chosen, as many as five simultaneous steady-

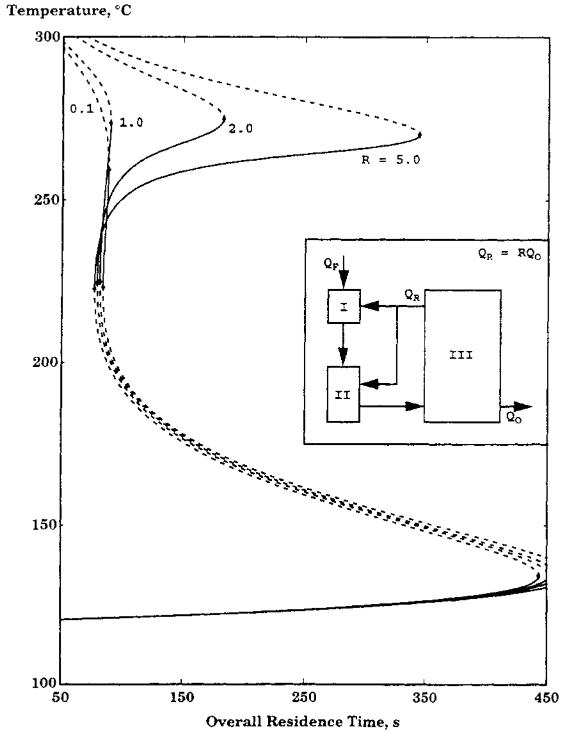

Figure 5. Effect of residence time on outlet temperature at low values of recycle ratio *R* for the imperfect mixing model.

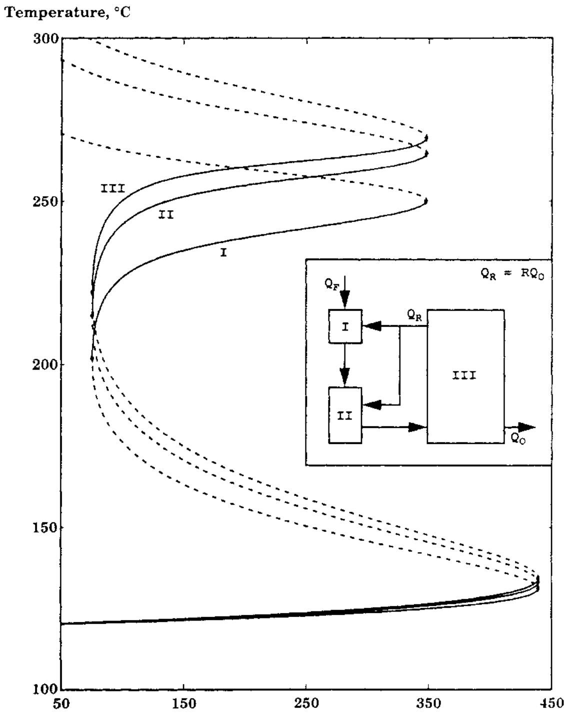

Figure 6a. Operating temperature in all compartments at an intermediate recycle ratio $R = 10$.

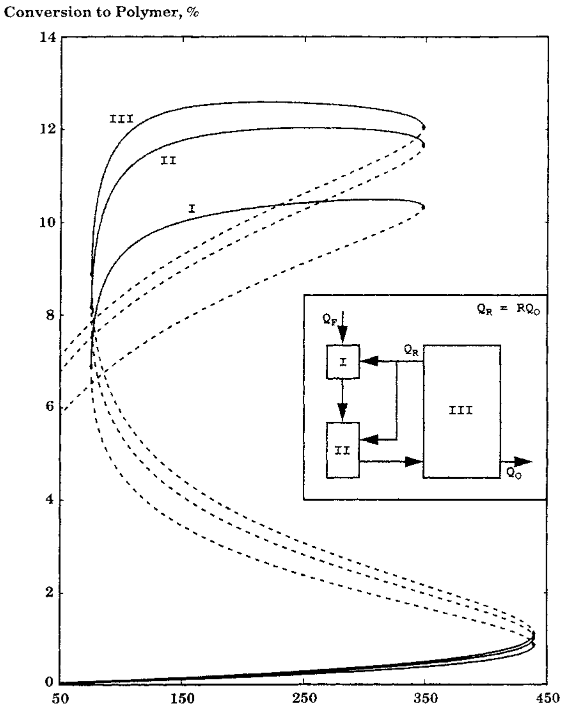

Figure 6b. Conversion to polymer in all compartments at an intermediate recycle ratio $R = 10$.

state solutions are possible for this system. In this study, we will focus on the four lower branches because they are in the normal operating range.

Figure 4a reveals the strong influence that the recycle ratio $R$ has on the open-loop behavior of the system at temperatures between 220 and 300°C. Note that a very high value of $R$ corresponds to near perfect mixing, while for lower values, there are various degrees of imperfect mixing. When the ratio is 10, the intermediate stable branch extends to residence times as high as 350 s and the reactor temperature is relatively insensitive to residence time. As $R$ increases, however, the interval of residence time covered by the intermediate stable branch shrinks more and more, until the behavior of the perfect mixing model is approached at a ratio of 500. Under these conditions, the reactor temperature is very sensitive to residence time and the intermediate region of stable operation has become tiny. Figure 4b shows that at high values of $R$, much of the monomer is decomposing leading to runaway at much lower temperatures than for $R = 10$.

Figure 5 shows how the continuation diagram evolves as $R$ is reduced below 10. In this case as the value of $R$ becomes 1 or less, the stable operating region becomes very small, similar to the behavior of the perfect mixing model. This is because at very low values of the recycle ratio, the imperfect mixing compartment model resembles a system of three reactors in series, with very little happening in the first two small

Table 3. Monomer and Initiator Consumption in Each Mixing Zone*

| Variable | Zone I | Zone II | Zone III |
|---|---|---|---|
| Temperature, °C | 231 | 247 | 254 |
| Initiator, % of total consumed | 30 | 38 | 32 |
| Monomer, % of total consumed | 14 | 19 | 67 |

*Residence time of 120 s; other conditions as listed on Table 1.

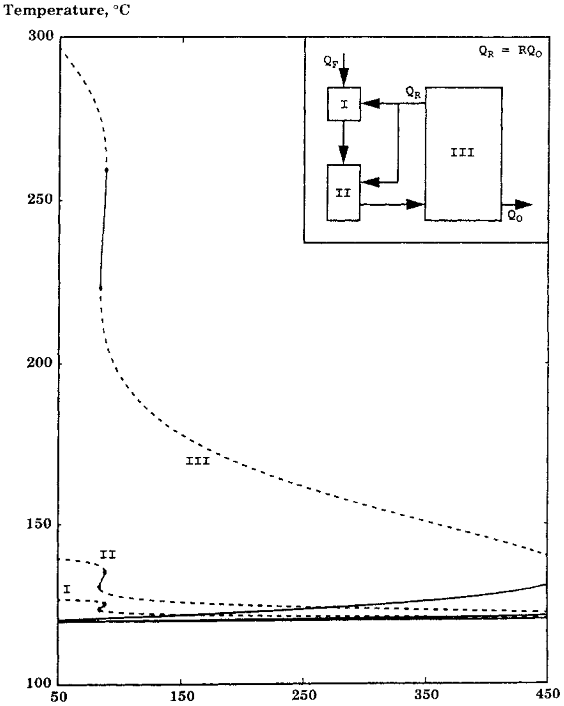

Figure 7. Operating temperature in all compartments at a low recycle ratio of $R = 0.1$.

reactors, with most of the initiator and monomer being consumed in the third perfectly mixed reactor. This raises an important issue in using compartment models: that is, the size of the plume compartments will, in principle, change with the degree of mixing ($R$ in this case). This effect will not be very significant except when $R$ is small because the plume compartments would grow quite large in this case.

The results shown in Figures 4a through 5 indicate that values of $R$ in the range 2–20 yield relatively stable open-loop operation at $T \sim 250–270°C$. It is interesting to note, however, that reported values of $R$ fit to plant data for initiator consumption also yield $R$ in the range from 2 to 20, corresponding to the relatively stable operating region (Marini and Georgakis, 1984a; Ochs et al., 1996).

It is important to understand the physical basis of the stabilizing effect that an optimum level of imperfect mixing has on the autoclave reactor. This can be explained by the results shown on Figure 2, generated by the imperfect mixing model at temperatures in the range from 200 to 320°C. The values of initiator consumed per unit amount of polymer produced indicate that, for the perfectly mixed reactor, the higher the reactor temperature the more effective the initiator is in increasing that temperature. By contrast, for the imperfectly mixed reactor, the two feed plume compartments have low initiator efficiencies because of the lower temperature and high initiator and free-radical concentration. Thus, a large fraction of feed initiator is wasted in the feed plume compartments. As can be seen in Figure 2, the specific initiator consumption begins to increase sharply beyond a certain operating temperature. The feed plume region thus acts like a feedback controller that reduces initiator effectiveness as temperature increases just in the same way that the reactor controller reduces the feed initiator concentration as the reactor temperature rises.

In trying to understand the stabilizing effect of the injection zone, it is helpful to look at the results listed in Table 3, which correspond to a residence time of 120 s for the imperfect mixing model when $R = 10$ and decomposition reactions are absent. Note that the operating temperatures in all compartments are too low for ethylene decomposition reactions to play a significant role, but the stabilizing effect is already responsible for a significant departure from the behavior of the perfect mixing model. As illustrated by the quantities listed in Table 3, temperatures in the feed plume are high enough for more than two-thirds of the initiator to be consumed there; however, monomer conversion to polymer, on the other hand, occurs predominantly in the main reactor compartment.

Our understanding of the stabilizing mechanism in terms of Figure 2 raises another important point. The shape of the initiator effectiveness curve depends on the choice of initiator, and producers normally use a mix of initiators in an attempt to increase initiator effectiveness at higher temperatures. While this may reduce initiator cost and enhance productivity, it will also have a significant effect on reactor stability. We will explore this point in a later section of this article.

At a recycle ratio of 10, Figures 6a and 6b show the operating temperatures and conversions to polymer, respectively, in the three compartments of the imperfect mixing model. Our simulations show that as $R$ increases, the three curves approach each other until they become almost identical at a value of 500. As $R$ is reduced, the curves corresponding to the first two compartments move away from the curve repre-

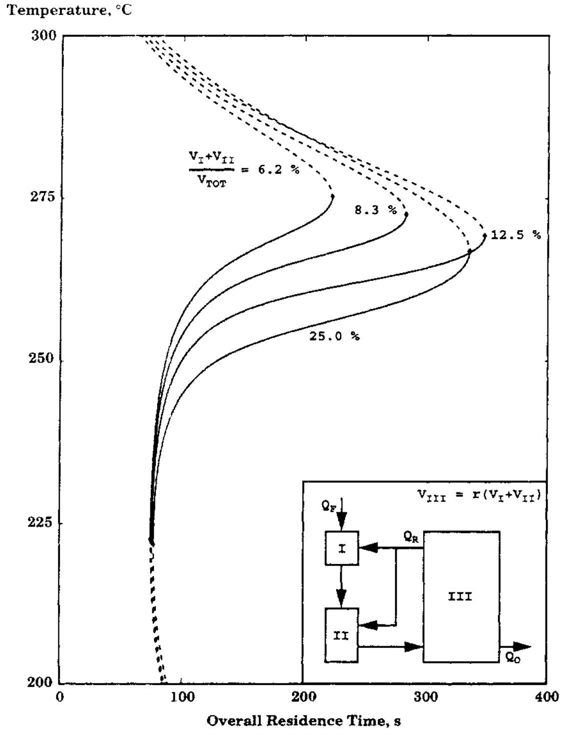

**Figure 8a. Effect of residence time on outlet temperature at various values of volume of the plume region and a recycle ratio $R = 10$.**

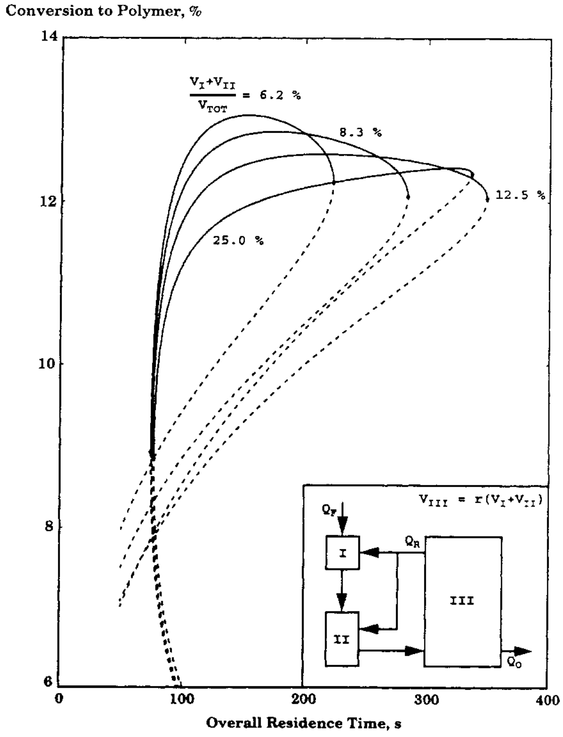

**Figure 8b. Effect of residence time on conversion to polymer at various values of volume of the plume region and a recycle ratio $R = 10$.**

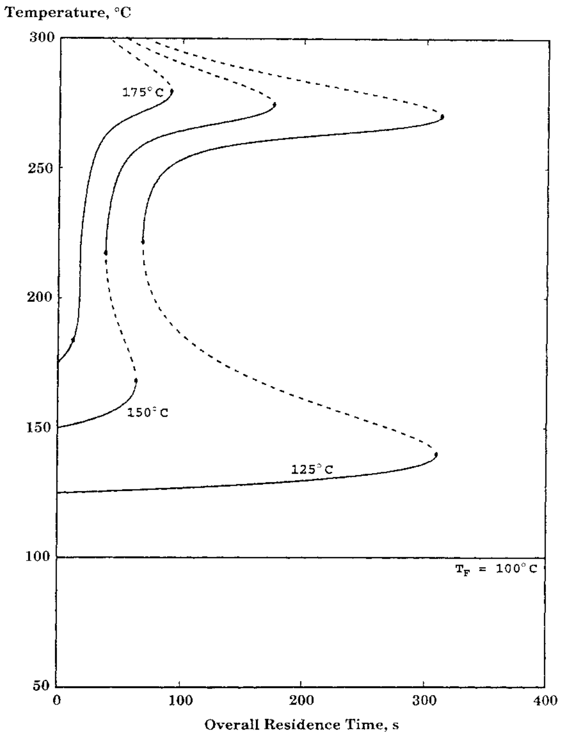

**Figure 9a. Effect of residence time on outlet temperature at various feed temperatures and recycle ratio $R = 10$.**

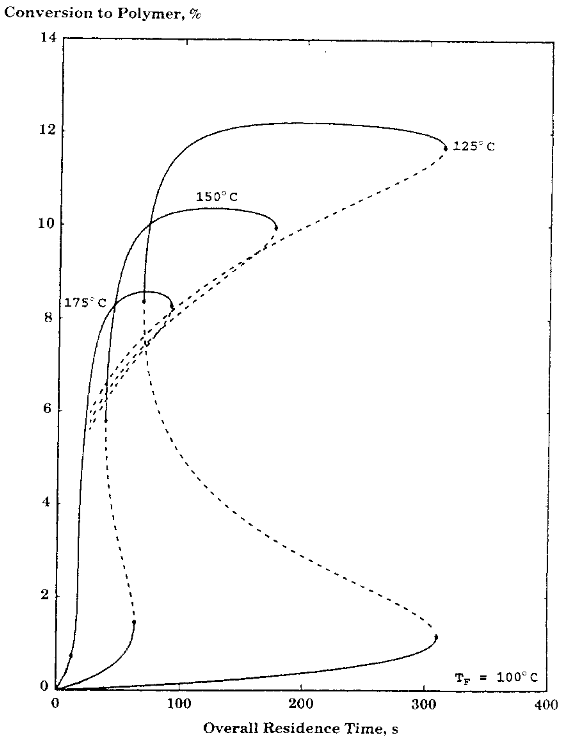

**Figure 9b. Effect of residence time on conversion to polymer at various feed temperatures and recycle ratio $R = 10$.**

senting the third compartment, until the results shown in Figure 7 are obtained at a value of 0.1. As pointed out earlier, very little seems to be happening in the injection region when the recycle ratio is very low.

It seems reasonable to expect the stabilizing effect provided by the injection zone of the model to depend on the size of that region relative to the size of the reactor. Figures 8a and 8b, created using a recycle ratio of 10 and depicting the intermediate stable branch and its surroundings, illustrate this dependency. It is interesting to note that, even when the injection zone accounts for as little as 6% or for as much as 25% of the total volume of the reactor, the stabilizing effect mentioned before is still significant; an increase in the size of the injection zone from 6 to 13% of the total volume, however, has a more significant impact on the stability of the system than a further increase from 13 to 25%. Previous workers (Kwag and Choi, 1994a) conclude that, when the volume of the injection zone is lower than 10% of the total volume of the reactor, the imperfect mixing model predicts similar reactor temperatures as the perfect mixing model; our results indicate that this may not always be true.

The feed temperature can also have an effect on the reactor stability behavior as shown in Figures 9a and 9b. Because the exit temperature is limited by the onset of ethylene decomposition reactions and the danger of runaway, reducing the temperature of the feed stream has the beneficial effect of allowing much higher degrees of conversion to polymer; going to very low temperatures, however, makes the reactor prone to extinction, as illustrated by the curves at a feed temperature of 100°C. The higher the temperature of the inlet stream, the lower that risk, but also the lower the maximum

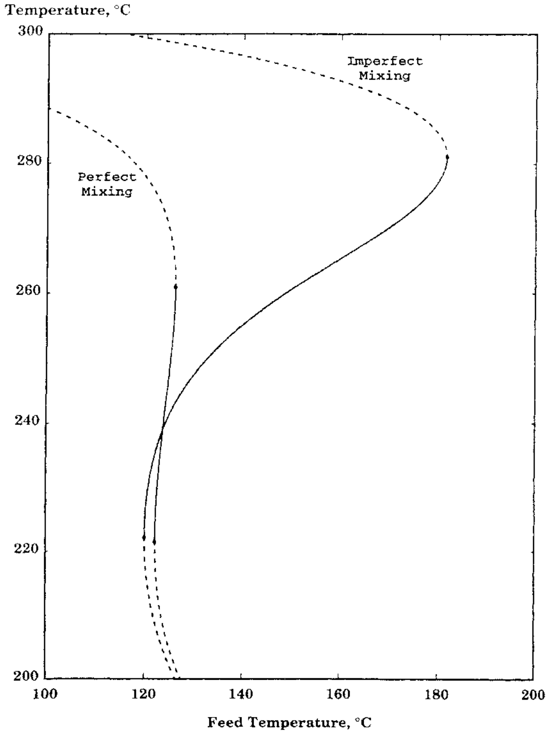

**Figure 10. Comparison of perfect and imperfect ($R = 10$) mixing models: effect of feed temperature on outlet temperature.**

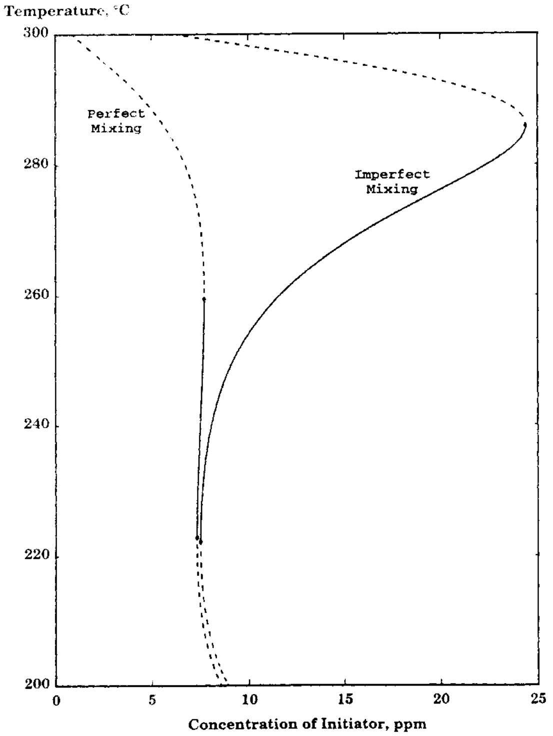

**Figure 11. Comparison of perfect and imperfect ($R = 10$) mixing models: effect of feed initiator concentration on outlet temperature.**

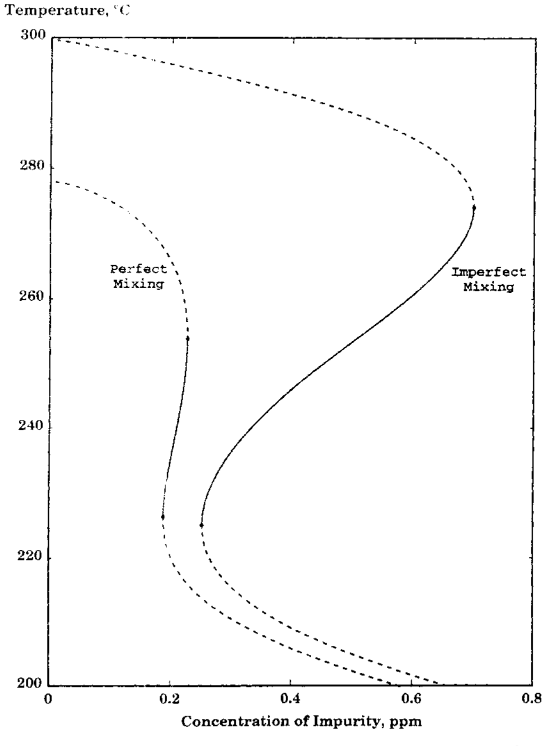

**Figure 12. Comparison of perfect and imperfect ($R = 10$) mixing models: effect of feed impurity concentration on outlet temperature.**

attainable conversion to polymer. Note that as the feed temperature approaches 175°C, the lowest of the unstable branches shrinks until it finally disappears, but, perhaps, the most significant change to note is the reduction in size of the interval of residence times covered by the intermediate stable branch.

The stabilizing effect of an imperfectly mixed feed zone compared to the perfect mixing case also carries over to other disturbances beyond reactor residence time. Figures 10, 11, and 12 illustrate that for $R = 10$, the imperfectly mixed reactor has a much wider range of stable operation for feed temperature, feed initiator, and reactive feed impurity (acetylene) disturbances.

Let us turn our attention to the control scheme mentioned earlier, where a feedback loop is used to control the reactor temperature by manipulating the amount of initiator in the feed. If the controller is sufficiently fast and has adequate span of control action, the controller dramatically increases the stability of the system, even when the perfect mixing model is used (Zhang et al., 1996). This helps explain why LDPE reactors can operate under disturbance conditions that would lead to unstable behavior in the absence of a controller (Chan et al., 1993).

Assuming the feedback loop responds quickly, we can analyze the steady-state span of the control problem by using the results from open-loop simulations such as shown in Figures 13a through 15. We observe the way the control loop introduces steady-state changes in the feed concentration of initiator, in an effort to keep the reactor temperature at the desired level, when steady-state perturbations are introduced in one of the following parameters; residence time, feed temperature, and concentration of impurity in the feed. Each of these parameters is used as a continuation parameter. By drawing horizontal lines at the desired reactor temperatures on Figures 13a, 14a, and 15, the feed concentration of initiator required for steady-state operation at a fixed temperature when other variables are perturbed is shown.

Consider first the difference in behavior between reactors that operate at temperature set points of 240 and 260°C, as illustrated by Figures 13a and 13b. The residence time is assumed to be the source of disturbance in this case. At the 240°C set point, even the smallest changes in reactor residence time will lead to significant changes in the amount of initiator in the feed necessary to maintain a constant steady-state temperature. The situation is very different at the 260°C set point, which shows that only very small changes in initiator are required to offset changes in reactor residence time. Higher conversions would be observed at the higher set point, another desirable condition, but decomposition problems would become more frequent at such a point. One can imagine, for instance, the problems associated with a change in set point, away from a value of 260°C, in a system that receives a feed containing 9 ppm of initiator; as indicated by Figure 13a, the residence time at these conditions is close to 150 s. Keeping the residence time constant during the set point change can make the reactor prone to either extinction or runaway as the control loop tries to reduce or increase the concentration of initiator beyond levels that are feasible for stable steady-state operation.

Consider now the results shown in Figures 14a and 14b, which try to illustrate the steady-state behavior of the reactor

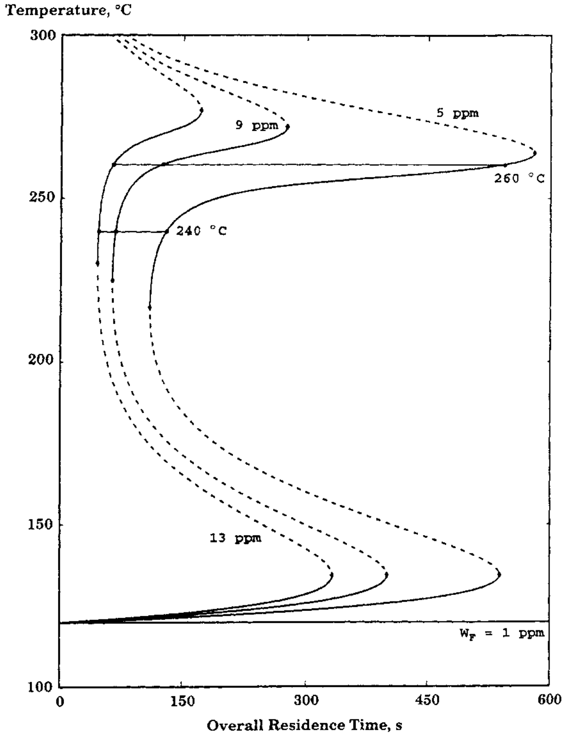

Figure 13a. Effect of residence time on outlet temperature at various feed initiator concentrations and recycle ratio $R = 10$.

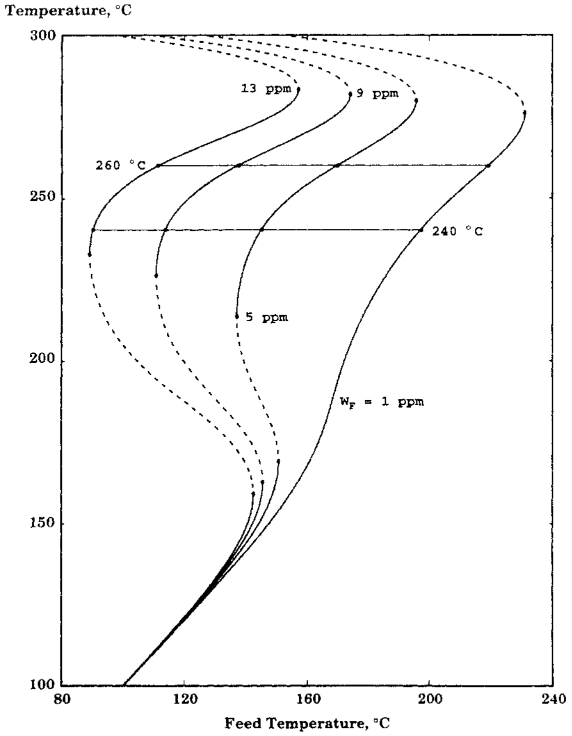

Figure 14a. Effect of feed temperature on outlet temperature at various feed initiator concentrations and recycle ratio $R = 10$.

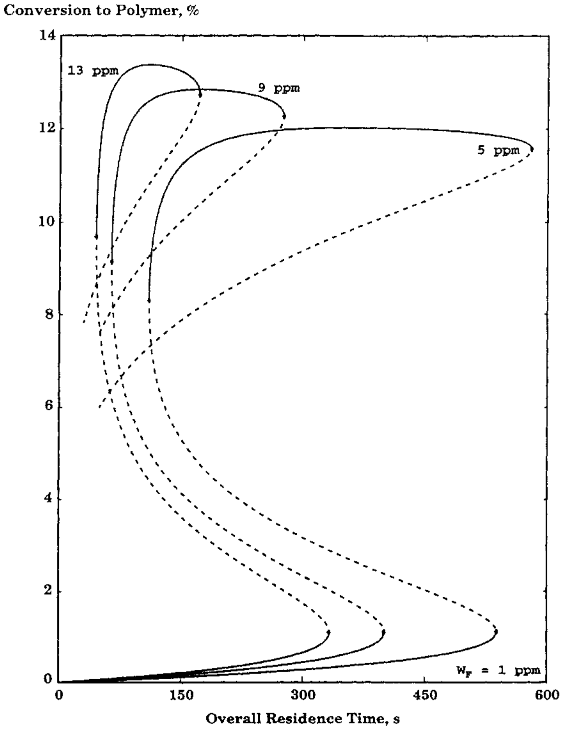

Figure 13b. Effect of residence time on conversion to polymer at various feed initiator concentrations and recycle ratio $R = 10$.

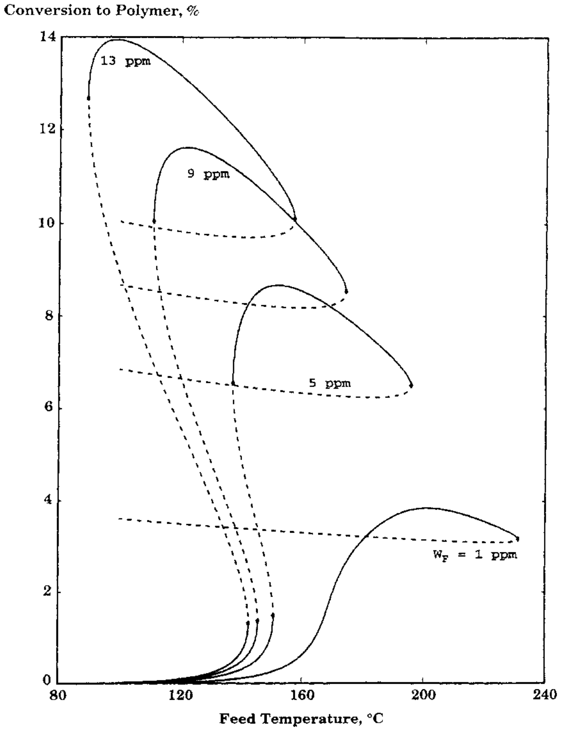

Figure 14b. Effect of feed temperature on conversion to polymer at various feed initiator concentrations and recycle ratio $R = 10$.

when the disturbance is coming from the feed temperature. When set points of 240 and 260°C are compared, the initiator change required in the face of steady-state changes in the temperature of the inlet stream are much smaller than the ones observed in the previous case. Note the significant decrease in the degree of conversion to polymer that results from increases in feed temperature—a consequence of adiabatic operation.

The last of the disturbed parameters chosen for this analysis is the concentration of reactive impurity (acetylene) in the inlet stream; the corresponding results are shown on Figure 15. It is interesting to see that, to be able to operate along the intermediate stable branch, the concentration of impurity allowed is limited by the concentration of initiator in the feed. When 7 ppm initiator enters the reactor, for example, no more than about 0.7 ppm impurity can be tolerated. Suppose now that a temperature set point of 260°C has been chosen and the concentration of impurity in the feed is at 0.6 ppm; the corresponding steady-state feed concentration of initiator should be set by the controller to approximately 7 ppm. A further increase in the amount of impurity entering the reactor would force a drop in the amount of initiator; unfortunately, for decreased initiator, the reactor also becomes more sensitive to fluctuations in the feed concentration of impurity. Going above 1.2 ppm impurity makes stable reactor operation impossible, as the intermediate stable branch disappears and there is inadequate span of control action to allow a stable steady state in the face of realistic dynamic disturbances.

Figures 16a and 16b are useful in analyzing the common practice of using more than one initiator so that as the tem-

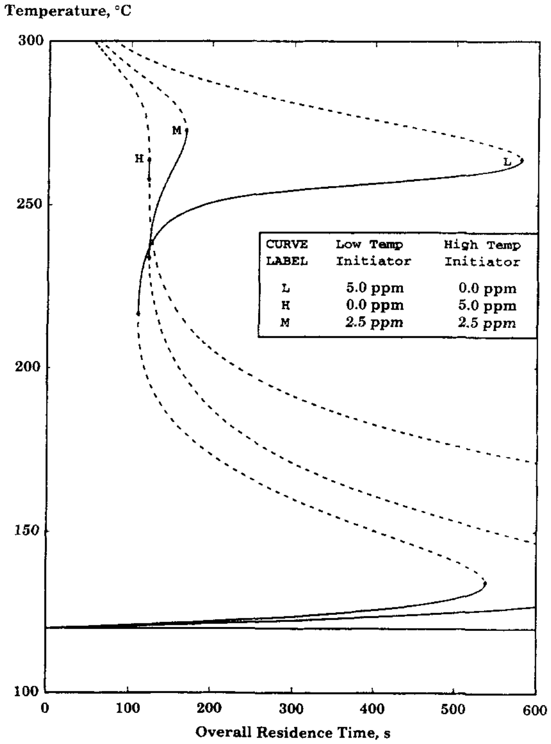

**Figure 16a.** Comparison of low ($k_d = k_{DTBP}$) and high ($k_d = 0.1k_{DTBP}$) temperature initiators at recycle ratio $R = 10$.

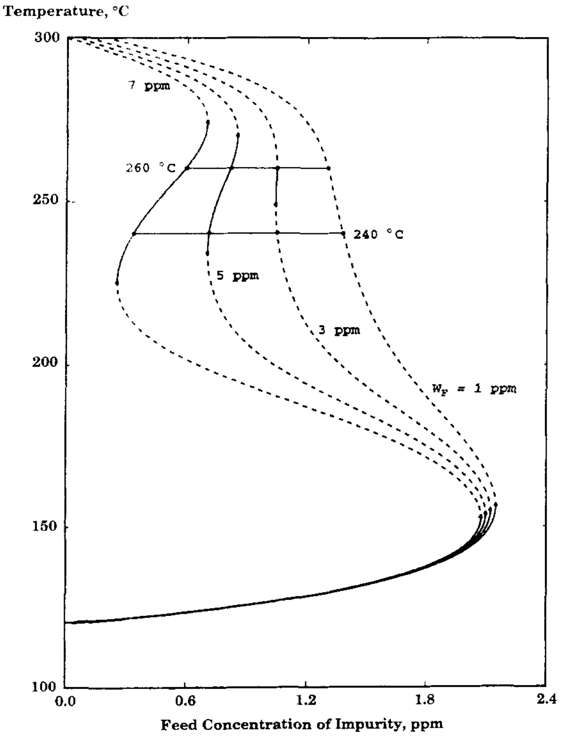

**Figure 15.** Effect of impurity concentration on outlet temperature at various feed initiator concentrations and recycle ratio $R = 10$.

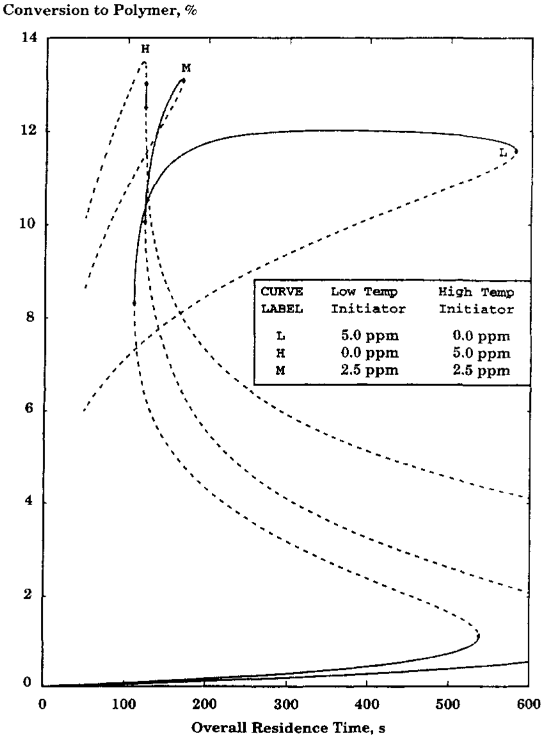

**Figure 16b.** Comparison of low ($k_d = k_{DTBP}$) and high ($k_D = 0.1k_{DTBP}$) temperature initiators at recycle ratio $R = 10$.

perature increases and the first initiator becomes ineffective, additional higher temperature initiators begin to generate free radicals. As shown, higher temperature initiators lead to higher conversions to polymer but the residence time interval for stable operation becomes very narrow (Curve **H**) when compared to the same interval for the lower temperature initiator (Curve **L**). Mixing equal amounts of initiators from these two groups (Curve **M**) provides the increase in initiator effectiveness that the LDPE producer expects but at the expense of operating the reactor under conditions that make it more sensitive than the lower temperature initiator to minor fluctuations in feed quantities like flow rate, temperature, and concentration of a reactive impurity. From this example, one can see that in designing initiator mixtures one must consider reactor stability issues.

## Conclusions

From the use of compartment mixing models, it is seen that a significantly larger domain of stable operation is observed in LDPE autoclave reactors when there is an optimum level of imperfect macromixing. These results are directly related to the initiator effectiveness curves shown in Figure 2 which provide self-regulation of reactor temperature in the face of disturbances.

Other parameters determine the location of the interval of stable operation of LDPE autoclave reactors. The relative size of the injection zone, for example, causes the stable operation interval to grow or shrink. However, even when the injection zone accounts for as little as 6% or as much as 25% of the total volume, a rather broad interval of stable operation is observed at an optimum level of imperfect mixing. It is thus important to keep in mind that the increased stability of the imperfect mixing model is caused by multiple factors and not just by the size of the feed compartments.

It is shown in this work that industrial measures for increasing the temperature interval for productive operation, by using initiators that decompose at higher temperatures and mixed initiators, lead to higher initiator effectiveness but the domain of stable operation shrinks and the reactor becomes more sensitive to disturbances in operating conditions. Thus, there is a trade-off between reducing initiator consumption and enhancing reactor stability.

In this work we have focused on the effects of imperfect macroscale mixing which can be represented reasonably well by compartment models. Macromixing is known to be important from time-scale comparisons of initiator half-lives and feed plume mixing times, as well as from CFD calculations. Another factor which is not considered here, but which will be treated in a future article, is the question of hot spot formation, subsequent quenching or expansion to global deflagration as an alternate route to reactor decomps and "color shot" product. Depending on the size scale of the hot spot, either macro-, meso-, or microscale mixing could be important. Because microscale hot spots are more likely to be quenched by their surroundings, it is likely that meso- and macroscale hot spots are the only ones likely to lead to reactor runaway. More will be said about this in the future.

This work shows that a better understanding of mixing phenomena would be valuable in making the right choice of initiator mixtures, agitator design, and feed inlet configuration since these have a dramatic impact on reactor stability and, of course, on product quality. Compartment imperfect macromixing models provide a quick way to explore the effects of these factors and of various operating conditions on LDPE autoclave reactor behavior. A combination of these with the more demanding, but more detailed, descriptions provided by CFD simulations can be used to improve reactor design for better product quality, improved productivity, and more stable reactor operation.

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