# Continuous Soluble Ziegler-Natta Ethylene Polymerizations in Reactor Trains, 3 – Influence of Operating Conditions upon Process Performance

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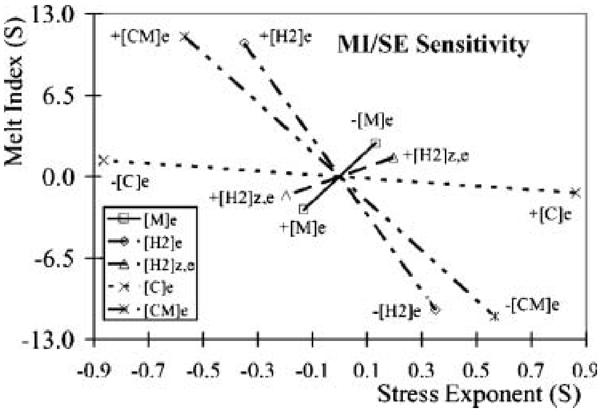
The behavior of continuous solution ethylene/but-1-ene polymerizations through Ziegler-Natta catalysts is analyzed, based on a previously developed mathematical model. In order to do that, dynamic simulations are carried out and process responses are analyzed as functions of process operating policies and flowsheet configuration, at conditions that resemble the actual operation of industrial sites. It is shown that system responses are highly nonlinear and very sensitive to disturbances of the operating conditions and that catalyst decay is of fundamental importance for proper understanding of process behavior. Results indicate that mixing conditions inside the reactor vessels exert a significant impact upon the final polymer quality and can be manipulated for in-line control of final resin properties. Finally, it is shown that the development of feed policies, based on the use of lateral feed streams, allows the simultaneous control of melt flow index, stress exponent and polymer density of the final polymer resin.



## Introduction

In spite of the commercial importance of continuous ethylene polymerization processes through homogeneous Ziegler-Natta catalysts, the performance of soluble Ziegler-Natta polymerization processes has not been discussed in detail in the open literature. Choi studied the solution ethylene polymerization in continuous stirred tank reactors using Ziegler-Natta catalysts and developed a kinetic model which allowed fair description of the reactor operation and the development of control policies for proper control of the MWD of the final polymer.[1] Cozewith studied the ethylene/propylene/ethylidene terpolymerization in solution and developed a mathematical model based on a very detailed kinetic mechanism for industrial Ziegler-Natta continuous stirred tank reactors, which allowed good description of transient responses of actual polymerization reactions.[2] Kim and Choi studied the Ziegler-Natta solution ethylene/but-1-ene copolymerization in continuous stirred tank reactors and developed a kinetic model that allowed for good prediction of available

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*Macromol. React. Eng.* **2008**, *2,* 161–175

DOI: 10.1002/mren.200700047

industrial data.[3] More recently, Pourhossaini et al. developed a model to describe semibatch olefin polymerizations performed with soluble Ziegler- Natta catalysts in stirred tank reactors.[4] However, although the solution technology generally comprises different non- ideal reactor vessels that may be operated independently or in series, the publications available in the field are focused on the performance of single ideal reactor vessels, which cannot reproduce the operating flexibility and performance of actual industrial sites.

Embiruçu et al. developed a detailed mathematical model to describe the operation of soluble ethylene/but-1-ene solution polymerizations through Ziegler-Natta catalysts.[5,6] The model describes the dynamic responses of both process operating conditions and important end-use polymer properties [melt flow index (MI), stress exponent (SE) and polymer density ($\rho$)] as functions of flowsheet configuration and operating policies. Model parameters were estimated based on actual industrial data and the model was validated at the plant site.[7,8] Results obtained showed that the model allowed for very good description of plant performance in very complex situations, where different flowsheet configurations, different catalysts and different feed policies were used.

The main objective of this paper is to analyze the behavior of continuous solution ethylene/but-1-ene polymerizations through Ziegler-Natta catalysts, based on the previously developed mathematical model. In order to do that, dynamic simulations are carried out and process responses are analyzed as functions of process operating policies and flowsheet configuration, at conditions that resemble the actual operation of industrial sites. It is shown that system responses are highly nonlinear and very sensitive to disturbances of the operating conditions. Besides, it is shown that catalyst decay is of fundamental importance for proper understanding of process behavior. Results also indicate that mixing conditions inside the reactor vessels exert a significant impact upon the final polymer quality. For this reason, mixing conditions can be manipulated for in-line control of final resin properties. Finally, it is shown that the development of feed policies, based on the use of lateral feed streams, allows the simultaneous control of MI, SE and $\rho$ of the final polymer resin.

## Process Description

The process studied is described in detail elsewhere,[5,6] so that only the main points will be emphasized here. The feed stream is a mixture of ethylene, but-1-ene, cyclohexane, a mixture of Ziegler-Natta (ZN) catalysts and cocatalysts and hydrogen. Feed streams with different compositions may be inserted into different process locations, so that feed policies are very flexible. The catalyst feed is a mixture containing varying amounts of transition metals (ZN) as active catalyst species, which must be activated by cocatalysts prior to polymerization. The process flowsheet is composed of two tubular reactors (Reactors 1 and 3) and a non-ideal stirred tank reactor (Reactor 2). The operation is adiabatic and cooling devices are not used. The basic process configuration is shown in Figure 1. As shown in Figure 1, different operating modes may be used in this system, as all reactor vessels are equipped with injection points for almost all chemical species. The agitators of Reactor 2 may be turned off in order to allow the operation of this vessel as a tubular reactor of large diameter. Therefore, depending on the mode of operation, the process may be composed of a series of tubular reactors, a continuous stirred tank reactor or some other type of mixed configuration. By changing the mode of operation, significant changes of the MWD of the final polymer may be obtained, allowing the production of many resin grades.

Two operating modes are used most often: the agitated mode and the tubular mode. In the agitated mode, Reactor 1 is not used and the agitators of Reactor 2 are turned on. The degree of mixing is controlled through the manipulation of the agitator speed and the lateral feed flow rates. The process is composed of a non-ideal stirred tank and a tubular reactor in series and is used to produce polymer grades with narrower molecular weight distributions. In the tubular mode, monomer and catalysts are injected into Reactor 1 and hydrogen is injected along the reactor train to control the MWD. The agitators of Reactor 2 are turned off, so that the process is composed of three tubular reactors in series. The proper control of the feed temperature is of fundamental importance in this mode, to avoid polymer precipitation inside the reactor. This mode of operation is used to produce polymer grades with broader molecular weight distributions.

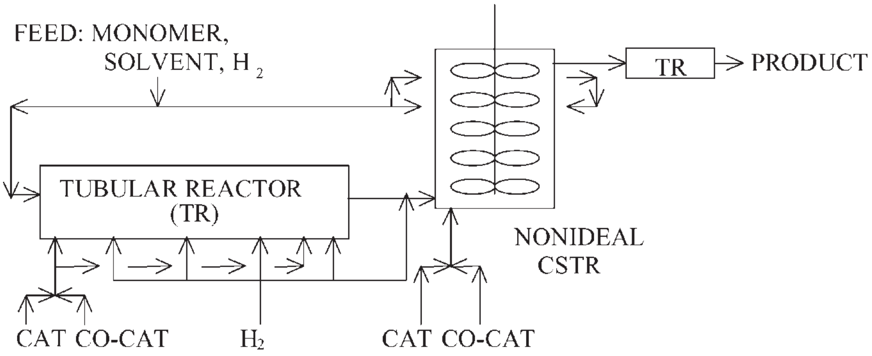


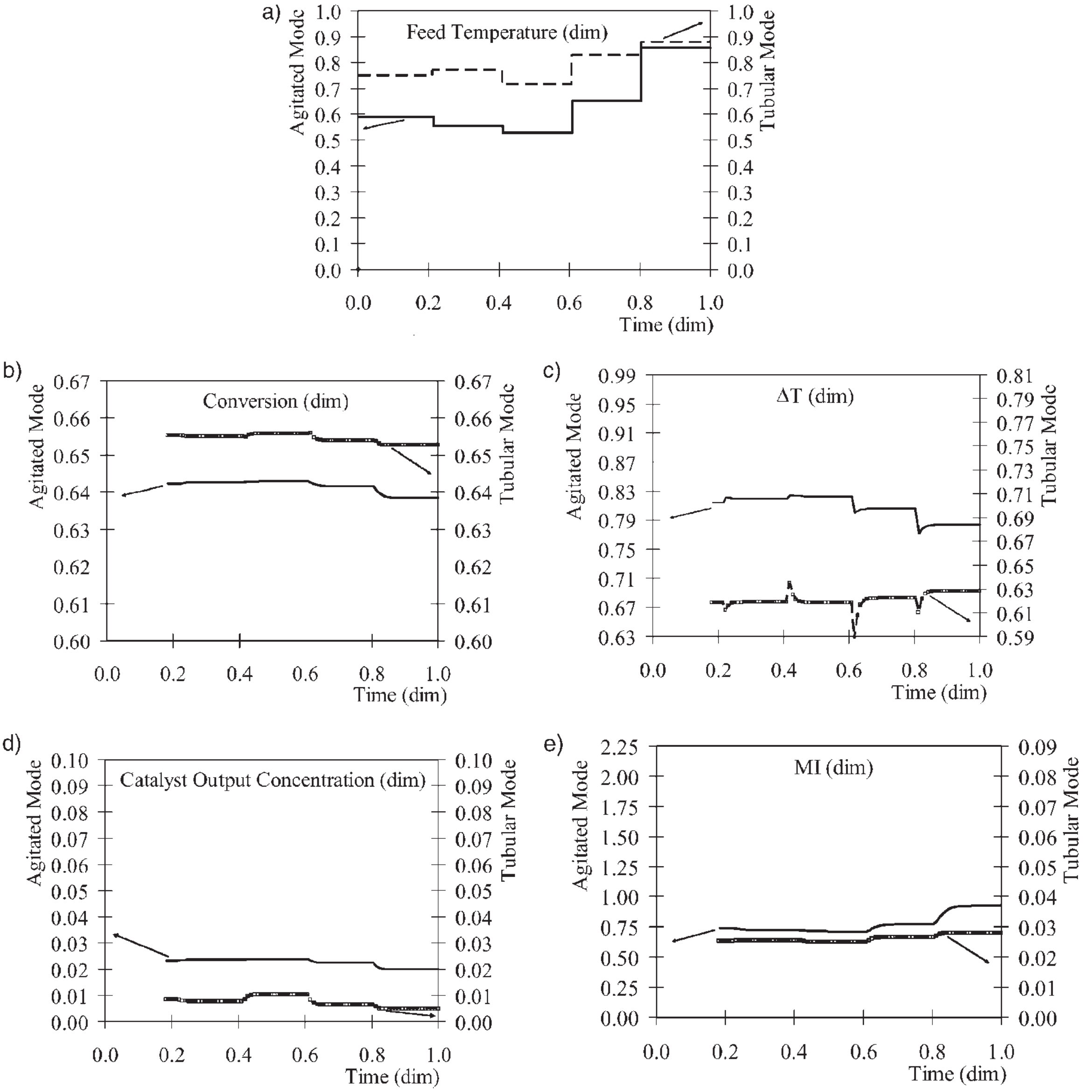
*Figure 1.* Basic process configuration.

### Simulation Conditions

Due to the large number of independent process variables, simulation studies were carried out based on dynamic responses to series of step perturbations of process inputs, instead of using formal bifurcation analysis.[9] Besides, as pointed out by Kim and Choi[3] bifurcations to multiple steady state and self-sustained oscillatory responses are unlikely for these systems. Step perturbations were defined in accordance with available process operating data.[5–7] Perturbations were defined within the range of variation of the process inputs and the magnitudes of the input perturbations simulate actual grade transitions practiced at the plant site. For proprietary reasons, data are presented in coded form, where 0 and 1 represent the minimum and maximum reference values respectively. Typical process operating conditions and parameters needed for simulation are presented in the literature.[5–8]

## Results

Simulation results are presented in three distinct sections. Process responses to changes of input process variables are presented first, to allow the identification of their effects and the definition of the most important inputs. Afterwards, process responses to changes of the basic flowsheet



configuration are analyzed, in order to characterize process operating flexibility. Finally, detailed sensitivity analysis is carried out, in order to provide additional insight and to speculate about possible control configurations for the many process variables analyzed. Results for both agitated and tubular operating modes are presented simultaneously, in order to compare the performances of the usual modes of operation more easily.

### Variable Effects

One of the most important features of the studied process is the proper control of reaction temperatures. If inlet temperature is too low (in tubular mode) or outlet reaction temperatures increases too much (in both modes), phase separation may occur, leading to severe operating problems.[5] As feed temperature is also manipulated to control grade transitions, the impact of feed temperature variations upon process performance is very important. Figure 2a shows the feed temperature profiles used for simulation studies for both the agitated and the tubular operating modes. Figure 2 also presents process responses to the series of input perturbations in the agitated mode. It is interesting to observe that monomer conversion decreases with the increase of the feed temperature, due to the very strong catalyst decay observed for soluble Ziegler-Natta catalysts. As the activation energy for catalyst decay is much larger than the activation energy for propagation,[5–7] the temperature increase is normally followed by a decrease in monomer conversion. This means that reactor run-away and thermal instabilities are unlikely.[3] This also means that the impact of feed temperature variations upon the output temperature is greatly minimized, making control of solution stability much easier. The increase of feed temperatures also lead to increase of MI (and consequently to the increase of $\rho$ and decrease of pressure losses), due to the higher activation energies of the chain transfer reaction steps, when compared to the propagation reaction steps.[5–7] The general picture is not much different in the tubular mode, as also shown in Figure 2. However, it is interesting to observe that the dynamic profiles obtained for the temperature difference between the outlet and inlet streams of the system, generally used to control the polymer productivity, present large inverse responses, due to the distributed nature of the reaction vessels. In the tubular mode, the dynamic behavior is influenced by the finite speed of the wave propagation of feed perturbations along the tubular vessels. This feature should not be disregarded if $\Delta T$ is used for control purposes, as usually made at the plant site.

Monomer feed concentrations are manipulated at the plant site to control polymer productivity and production schedules. Therefore, the analysis of the influence caused

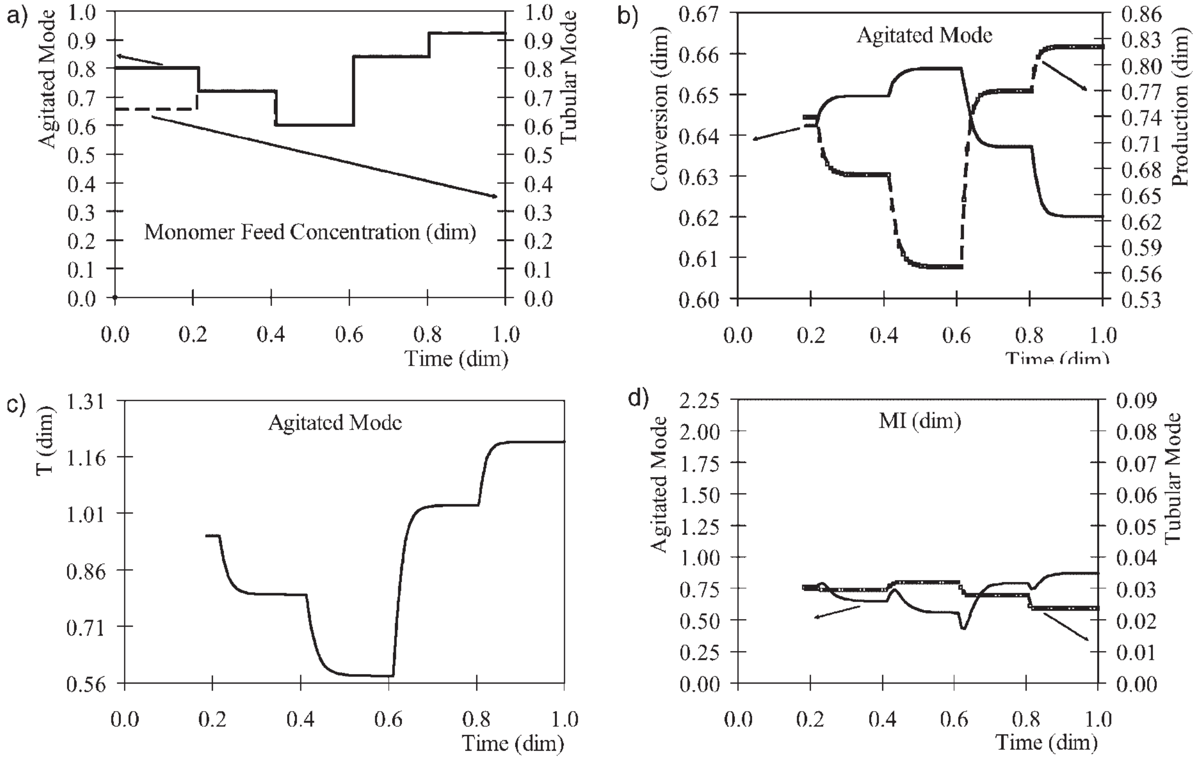


*Figure 3.* Step perturbations of the monomer feed concentration (a) and process responses (b–d).

DOI: 10.1002/mren.200700047

by variations of the monomer feed concentrations on the polymerization conditions is very important. Figure 3a shows the sequences of step perturbations used to characterize the influence of monomer feed concentrations on process performance for both the agitated and the tubular operating modes. Figure 3 also shows that the process dynamics observed for the agitated mode are greatly influenced by the temperature increase that follows the increase of the monomer feed concentration. This leads to the decrease of monomer conversion (despite the obvious increase of polymer production) and to the increase of the MI. Observe, though, that the MI dynamic profiles present small inverse responses, due to the higher thermal capacitance of the polymerization system. As monomer concentrations increase faster than reactor temperatures when the monomer feed increases, one observes the decrease of the MI before the stabilization at higher MI values. Figure 3 shows that the MI dynamic profiles are different in the tubular mode. Due to the much lower degree of mixing, the combination of higher monomer concentrations and relatively low reaction temperatures lead to the decrease of the MI when the monomer feed concentration increases.

Total feed flow rates (feed compositions are kept constant) are manipulated at the plant site mostly to control production schedules between grade transitions. The influence of total feed flow rates upon process performance is presented in Figure 4. Figure 4a presents the sequence of step feed flow rate perturbations, while the rest of Figure 4 shows results obtained for the agitated

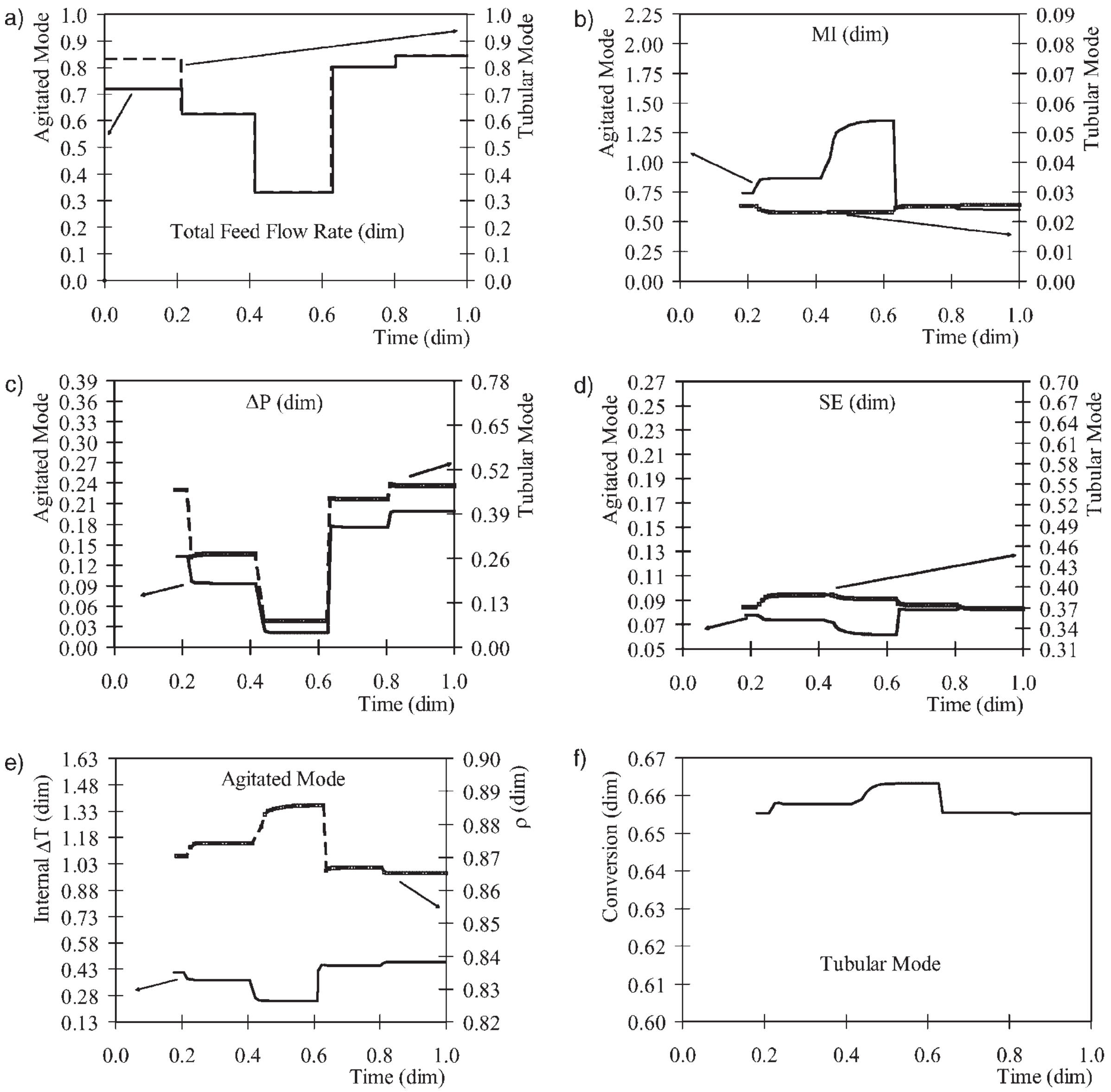


*Figure 4.* Step perturbations of the total feed flow rate (a) and process responses (b–f).

and tubular modes. It can be seen that the increase of the total feed flow rate leads to the increase of the temperature gradient observed in the agitated mode. This is caused mostly because a larger amount of polymer of high molecular weight (low MI) is produced at the first sections of Reactor 2, leading to a decrease of the degree of mixing. This also leads to the increase of the polymer polydispersity (increase of SE) and decrease of the polymer density. In spite of the lower MI, an increase of the head losses in the system, due to the higher production rates, is observed. In spite of that, the total monomer conversion decreases, due to the smaller residence times. The influence of the total feed flow rate on the process performance in the tubular mode is much smaller (see, for example, MI and SE profiles). This occurs because the increase of the feed flow rate in this case is equivalent to the decrease of the tubular reactor length, so that the main effects observed regards the loss of monomer conversion. A small effect can also be observed in the polymer polydispersity, as reaction conditions become more uniform when feed flow rates increase.

Hydrogen feed concentration is manipulated at the plant site to allow the control of the MI of the final polymer resin. Figure 5 shows the sequence of step perturbations of the hydrogen feed concentration used for simulation studies in the agitated mode and in the tubular mode and presents the results obtained. As expected, the MI (and consequently also $\rho$) increases very significantly with the increase of the hydrogen concentration in both operating modes. In the agitated mode, this is also followed by smaller gradient temperatures and head losses, due to the much better mixing conditions when the MI increases. The effect on polymer productivity and monomer conversion, though, is very small. In the tubular mode, the increase of the MI is followed by strong increase of the polydispersity, due to the increase of the gradient of chain transfer reaction rates along the tubular vessel. This is a very important subject, because this implies that MI and SE cannot be controlled simultaneously, unless some other control strategy is devised for the MI.

Catalyst and cocatalyst concentrations are manipulated at the plant site to compensate for variations of the catalyst activity and cocatalyst efficiency. Most of the time, such variations are induced by variations of the undesired catalyst and cocatalyst poison concentrations, which cannot be controlled and most of the times are unknown. Figure 6a and 7a display the series of steps perturbations used for simulation for both catalyst and cocatalyst concentrations. In the first case, cocatalyst concentration was also varied proportionally, which means that the ratio cocatalyst/catalyst was kept constant. In the second case, the catalyst concentration was kept constant, which means that the ratio cocatalyst/catalyst was allowed to vary. Results obtained for the agitated mode and the

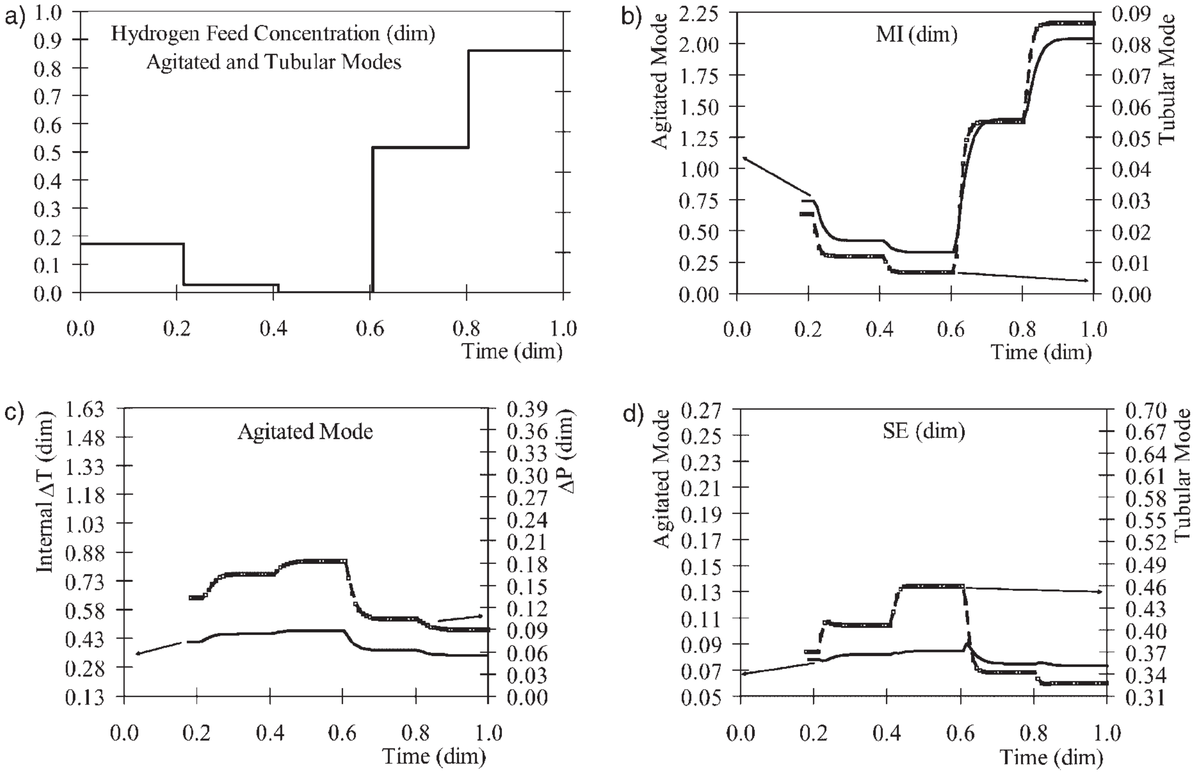


*Figure 5*. Step perturbations of the hydrogen feed concentration (a) and process responses (b–d).

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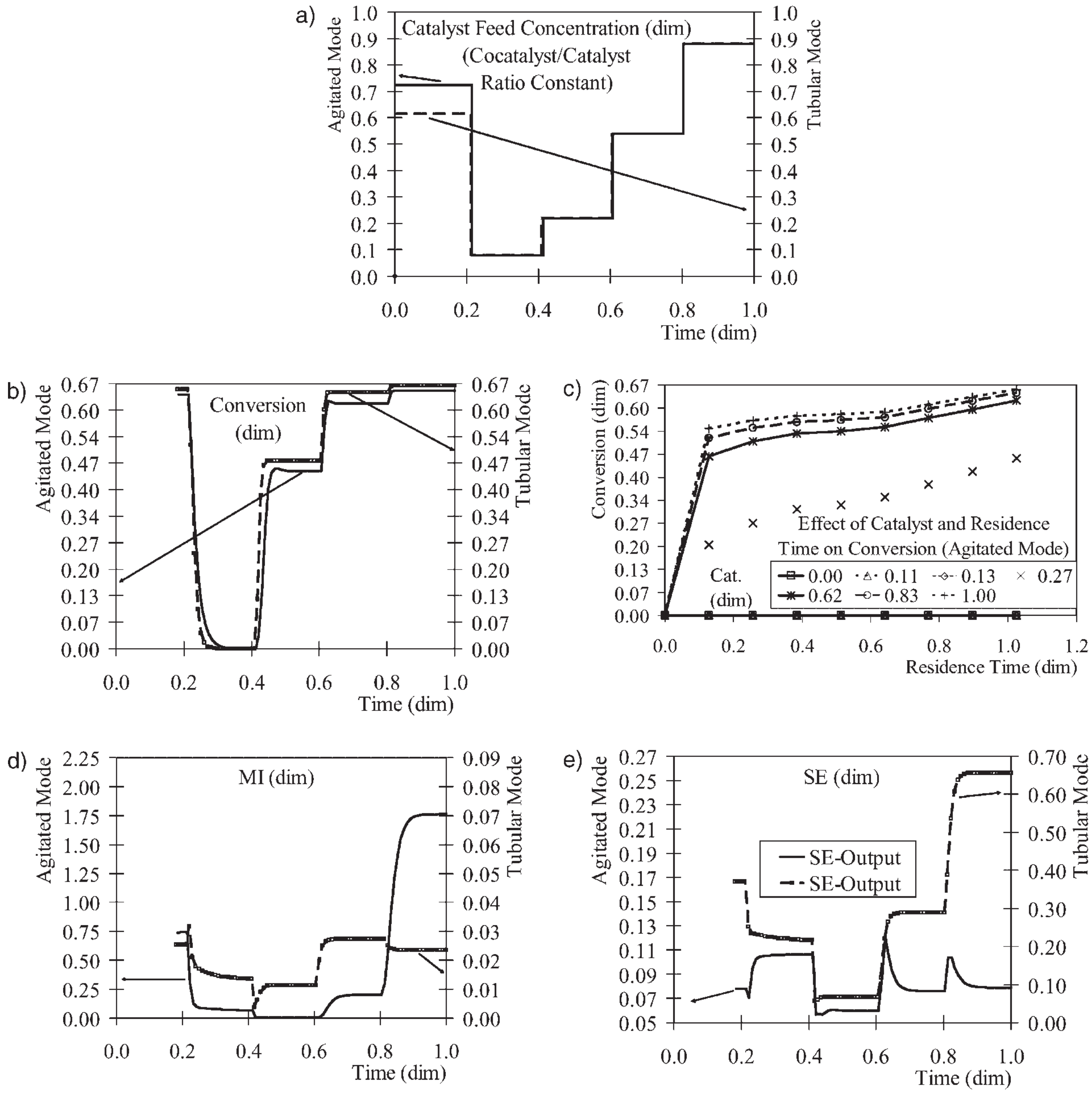

*Figure 6*. Step perturbations of the catalyst feed concentration (cocatalyst/catalyst ratio constant) (a) and process responses (b–e).

tubular mode are also presented in Figure 6 and 7. Figure 6 shows, for both operating modes, that monomer conversion initially increases very fast with the increase of catalyst concentration, but afterwards tends to stabilize. This is mainly due to the increase of reactor temperature and catalyst decay. Therefore, from a practical point of view, there is a very sharp optimum value for catalyst concentration in both operating modes, beyond which no significant gain in polymer production is obtained due to catalyst decay. It is also interesting to observe that the increase of catalyst concentration is followed by a very sharp increase of both MI and SE, due to the larger temperature and monomer concentration gradients obtained. Figure 7 shows that, as the cocatalyst concentration increases, both MI and SE also tend to increase, because the cocatalyst molecules act as chain transfer agents and therefore affect the molecular weight distribution of the final polymer chains.[5–7] However, it is very interesting to observe that if the cocatalyst concentration falls below a certain minimum value, monomer conversion may drop dramatically (this is confirmed by plant experience). This occurs because of the unavoidable presence of catalyst and cocatalyst poisons in the reaction environment. If cocatalyst is not added in excess in regard to the polymerization

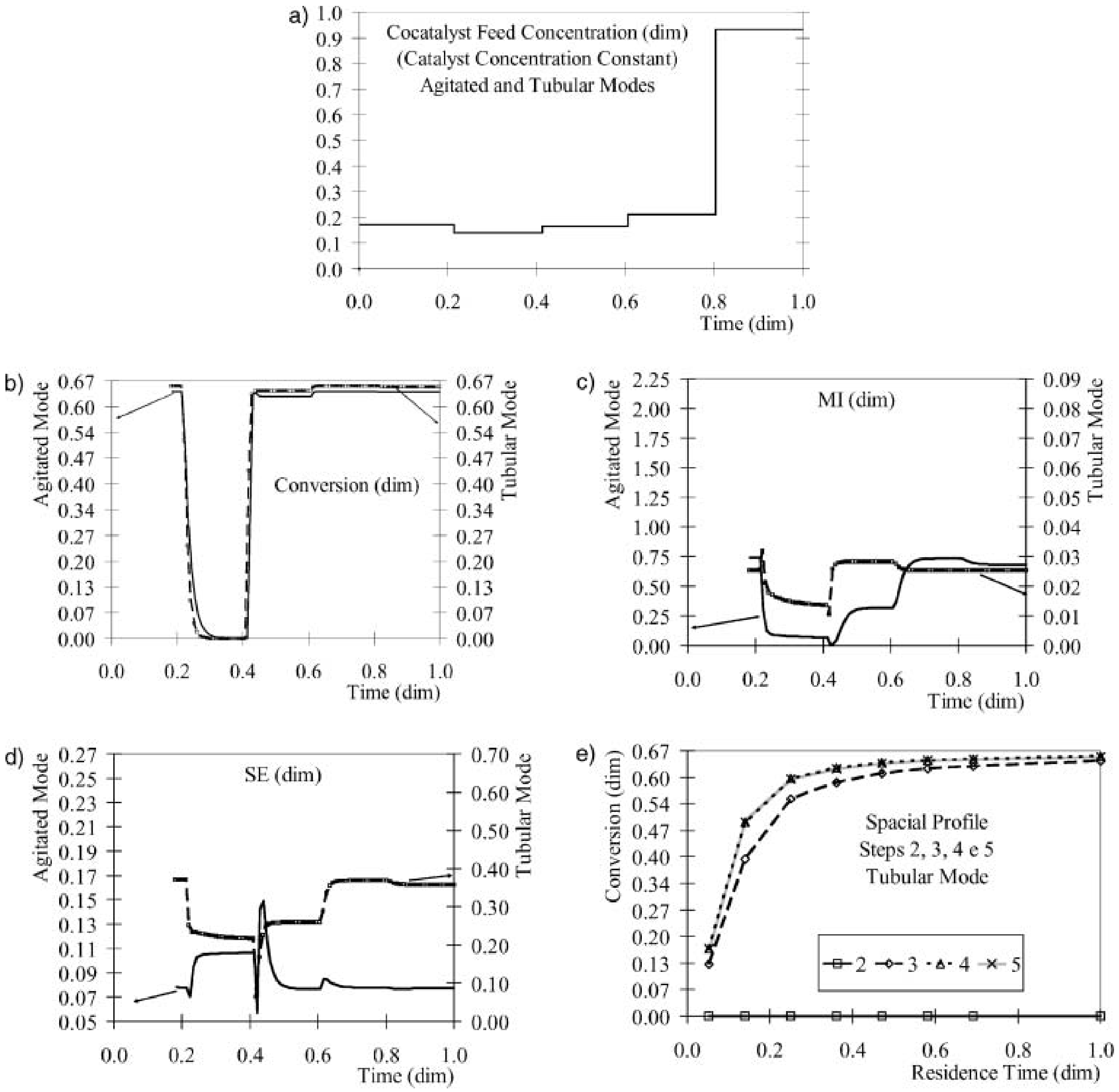

*Figure 7.* Step perturbations of the cocatalyst feed concentration (catalyst concentration constant) (a) and process responses (b–e).

poisons, catalyst activation does not occur adequately and reaction rates decrease very significantly.

Figure 8 shows the effect of the simultaneous variation of catalyst and cocatalyst feed concentrations upon the monomer conversion. Figure 8 shows that there are minimum catalyst and cocatalyst feed concentrations needed to reach any specified monomer conversion level. However, as drop of monomer conversion is dramatic below these minimum levels, both catalyst and cocatalyst feed concentrations are always added in excess in regard to these minimum amounts. Figure 8a and b also shows that there is an optimum cocatalyst feed concentration for each catalyst feed concentration specified, which leads to maximum polymer productivity. Once more, the optimum is placed very close to the boundary where the sharp decrease of monomer conversion begins. Therefore, cocatalysts are also added in excess in regard to this optimum level, which does not cause significant reduction of polymer productivity. Figure 8b also shows the geometric place of optimal cocatalyst/catalyst ratios. It may be observed that this optimum varies, as a consequence of catalyst decay and type and concentration of impurities.

Figure 9 shows how monomer conversion responds to simultaneous changes of the catalyst feed concentration and total feed flow rate (residence time). It may be observed that, in order to reach a specified monomer conversion level, there is an optimum operating condition constituted by a minimum amount of catalyst required and a

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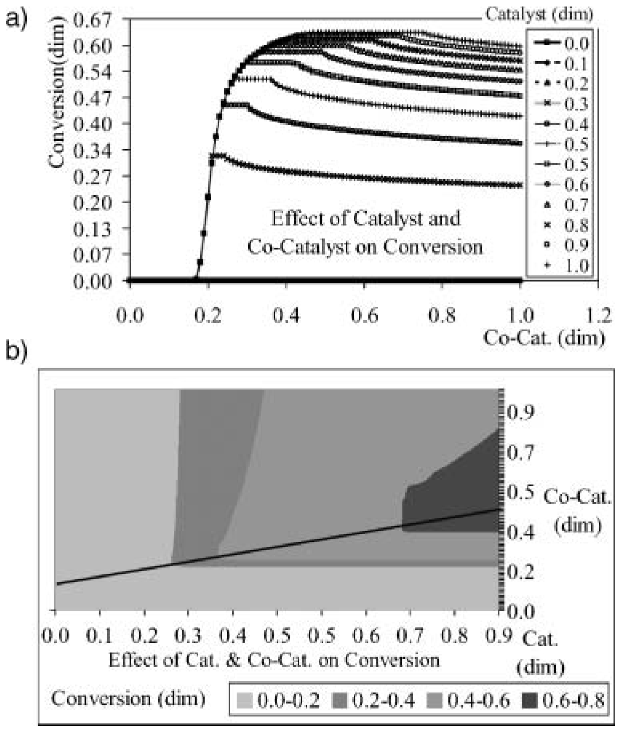

*Figure 8.* Process responses to simultaneous changes of catalyst and cocatalyst feed concentrations in the agitated mode.

minimum residence time (maximum polymer production). Above the minimum residence time level, conversion increase is very small, so that the process should be operated close to the point of minimum to maximize polymer throughput. Above the minimum catalyst concentration level, the monomer conversion increase is also very small, as already observed in the previous paragraph. Observe that monomer conversion is also very sharp below the minimum residence time level, as observed previously for catalyst and cocatalyst concentrations. Therefore, feed flow rates should be kept below the optimum value to avoid too much variation of polymer production rates due to process disturbances, such as catalyst and cocatalyst poisoning.

It is important to say that process responses to variations of catalyst feed concentration, cocatalyst feed concentration and feed flow rates are largely influenced by the catalyst decay. When catalyst and cocatalyst feed concentrations increase, polymer production also increases, leading to the increase of reaction temperature. Beyond a certain limit, monomer conversion is limited by the strong increase of the rates of catalyst decay, as the system operates adiabatically. Similar behavior is observed when the feed flow rates decrease (and feed composition is kept constant) and monomer conversion increases.

In the industrial practice the comonomer/monomer feed ratio is manipulated to control polymer density.[5,8]

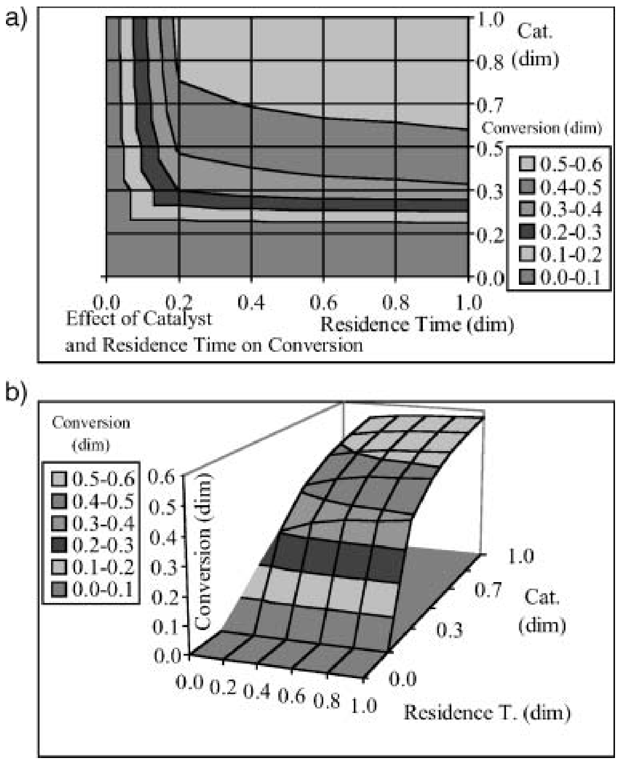

*Figure 9.* Process responses to simultaneous changes of catalyst feed concentrations and total feed flow rates in the agitated mode.

The but-1-ene comonomer introduces small branches into the polymer chains, yielding a resin with lower density. Figure 10 illustrates that the model is able to predict the expected behavior for both operating modes, when step changes are introduced in the comonomer/monomer feed ratio. The comonomer also modifies the overall rates of propagation and chain transfer reactions, affecting the evolution of the MI. Figure 10 shows that the decrease of the average molecular weight of the polymer, caused by the increasing comonomer compositions, leads to the increase of the MI of the final resin.

Given the importance of the degree of mixing to explain process variations, Figure 11 shows process responses to changes of the degree of mixing presented in Figure 11a, using the basic tubular configuration. It is very interesting to observe that the impact of the degree of mixing on the process performance is very small, if no other process input is changed. This shows very clearly that the mixing conditions tend to magnify the influence of process perturbations, but cannot be used as a control tool without simultaneous manipulation of other process variables. At best, the degree of mixing can be used for fine tuning of process operating conditions, but not for design of resin grades, for instance.

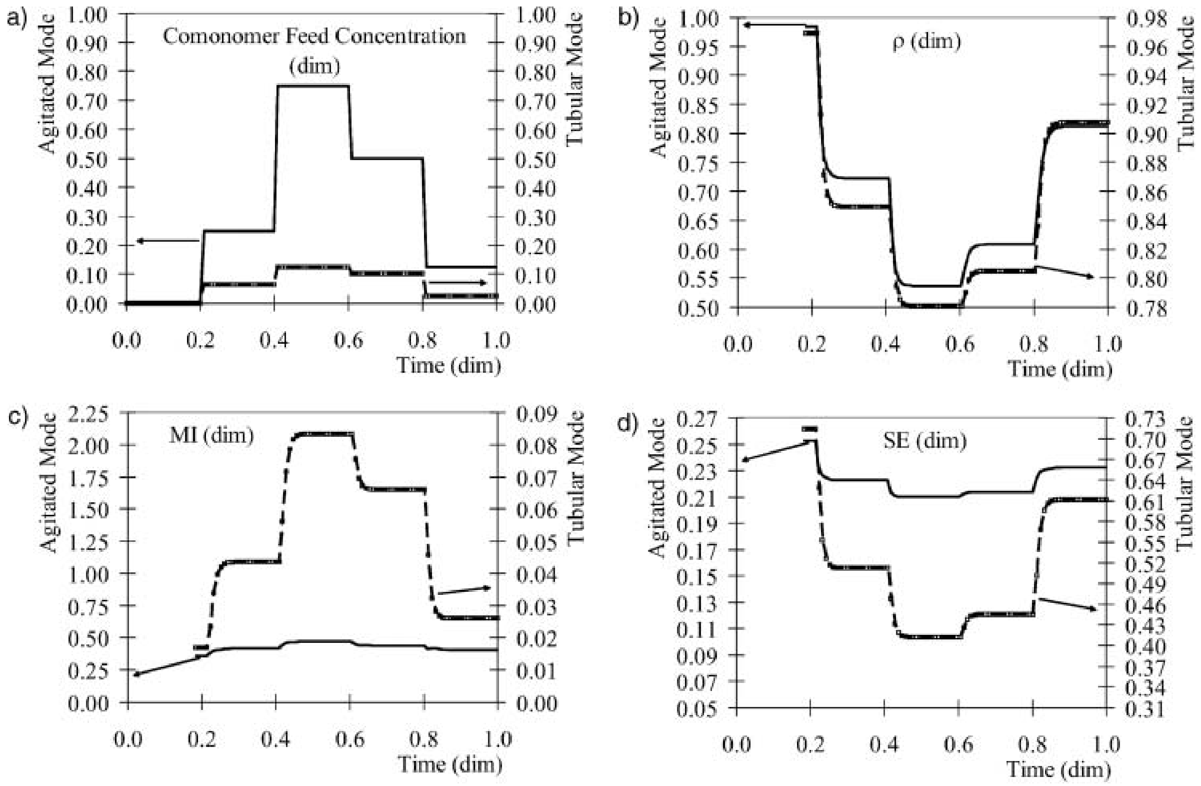

*Figure 10*. Step perturbations of the comonomer feed concentration (a) and process responses (b–d).

The results of this section show very clearly that process responses to feed perturbations are very nonlinear. As shown in these figures, response gains to increasing input values may be very different from response gains to decreasing input values at nominal conditions. This nonlinear behavior is largely determined by the catalyst decay, but is also determined by the natural nonlinear characteristics of the MI and SE functions.[5–7] Therefore, nonlinear and varying response gains should not be disregarded during the development of control strategies for in-line process control.

## Flowsheet Effects

An interesting feature of industrial solution Ziegler-Natta polymerization processes is the possibility of modifying the reaction environment through addition of lateral feed streams. Figure 12a shows the sequence of perturbations of the lateral feed flow rate used to analyze process responses in the agitated mode. Figure 12b shows process responses obtained when the lateral feed stream is inserted at different zones of the agitated reactor vessel. It is important to observe that the process responses are sensitive to changes of both the lateral feed flow rate and the feed location. Even more important is the fact that modifications of the lateral feed flow rate cause MI and SE to vary along opposite directions. As observed previously, process changes usually tend to cause the simultaneous increase or decrease of both MI and SE. However, the manipulation of the lateral feed flow rate allows the reduction of SE and increase of MI simultaneously, which means that this is an important control variable for design of resin grades and independent manipulation of MI and SE. It is also important to observe that process responses to changes of the lateral feed flow rate depend on the feed location, which adds additional flexibility to the control problem. In this sense, Figure 12 reveals an interesting nonlinear effect. Zones 4 and 5 interchange its influence on the properties, depending on the lateral feed level.

Figure 13 shows a similar study for the tubular mode. However, in this case only hydrogen is partially fed through a lateral feed stream. Figure 13 shows that variations of the hydrogen feed flow rate and of the feed location may cause a tremendous impact upon the properties of the final polymer resin. Besides, it is shown again that MI and SE respond differently to the process perturbations, which means that the use of lateral feed streams adds enormous flexibility to the production of different polymer grades. For instance, it can be seen that variations of the hydrogen feed flow rate at an intermediate position of feed tubular reactor (variation 2) has a

DOI: 10.1002/mren.200700047

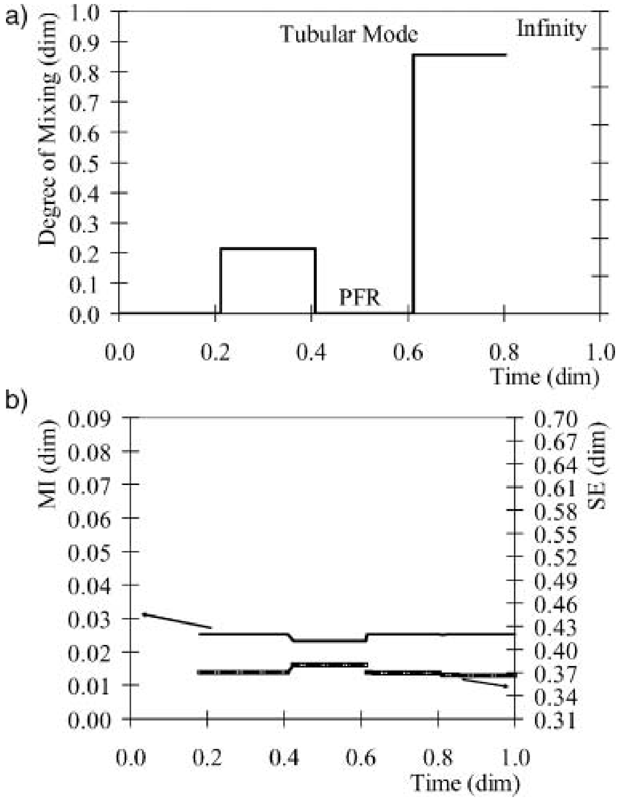

*Figure 11*. Step perturbations of the degree of mixing for the tubular configuration (a) and process responses (b).

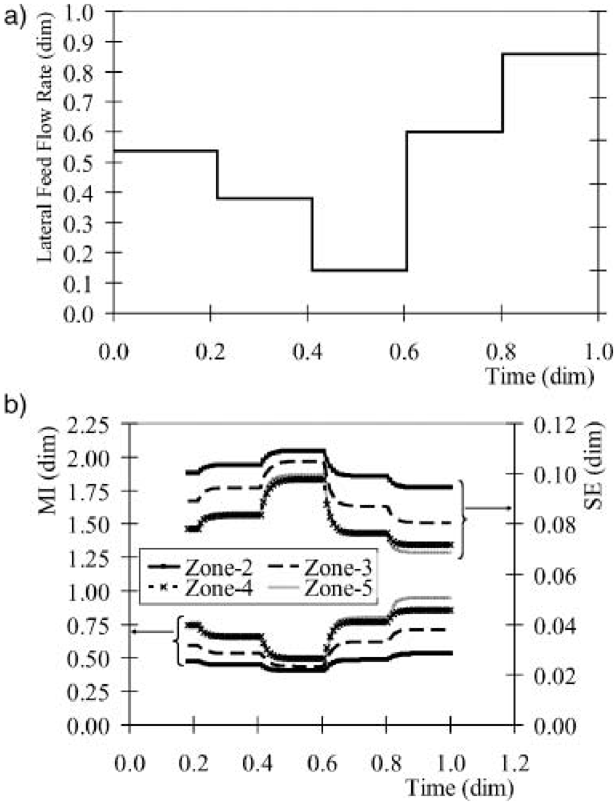

*Figure 12*. Step perturbations of the lateral feed flow rate for simulation studies in the agitated mode (a) and process responses to changes of the lateral feed flow rate at different feed points (b).

great effect on MI, whereas similar variations at the feed of stirred reactor (variation 1) has a negligible effect. Moreover, an important nonlinear effect is observed. When hydrogen is fed at the beginning of the system (first point in both simulations, variations 1 and 2), SE decreases with increasing hydrogen, whereas an opposite effect is observed when the hydrogen injection is made in an intermediate position (in either case, at intermediate position of feed tubular reactor, variation 2, as well as at the feed of stirred reactor, variation 1). In the former case, the hydrogen at the beginning of the system compensates the high temperature of the end of the system, narrowing the MWD. In the second case, two very distinct polymers are produced, which broads the MWD. This result is in agreement with experimental observations.

The number of reactor zones used in the agitated mode may be varied through manipulation of the axial agitation profiles. Figure 14 shows process responses to variations of the number of reaction zones. As it may be observed, monomer conversion levels are not too sensitive to changes of the number of reaction zones. However, MI and SE change considerably when the number of reaction zones changes. It may be observed again that MI and SE vary along opposite directions. Therefore, manipulation of the axial agitation profiles also adds an interesting control window for design of polymer grades. If the agitation speed is varied simultaneously with the number of reaction zones, then process responses may be magnified even further, as shown in Figure 14.

In all cases analyzed in this section, the extra degree of freedom for independent control and design of resins with different MI and SE is added by the possibility of controlling the axial concentration profiles along the reaction vessels. As shown in Figure 12–14, this may be achieved through manipulation of lateral feed flow rates or through manipulation of axial mixing profiles. This means that the sequence of reactors presented in Figure 1 may be operated as if different reactor vessels of different sizes were aligned for polymerization through the manipulation of the axial mixing profiles.

## Sensitivity Analysis

Finally, a series of dynamic simulations were performed, where process inputs were perturbed individually as a series of step perturbations, in both directions (increasing and decreasing values), covering the whole range of industrial interest.[5] Based on the steady state values,

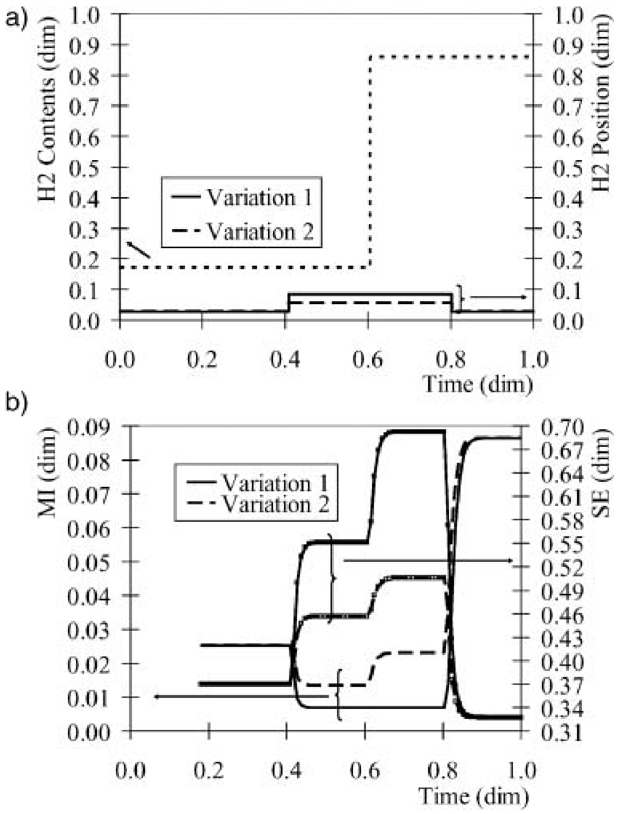

*Figure 13.* Step perturbations of the lateral hydrogen feed flow rate and of feed location for simulation studies in the tubular mode (a) and process responses (b).

sensitivity factors were defined as:

$$S_{y,x} = 100 \cdot \frac{y_i - y_0}{y_0 \cdot (x_i - x_0)} \qquad (1)$$

where $S_{y,x}$ is the $y$-process output sensitivity to variations of the $x$-process input, $x_0$ and $y_0$ are the reference initial values for process inputs and outputs, respectively, and $x_i$ and $y_i$ are the observed input and output values obtained after perturbation. As all process inputs were normalized to be in the interval [0,1], the sensitivity factors are defined as relative variations of process outputs when subject to process input perturbations in the normalized process input range. As the process is very non-linear, results were averaged in the whole process input range. Average results obtained for the agitated and tubular modes are presented in Table 1 and 2.

Table 1 shows that the most important process inputs for the agitated mode are the catalyst feed composition (which may be used to fine tune the reaction temperature), the monomer feed composition (which may be used to define the polymer production) and the cocatalyst feed composition (which may be used to control the monomer conversion). In this case, it is implicitly assumed that the residence time (total feed flow rate) is placed at the optimum value in order to minimize catalyst consumption, as discussed in the previous sections. The remaining variables are largely controlled by these three process inputs, if the flowsheet configuration is kept constant. For this reason, any modification of catalyst activity, induced by the increase of the inhibition rates or by the increase of catalyst and/or cocatalyst poison concentrations, may cause simultaneous decrease of polymer production and loss of control of final properties of the polymer resin. Therefore, catalyst activity (and monomer conversion) must be controlled very tightly.

Due to the large influence that the input variables normally used to control polymer productivity also exert upon the final polymer properties, the hydrogen feed concentrations must be manipulated to allow the control of the final MI and SE of the polymer resin. In this case, lateral feed flow rates and axial agitation profiles must then be used to fine-tune the MI and SE values of the polymer grades, as discussed previously. As the density of the final homopolymer resin is basically defined by the MI and SE of the polymer material, no sort of independent control may be devised for this variable. However, the density can be made smaller, if a varying amount of comonomer is added to the feed stream.[5,8] From the control perspective, it is very interesting to observe that grade transitions are usually determined by changes of the feed policy and of the mixing profiles, and not only by changes of the hydrogen and comonomer feed concentrations, as normally performed in Ziegler-Natta processes.

Table 1 also shows that $\Delta P$ and $\Delta T$ may be used very effectively to monitor the performance of the process operation, given the very high sensitivity to changes of the catalyst activity. This is in fact used at the plant site for detection of abnormal operating conditions and fast in-line correction of catalyst activity and resin properties.

Table 2 shows that the general process behavior is almost the same when the plant is operated in the tubular mode. Figure 15 depicts the sensitivity of the most important variables to control MI and SE. This diagram is useful to determine compensatory actions to adjust both properties simultaneously. It shows, once more, that catalysts, and mainly hydrogen, are the most important methods to control resin properties.

## A Comparison between Agitated and Tubular Modes

Since both modes present operational restrictions on the maximum outlet temperature, due to phase separation problems, and the tubular one presents an additional constraint on the minimum inlet temperature, also due to phase separation problems, the available temperature rise

DOI: 10.1002/mren.200700047

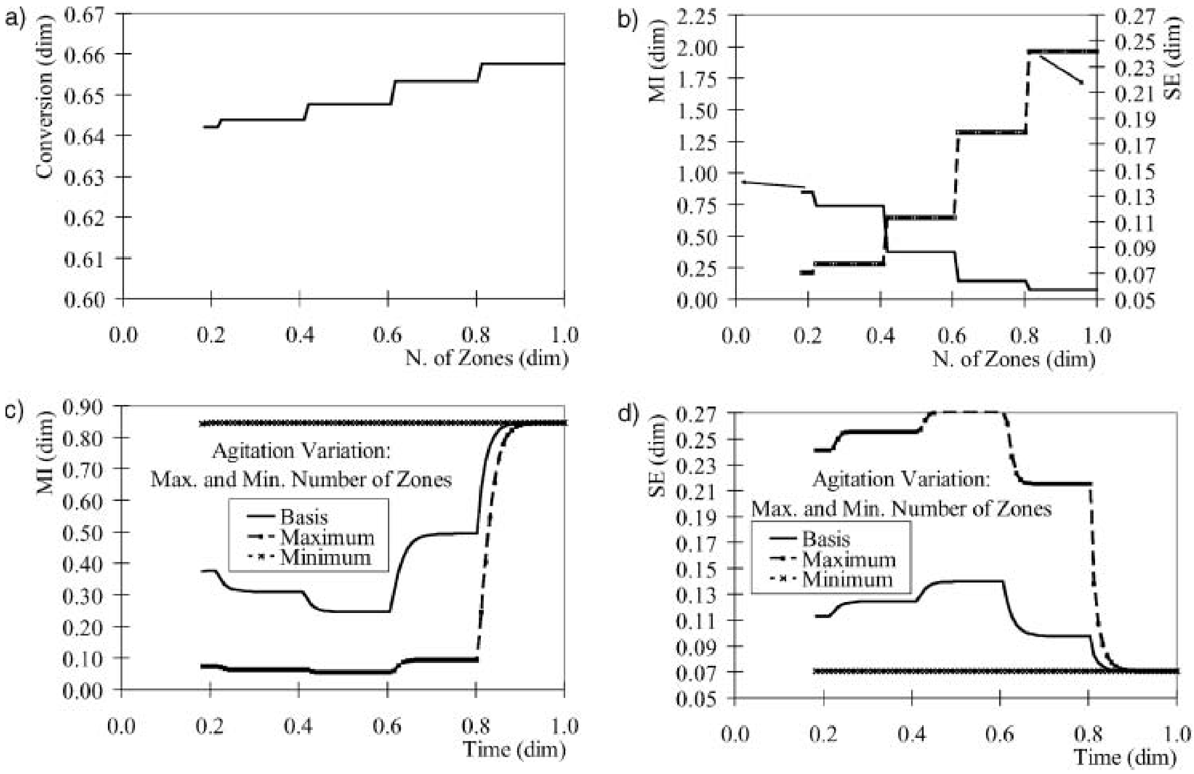

*Figure 14.* Process responses to changes of the number of reaction zones and to simultaneous changes of the number of reaction zones and of the agitation speed in the agitated mode.

is lower in tubular mode. Therefore, the agitated mode allows higher production rates. On the other hand, higher conversions are achieved in the tubular mode, since it must operate with lower monomer concentrations and/or lower flow rates.

In the case of polymer properties, there are important dissimilarities. Due to its distributed characteristic, and a combination of low temperatures and high monomer concentrations at the beginning, and high temperatures and low monomer concentrations at the end of the system, a broad MWD material is produced in the tubular mode. On the other hand, a low SE resin is produced in the agitated mode. Moreover, at least in the strict sense of the polymerization reaction, the tubular mode allows the production of lower MI resins, since a significant amount of reaction occurs in mild temperature conditions, which propitiate the production of high molecular weight polymers. These facts imply in slightly higher densities in the agitated mode, is spite of a lower SE, and a higher head loss in the tubular mode, in spite of a lower production rate.

Besides the differences mentioned above, it might be observed that the gain directions of some input variables are different in the two modes, at least in the operating condition selected. Some examples of these opposite phenomena are:

- The increase of feed temperature leads to a slight SE increase in tubular mode, and a slight SE decrease in the agitated one;
- MI decreases with the increase of monomer amount in the tubular mode;
- The flow rate decrease results in a lower MI and higher SE material in the tubular mode; and,
- The increase of co-catalyst amounts may causes a MI decrease in the tubular mode.

Most of the described effects, however, seem to depend greatly on the particular steady-state around which the process is operated. In other words, the gain directions may change, depending on the specific situation. In this sense, the tubular mode seems to present an even greater non-linear behavior than the agitated mode.

Another important difference between the two modes is the SE sensitivity. As pointed out earlier, this variable is much more sensible, and therefore much more controllable, in the tubular mode. From the dynamic point of view, in spite of a greater time delay in the tubular mode, similar behaviors are observed for both setups.

In brief, given the distinct behaviors of both configurations, it is possible to say that the usage of the different

*Table 1.* Average sensitivity factors for the agitated mode. Suggested pairings for control purposes are in **bold**, the most important input effects on outputs are in *italic*, and the most important input effects for particular outputs are underlined.

| | $x$ | $W_u$ | Cat. | $\Delta T_{Int}$ | $T$ | MI | SE | $\Delta T_{Tot}$ | $\Delta P$ | $\rho$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $[CC]_e/[C]_e$$^{a)}$ | **2.268** | 2.266 | 3.069 | 23.35 | 2.174 | *63.64* | 0.086 | 2.518 | 36.95 | 0.174 |
| $[M]_e$ | −0.738 | **4.250** | −*25.689* | 8.754 | 4.207 | 5.944 | −0.035 | 4.874 | 6.076 | 0.011 |
| $W_e$ | 0.027 | 0.891 | ***2.322*** | 0.974 | 0.026 | −1.091 | 0.019 | 0.030 | 2.063 | −0.002 |
| $F$ | −0.031 | −0.031 | 0.819 | ***−4.233*** | −0.031 | 1.869 | −0.059 | −0.036 | −0.863 | 0.003 |
| $[C]_e$ | 0.586 | 0.586 | 0.950$^{a)}$ | −3.471 | **0.506** | *9.845* | 0.022 | 0.586 | −5.797 | 0.027 |
| $[H_2]_e$ | 0.002 | 0.002 | 0.466 | −2.156 | 0.000 | ***8.130*** | −0.038 | 0.000 | −3.569 | 0.015 |
| $[CM]_e$ | −0.542 | 0.551 | −0.970 | −0.498 | 0.029 | 0.784 | −0.071 | 0.163 | −0.985 | ***−1.235*** |
| $T_e$ | −0.026 | −0.026 | −0.714 | −0.070 | 0.136 | *1.039* | −0.005 | −0.227 | −0.435 | 0.002 |
| Ag. | 0.000 | 0.000 | 0.100$^{a)}$ | *−0.231* | 0.000 | 0.064 | −0.003 | 0.000 | −0.025 | 0.000 |

$^{a)}$Average of absolute values.

*Table 2.* Average sensitivity factors for the tubular mode. Suggested pairings for control purposes are in **bold**, the most important input effects on outputs are in *italic*, and the most important input effects for particular outputs are underlined.

| | $x$ | $W_u$ | $\Delta T_{Tot}$ | Cat. | $\Delta T_{Int}$ | $T$ | MI | $\Delta P$ | SE | $\rho$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $[CC]_e/[C]_e$ | **2.010**$^{a)}$ | 2.018$^{a)}$ | 2.490$^{a)}$ | −10.427 | *64.48*$^{a)}$ | 1.627$^{a)}$ | −*12.67*$^{a)}$ | 8.390$^{a)}$ | 6.645$^{a)}$ | 0.091$^{a)}$ |
| $[M]_e$ | −0.823 | **5.042** | 4.184 | *13.57*$^{a)}$ | 12.757 | 2.780 | −2.650 | 11.999 | 0.134$^{a)}$ | −0.007 |
| $W_e$ | −0.010 | 0.745 | −0.013 | ***2.568*** | 1.766 | −0.008 | 0.326 | 1.224 | −0.033 | 0.000 |
| $[C]_e$ | 0.608 | 0.609 | 0.678 | *−3.415* | *−8.825* | **0.443** | 1.792$^{a)}$ | 1.091 | 1.048 | 0.019 |
| $[H_2]_e$ | −0.013 | −0.013 | −0.021 | 1.082 | −0.787 | −0.014 | ***10.659*** | −5.494 | −0.350 | 0.017 |
| $[H_2]_{z,e}$ | −0.001 | −0.001 | −0.004 | −0.004 | −0.077 | −0.002 | *1.533* | −0.412 | **0.196** | 0.006 |
| $[CM]_e$ | −0.240 | 1.045 | 3.571 | −6.069 | 2.689 | 0.187 | *11.191* | −7.140 | −0.567 | **−9.053** |
| $T_e$ | −0.017 | −0.015 | −0.180 | *−2.005* | −0.909 | 0.200 | 0.769 | −0.318 | 0.028 | 0.002 |
| Ag. | −0.002 | −0.002 | −0.003 | *0.228* | −0.114 | −0.002 | 0.000 | −0.004 | 0.000 | 0.000 |

$^{a)}$Average of absolute values.

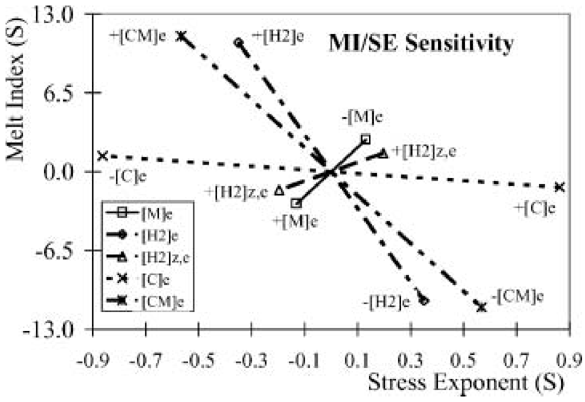

*Figure 15.* General trends in the control of MI and SE in the tubular mode.

modes, besides other intermediate ones, furnishes a great flexibility and an excellent alternative to produce a variety of different grades, within a large range of property values.

## Conclusion

The behavior of continuous solution ethylene/but-1-ene polymerizations through Ziegler-Natta catalysts was analyzed, based on a previously developed mathematical model. Dynamic simulations were carried out and process responses were analyzed as functions of process operating policies and flowsheet configuration, at conditions that resemble the actual operation of industrial sites. It was shown that system responses are highly nonlinear and very sensitive to disturbances of the operating conditions

DOI: 10.1002/mren.200700047

and that catalyst decay is of fundamental importance for proper understanding of process behavior. Results indicated that process responses are largely dominated by fluctuations of the input variables that normally define the polymer throughput, so that catalyst activity and monomer conversion must be controlled very tightly at the plant site. Besides, it was shown that mixing conditions inside the reactor vessels exert a significant impact upon the final polymer quality and can be manipulated for in-line control of final resin properties. However, mixing effects are greatly magnified if other process inputs are manipulated simultaneously and if it is possible to impose different axial mixing profiles upon the reaction line. In this case, it was shown that the development of feed policies and axial agitation profiles, based on the use of lateral feed streams and variation of number and agitation conditions of the reaction zones, allows for simultaneous control of MI (melt flow index), SE (stress exponent) and $\rho$ (polymer density) of the final polymer resin.

## Nomenclature

| | |
|---|---|
| C | Catalyst; |
| CC | Co-catalyst; |
| CM | Comonomer; |
| $F$ | Lateral feed; |
| H | Hydrogen; |
| M | Monomer; |
| MI | Melt index; |
| $P$ | Pressure; |
| $S$ | Sensitivity coefficient; |
| SE | Stress exponent; |
| $T$ | Temperature; |
| $W$ | Mass flow; |
| $x$ | Conversion; |
| $x$ | Input variable; |
| $y$ | Output variable; |
| [] | Concentration. |

### Greek Letters

| | |
|---|---|
| $\Delta$ | Difference Operator; |
| $\rho$ | Density. |

### Subscripts

| | |
|---|---|
| 0 | Basis point for sensitivity calculations; |
| e | Feed, input; |
| $i$ | Generic point for sensitivity calculations; |
| u | Dead polymer; |
| $x$ | Input variable; |
| $y$ | Output variable; |
| $z$ | Intermediate position. |

### Abbreviations

| | |
|---|---|
| Ag. | Agitation; |
| Cat. | Catalyst; |
| Co-Cat. | Co-Catalyst; |
| CSTR | Continuous Stirred Tank Reactor; |
| Dens. | Density; |
| dim | Dimensionless; |
| Int | Internal; |
| Max. | Maximum; |
| Min. | Minimum; |
| MWD | Molecular Weight Distribution; |
| N | Number; |
| PFR | Plug Flow Rector; |
| RT | Residence Time; |
| Tot | Total; |
| TR | Tubular Reactor. |

Acknowledgements: We thank *CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico* – and *FAPESB* for supporting our work and for providing scholarships for the authors. We also thank *Braskem* for providing technical information and extensive plant data. Finally, we thank *CADCT*, *PADCT* and *PRONEX* for supporting our research activities.

Received: November 19, 2007; Revised: January 17, 2008; Accepted: January 18, 2008; DOI: 10.1002/mren.200700047

Keywords: ethylene; polymerization; process operation; soluble; Ziegler-Natta

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