On-Line Parameter Estimation in a High-Pressure Low-Density Polyethylene Tubular Reactor

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The high throughput and operating cost of the reactor provide the economic incentive in considering the on-line optimization of the LDPE tubular reactor. For an on-line optimization procedure it is crucial to develop a flexible and adaptive on-line parameter estimator, which based on the appropriate measurements from the reactor will adjust certain key model parameters so that the model can capture the actual reactor operation and reliably be used for the real-time optimization of the reactor performance. Various issues involved in developing the on-line estimator for such applications as the mathematical modeling of the reactor, the selection of the adjustable model parameters and reactor measurements, the decomposition of the problem according to the characteristic time constants of various disturbances, and the efficient and robust solution of the mathematical problem are discussed. The tools developed were successfully used on an EXXON high-pressure LDPE tubular reactor. Results from the numerical experiments that are compared with scaled data from a real reactor show that the estimated temperature profiles agree remarkably with those observed at various phases of the reactor operation.

Introduction

The annual production of low-density polyethylene (LDPE), that includes homopolymer and copolymer grades with densities ranging from 0.91 to 0.93 g/cm^3, is estimated to be over 15 Mt/yr, a figure that represents almost a quarter of all commodity polymers industrially manufactured. LDPE is mainly produced in high-pressure tubular or autoclave reactors by free-radical polymerization, initiated by oxygen or the chemical decomposition of peroxides and/or azo compounds. A multitude of LDPE grades is usually produced from a single reactor line. The properties of these grades are to a great extent determined by the operating conditions within the reactor.

The multiproduct operation of the high-pressure LDPE reactors is imposed by two critical factors, namely:

1. The extreme operating conditions (e.g., pressures 2,500–3,000 atm and temperatures 250–300°C) required for the free-radical polymerization of ethylene.
2. The wide spectrum of the LDPE products with relatively close molecular and morphological properties, yet with distinct end-use applications.

The two major tasks in the operation of a tubular LDPE reactor are the minimization of off-spec polymer production during a grade transition and the selection of the optimal operating conditions to ensure the production of a certain polymer grade. The latter is quite a nontrivial problem for a tubular LDPE reactor due to the significant variability of the reactor performance, which is gradually manifested within the time horizon of a single polymer grade production.

The major sources of this variability are the fouling of the inner wall surface due to polymer deposition (Hwu and Foster, 1982), and the accumulation of impurities due to ethylene recycling. Note that the ethylene conversion achieved in

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the reactor is about 20–30% per pass. As the state of the reactor changes (such as fouling and level of impurities), the operating conditions (such as initiator and coolant flow rates) are to change accordingly to keep the production within the desired specifications. This necessitates the revaluation of the reactor state in time intervals determined by the timing of its variability and the reset of the manipulated variables.

The current practice in the industry undertakes this task with a net of complex recipes that includes trains of control actions, based on the expertise developed around the operation of such reactors. Taking into account the complexity of the phenomena occurring within the reactor, the optimality of such operating decisions can be hardly claimed. Considering though the high throughput of the LDPE tubular reactors together with the significant operating costs and the tight profit margins of the LDPE market, the economic incentive in seeking optimal operating conditions becomes obvious. Furthermore, the technical feasibility of such an endeavor is substantiated on the dynamic characteristics of the process and its variability.

An on-line optimization scheme can be generally applied to processes with fast dynamics that are subject to slow and persistent disturbances. The persistency of the disturbances is the feature that imposes the need for the on-line optimization of the operating conditions. The requirement for the mentioned relation between the characteristic time constants of the process and those of the disturbances is based on the fact that any manipulation of the process can only make sense if the process can absorb the intended manipulation before the disturbance changes significantly or ceases to exist.

A tubular LDPE reactor consists of a number of reacting and cooling zones arranged in a certain sequence according to the reactor design and product specifications. The total length of the tube is about 2 km and the mean residence time is about one minute. In the reacting zones very fast chemical reactions are taking place in short space times. These design and operating features result in fast dynamic responses. On the other hand, the process disturbances are orders of magnitude slower, since the reactor fouling and the impurities accumulation take hours in their gradual buildup. Conclusively, the LDPE tubular reactor presents itself as a role model candidate for the application of an on-line optimization scheme.

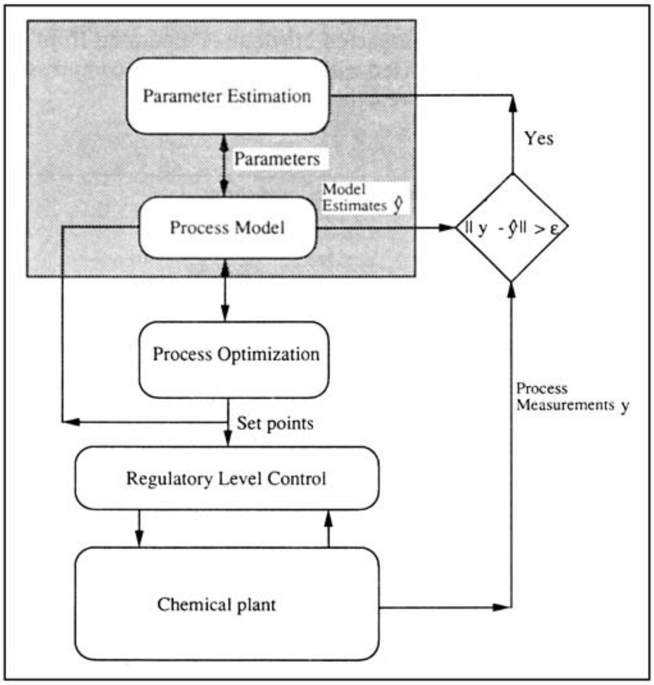

Figure 1. Hierarchical decomposition of the on-line optimization problem.

In the chemical engineering literature, the problem of the on-line optimization of the operation of a process has been motivated either by a change in the optimization objective, or by a change in the process characteristics (Cutler and Perry, 1983; Schuler and Schmidt, 1992). The on-line optimization level of a process operational scheme lies between the scheduling and the regulatory control problem, and its goal is to estimate within the framework of the process functioning determined at the scheduling level, the optimal operating policy to be carried out by the regulatory level controllers (Kiparissides and Ponnuswamy, 1981). A typical on-line optimization procedure, as is suggested by the consensus of the literature in the field (Jang et al., 1987; Robert and Williams, 1981; Krishnan et al., 1992), is based on the separation hypothesis and is organized in two basic phases (see Figure 1):

1. The elimination of process/model mismatch (on-line parameter estimation).
2. The determination of the optimal operating conditions based on the adapted mathematical model and a prespecified optimization objective.

The main attributes that the solution of an on-line parameter estimation problem has to observe, seen from the point of view of the on-line optimization, is to make the mathematical model of the process adapt in timely way to the process variability and predict accurately the performance of the process. Inaccurate predictions result in a suboptimal performance that defeats the purpose of the on-line optimization altogether, and loss of timing with the process results in unsynchronized optimization moves that may be obsolete at the time of their application.

The mathematical aspects of the on-line parameter estimation problem have been mainly addressed in the literature in the context of the general off-line parameter estimation problem that has an identical mathematical representation. Reviews on this problem can be found in Bard (1974), Biegler et al. (1986), Biradello et al. (1993), Tjoa and Biegler (1991), or in the context of the chemical process simulation and optimization, in Dovi and Reverberi (1993), Byrne and Ponzi (1988), Renfro et al. (1987), and Pantelides and Barton (1992). The scope of the general off-line parameter estimation problem is to validate, using process data, mathematical models describing the dynamic or steady-state behavior of a process by estimating the unknown model parameters (such as the kinetic rate constants and the heat transfer coefficient). In this sense, it is a problem that precedes its on-line counterpart. For the tubular LDPE reactor, such an off-line parameter estimation utility can be employed to estimate the various polymerization kinetic rate constants (initiator decomposition rate constants, propagation and termination rate constants, transfer to polymer rate constants, and so on) from off-line measurements on monomer conversion, molecular weight distribution, degree of branching, copolymer composition, and so forth.

The present work addresses the various aspects of the on-line parameter estimation problem as this is posed in a high-pressure tubular reactor. Any methodological inferences resulting from this study are appropriately underlined.

Problem Statement

The issues that have to be addressed in an on-line parameter estimation problem include the appropriate model description of the process, the selection of the model parameters and the process measurements and, finally, the identification of a robust optimization algorithm to solve efficiently the problem at hand. Specifically, these issues can be stated as follows:

1. Select the type of the mathematical model representation (steady-state vs. dynamic) to describe the process behavior in terms of process operating conditions. Check and validate the assumptions made in the modeling of the process against the expected and required accuracy of its performance.
2. Select the key model parameters to be regularly updated and the process measurements based on which the model parameters will be estimated.
3. Investigate the possible decomposition of the problem and synchronize the model parameter estimation based on the characteristic time constants of the process.
4. Formulate the optimization problem and select the most suitable numerical algorithm.

The issue of the model selection has been often discussed in the literature. The choice between steady-state and dynamic representation of a process is conjugated with the dynamic features of the process. For the tubular LDPE reactor, the dynamic response of the process is orders of magnitude faster than the grade shifts and the time constants of the varying process parameters. Thus, the steady-state representation of the LDPE reactor is judged to be adequate (Kiparissides et al., 1993). The use of a linearized dynamic model has also been suggested in the literature (Schbib et al., 1992), but given the nonlinear features of the reactor, such a choice cannot be considered in the present work.

As for the complexity of the process model to be employed, the trade-off between model accuracy and computational speed, generally results in assuming a simplified or a phenomenological model of the process (Rhinehart and Riggs, 1991; Jang et al., 1986). However, for the problem at hand, there are two basic reasons for disregarding this prejudice. The first is the complex interrelations between the various process variables and the stiffness in their variability, features that are bound to be distorted in an oversimplified model. The second is the availability of only secondary process measurements, a fact that enlarges the distance to be covered by the model and extends the problem addressed to one of a combined parameter and state estimation.

Regarding the selection of the key model parameters and the process measurements, Krishnan et al. (1992) presented a well-founded and integrated scheme for this stage of parameter estimation. The present work stands critically on the methodology of Krishnan et al. and, at least as far as the key parameter selection is concerned, presents several alternative criteria in a subsequent section.

The issue of the system decomposition and synchronization with the process has been mainly addressed in the literature in the context of control structures development (Morari and Stephanopoulos, 1980), yet the timing of the parameter estimation procedure to that of the process is of paramount importance in the actual implementation of the on-line optimization algorithm.

The optimization problem can be stated in a fairly general mathematical representation, as follows:

$$\min_{\theta} \Phi = \Phi(\|y - \hat{y}\|; \boldsymbol{\theta})$$

$$\text{.t.} \quad \frac{ds}{dx} = f(x, y, s, \boldsymbol{u}, \boldsymbol{m}, \boldsymbol{\theta})$$

$$g(x, y, s, \boldsymbol{u}, \boldsymbol{m}, \boldsymbol{\theta}) \leq 0$$

$$h(x, y, s, \boldsymbol{u}, \boldsymbol{m}, \boldsymbol{\theta}) = 0$$

where s denotes the vector of state variables, $\hat{y}$ and y are measured and estimated by the model output variables, respectively, $\boldsymbol{u}$ is the vector of the input variables, $\boldsymbol{m}$ represents the vector of manipulated variables, $\boldsymbol{\theta}$ denotes the unknown model parameters, and x is the independent variable (typically time or length). Φ is a norm (usually Euclidean) of the measured and estimated variable discrepancies.

Thus, the on-line parameter estimation of a tubular LDPE reactor ends up in the optimization of a quadratic objective function subject to a set of stiff implicit ordinary differential equations (see Appendix).

Presentation of the Engineering Problem

A typical production line of low-density polyethylene is shown schematically in Figure 2. The principal elements of the process include the ethylene compressors, the reactor line that consists of a long (up to 2 km), narrow, jacketed spiral tube and the flashes that separate the LDPE from the unreacted ethylene. The unreacted ethylene is separated from the polymer product, is mixed with fresh ethylene, is compressed, and is fed back to the reactor.

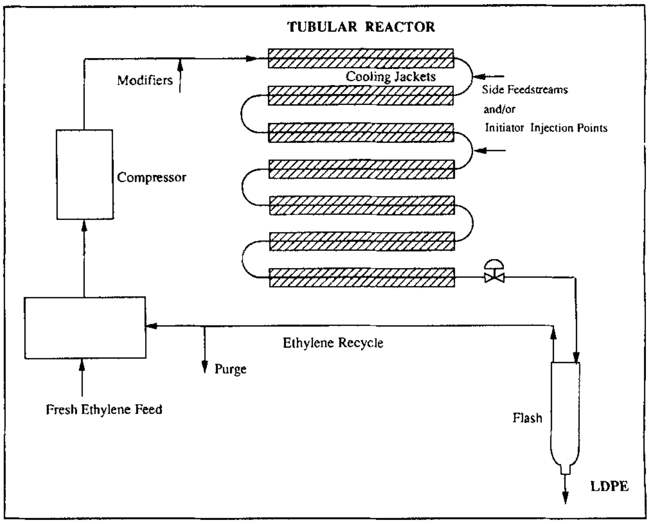

Figure 2. LDPE high-pressure tubular reactor production line.

The reactor usually has multiple ethylene, chain transfer agent (CTA), and initiator feed points. The reactor typically operates at pressures of about 2,500–3,000 atm and temperatures in the range of 150 to 300°C. The temperature ceiling is 340°C, above which ethylene is decomposed via a number of highly exothermic reactions to carbon, CH_4 and CO or CO_2, a thermal runaway that is catastrophic not only to the product but also to the reactor.

A number of grades can be produced from a single reactor line. The time scale of a grade shift is about 12 hours. The change in the grade production involves modifications in the feed streams and in the operating conditions. Although a grade change is generally performed through detailed and complex procedures, the reactor typically produces off-spec PE during transition phases.

While producing a single grade, the reactor line does not exhibit a typical steady-state operation, which is only interrupted by stochastic disturbances. During the reactor operation, the inner wall of the tube is relatively quickly fouled due to polymer deposition. The fouling of a reactor zone is partially overcome by a periodic increase of the reactor pressure by means of a control valve located at the reactor exit. The pulse motion of the valve results in an increase of the velocity, which tears away the polymeric deposits. However, the actual defouling of a reactor zone is principally effected by increasing the inlet temperature of the coolant in the relevant reactor jackets, which results in the melting of the polymer wall deposits. The time scale of the fouling–defouling cycles of the reactor operation is about 2–6 hours. Note that the increase in the coolant temperature necessitates a whole cycle of parallel control actions to ensure the safe operation of the reactor and the normal polyethylene production. In practice, this is the subject of present complex operational procedures.

Finally, due to the recycling of the unreacted raw material, impurities are accumulated in the system (Figure 2). It is important to note that the primary radicals produced by the chemical decomposition of the initiators are very sensitive to the presence of impurities, and their accumulation has an adverse effect on the overall efficiency of the initiators. In response to this slow changing disturbance, the reactor operation undergoes periods of impurities accumulation and purging. Furthermore, the actual initiator pump output, and consequently the concentration of the initiators in a reaction zone, can be subject to significant variations.

Overall, the operation of a high-pressure LDPE reactor is passing through regular cycles in its operational mode. Due to the extreme process conditions and the high throughput, the cost of a potential shutdown and start-up of the reactor is prohibitively high. All the operating cycles of the reactor line are performed in a nonstop manner by changing periodically the process conditions. This challenge is met in practice by the implementation, as mentioned earlier, of complex operational procedures based on the expertise developed around the reactor operation. The complexity of these procedures, the rigidity in their application, and their narrow scope are well understood if one considers the complexity and the degree of interaction of the manipulated and state variables. As a result, slight changes in the recipes might trigger unexpected and dramatic changes elsewhere in the process.

The ultimate goal is to have all these operational shifts performed automatically and optimally. This implies the development of an on-line parameter estimator capable of maintaining the model predictions in close agreement with process measurements despite the presence of time-varying process parameters.

Mathematical Model Developments

In the course of establishing an on-line parameter estimator the choice of a suitable model is the first and perhaps the most crucial decision. The main goal in any model development is the accurate representation of the physical and chemical phenomena taking place in the process. This means that a mathematical model for a high-pressure tubular LDPE reactor should include a detailed reaction mechanism, a system of differential equations describing the conservation of the various molecular species in the reacting mixture, and a number of algebraic expressions describing the varying physicochemical properties of the reaction mixture. The various model assumptions made are well accepted to have a marginal effect on the outcome of the model predictions. Although less execution time is always a valued merit in on-line implementation of a process model, the criterion for making any simplifying assumption should be based on the degree of its validity rather than on the reduction of the computational time.

In fact, the extensive and severe nonlinearities and the stiffness of the model magnifies the effect of an unwarranted assumption. Furthermore, the long distance between the available measurements and the control objectives, together with the rigidity of the control objectives, at least as far as the product quality is concerned, set a tight range for the allowable model inaccuracies.

Specifically, the available process measurements include the temperature profile along the reactor and the ethylene, solvent, and initiator input flow measurements. The control objectives include the ethylene conversion and the end-product properties (such as melt index and density). Between the former and the latter variables practically lies the whole of the reactor design and operation.

The most common physical and computational assumptions made in the development of a high-pressure LDPE reactor model include (Kiparissides et al., 1993):

1. One phase flow, which implies that in the range of the operating conditions of the reactor line, the ethylene–polyethylene mixture behaves as a supercritical fluid.
2. Stationary, plug flow conditions. This assumption is well justified for tubular LDPE reactors operating at high Reynolds numbers ($N_{Re} > 10^4$).
3. Quasi-steady-state approximation (QSSA) for the concentration of the primary radicals and the "live" polymer chains.
4. Negligible heat effects due to chain initiator, termination, and chain transfer reaction. Conventionally, all the heat of the polymerization reaction is assigned to the propagation step.

A detailed mathematical description of a high-pressure LDPE tubular reactor is presented in the Appendix. For more details, the reader can refer to Kiparissides et al. (1993) and Verros et al. (1993).

Solution approach

The set of the ordinary differential equations describing the steady-state behavior of an LDPE tubular reactor presents two serious complications. The first problem is that the system of the ODEs is substantially descaled and stiff. Temperature, pressure, and the concentration of the monomers and "dead" polymer chains on the one hand, and the concentration of the initiators and "live" polymer chains on the other, are of a substantially different order of magnitude both in their values and the rates of change. The second problem is related with the extremely fast reaction rates (initiators are consumed in less than 1 s). These problems are commonly addressed by the proper choice of the integration algorithm and/or the introduction of the QSSA.

Assuming that the QSSA is valid, then one can replace the moment differential equations for "live" polymer chains (see Eq. A8 in the Appendix) with the corresponding algebraic equations. Accordingly, the resulting differential algebraic equation (DAE) system can be expressed as follows:

$$\frac{ds_d}{dx} = f_1\left(\frac{ds_d}{dx}, s_d, s_a\right)$$

$$0 = f_2(s_d, s_a)$$

where

$$s_a = [\lambda_{i,i=0,1,2}^{j,j=1,2}, (\mathrm{R}\ )]$$

$$s_d = [\upsilon, y_{di,i=1,N_i}, y_{mi}, y_s, \mu_{i,i=0,1,2}, c_{LCB}, c_{SCB}, \theta, \theta_c, p]$$

where s_a and s_d denote the algebraic and the differential variables, respectively.

The more traditional approach in dealing with such a system has been that of solving the algebraic equations numerically to obtain the algebraic variables, s_a, in terms of the differential ones, s_d. The algebraic variables are then substituted into the differential equations, effectively converting them to a set of implicit ODEs in s_d, which can be solved using ODE numerical methods. However, since most ODE solvers require several solutions of the algebraic system as they calculate repeatedly the residuals of the differential equations, this approach may result in computationally expensive solutions. Alternatively, the simultaneous solution of the algebraic and the differential equations has been suggested (Brenan et al., 1989). Perregaard et al. (1992) conducted a comparative study of the two approaches and concluded that the relative efficiency of the two approaches depends on the relative number of the differential and the algebraic equations and the number of iterations required on the average to solve the algebraic system (see also Pantelides et al., 1988; Pontor and Gaethrop, 1991).

To minimize the computational burden in solving the system of DAE, it was assumed that the reaction rate of a P radical chain with an M_2 monomer is approximately equal to the reaction rate of a Q radical chain with an M_1 monomer. The last simplifying assumption, considered a corollary of the long-chain hypothesis (LCH), permits the analytical calculation of the ratio of the two zeroth moments λ_0^1 and λ_0^2 (Eqs. A26 and A27). Accordingly, substituting the analytical expressions for λ_0^1 and λ_0^2 into the original algebraic moment equations, the whole system is decomposed into two linear systems of two equations (λ_1^1, λ_1^2 and λ_2^1, λ_2^2) that can be solved analytically. The resulting system of implicit ODEs is adequately and efficiently solved using the Gears method as employed by the IMSL DGEAR routine.

For the solution of the optimization problem related to the parameter estimation, the general-purpose optimization routine DBCONF of IMSL and the GREG package were employed. The performance of both routines was proved to be equally acceptable for the cases studied.

Selection of the Model Parameters and Process Measurements

The selection of the key model parameters and process measurements is often a nonissue in most of the literature concerned with the on-line parameter estimation problem. The importance of this problem is underlined in the work of Krishnan et al. (1992, 1993) where a systematic methodology for the selection of the key parameters and the measured variables is described. According to this work, the key model parameters to be selected are those that have the greatest impact on the optimum operating conditions of the process. They are determined by performing a sensitivity analysis around the optimal operating point. As for the process measurements, their selection follows a series of nonnumerical and numerical steps.

The nonnumerical step is based on a structural analysis that analyzes the interrelationships among the process variables. This analysis establishes the connectivity of the measured variables and the adjustable model parameters by ensuring the accessibility of the measurements to the selected parameters, and the inclusion of all essential measurements, which is asserted by the rank of the observability matrix (e.g., full generic rank). The numerical phase of the procedure undertakes first a singular value analysis of the linearized transfer matrix that relates the measurements and the parameters, thus determining which measurements contribute to the larger singular values of the transfer matrix and so to accurate parameter estimates. Following the singular value decomposition, a confidence region analysis is carried out that selects, among the measurements that were not rejected by the previous steps, the set of measurements that have the smallest confidence region and induce the lowest interaction between the parameters.

Although this is a well-defined quantitative procedure for the selection of the adaptive model parameters and the process measurements, it is important to note that conceptually the whole procedure is structured around the optimization phase. In fact, the parameters are selected on the ground of their impact on the optimal operating conditions and the measurements are chosen on the basis of their ability to establish an accurate and reliable estimation of these parameters. Recognizing though that the process/model mismatch that is of concern in the on-line parameter estimation, is mainly due to the variability of the process itself, it is natural to select those model parameters that can actually describe the variability of the process.

The modeling of the process variability can be accomplished either by modeling its mechanism (mechanistic modeling of the variable initiator efficiency) or by representing phenomenologically this variability within the framework of a detailed process model (including a varying fouling factor in the estimation of the overall heat transfer coefficient). Alternatively, if the source of this variability is not known, one can choose empirical parameters that have an impact on the variables on which this variation is manifested, that is, the measured variables. The latter does actually correlate the parameters with the measurements, but in an inverse order to that proposed by Krishnan et al. (1992). Specifically, in the present work the parameter selection is based on the measurements that are principally affected by the long-term variability of the process.

The criterion proposed by Krishnan et al. (1992) and the one suggested here may result to similar choices for the estimated model parameters since both criteria will eventually resort to parameters that have the greatest impact on the process. However, it seems to be more appropriate to search for the adjustable model parameters within the context of the role they are called upon to play.

In an on-line optimization problem, the various process variables can be classified into:

- The input variables that include the process-manipulated variables (ethylene and side stream temperature), the process disturbances (fouling factors, impurities accumulation), and the model control variables (initiator, chain transfer agent, and coolant flows) used in the optimization.
- The state variables (pressure, the initiator, ethylene, comonomer, CTA and PE concentrations, and the polymer product macromolecular properties such as the molecular weight distribution (MWD), long-chain branching (LCB), and short-chain branching (SCB).
- The output variables that include process measurements (temperatures) and the variables that appear in the objective function formulation (melt index, density of PE, and monomer conversion).

From the process measurements, the level of the disturbances can be induced, and the adjustable model parameters can be estimated so that the model reproduces the performance of the real reactor (parameter estimation phase). Subsequently, the values of the control variables are estimated (optimization problem) by minimizing the chosen objective function.

Measurements and parameter selection for the LDPE reactor

Regarding the high-pressure tubular LDPE reactor, the selection of measurements is quite simple. Actually, as is widely mentioned in the pertinent literature, the only available measurements are the temperature profile of the reaction mixture and coolants in the various reactor zones and the melt flow index of the polyethylene product at the reactor exit.

Since the melt index measurements are available considerably less frequently than the temperature measurements, an inference technique (McAuley and MacGregor, 1991) can be employed in order to predict the desired properties based on easily available indirect process measurements. According to this scheme adjustable parameters in the property prediction equations are adapted on-line by a recursive least-squares method when the actual measurements become available.

As mentioned in the engineering problem presentation, the variability of the reactor can be identified in the fouling of the inner wall surface and the variation of the level of impurities. The reactor fouling per se can be represented within the model as an additional variable resistance in the estimation of the overall heat transfer coefficient (Eq. A24). It should be noted though that as the reactor wall fouling increases the temperature profile in the reactor changes, which affects the polymerization rate.

The impurities, on the other hand, depending on their nature, can either act as chain transfer agents, as radical generators, or they can act as inhibitors, deactivating the primary radicals produced by the decomposition of the initiators. Whichever is their actual impact on the reactor operation, it is the apparent concentration of the initiators on the one hand and the apparent concentration of the CTA on the other that influence the model predictive abilities to track the on-line reactor performance. The apparent concentration of the CTA is modeled by assuming $|c_s|_{\text{apparent}} = f_s c_s$, where c_s is the estimated CTA concentration based on the total solvent feed rate and f_s is a variable efficiency factor. The apparent concentration of the initiators, on the other hand, has been modeled by implanting a variable overall efficiency factor f in the total radical production term $\Sigma_{i=1}^{N_i} 2 f k_{d_i} c_{Ii}$ (Eq. A5), where c_{Ii} is the concentration of the ith initiator and k_{di} is the corresponding decomposition rate constant.

The effect of the impurities has been distributed in two distinct parameters, but this is not an arbitrary and convenient imposition; it actually reflects the different functionalities of the various species lumped under the term "impurities." Some of these species, for example, O_2, can either act as initiators or as inhibitors, and are consumed. On the other hand, other species, such as CH_4, can act as chain transfer agents and are therefore physically sustained and accumulated in the system.

Overall, the inner wall surface fouling along the reactor and the impurities accumulation are tracked by the adjustment of two distributed parameters and a global one. The distributed parameters are the overall initiator efficiency and the reactor fouling factor, which are allowed to change along the length of the reactor, whereas the global parameter is the CTA concentration efficiency, which assumes a single value throughout the entire reactor.

The choice of the preceding adjustable parameters has been presented from the point of view of the phenomenological representation of the reactor variability. It is useful though to note that their choice can be just as well substantiated on the ground of the essential functionalities of the reactor model, enabling them to make the mathematical model adapt to the observed variability of the reactor performance. Seen from this point of view, the parameters selected, can control the polymerization rate, the heat transfer rates in the reaction and cooling zones, and the product quality.

The polymerization rate is monitored by the effective concentration of the initiators and thus the net generation rate of the primary radicals that trigger the polymerization process. The heat transfer rate is controlled by the overall initiator efficiency at the reaction zones and by the fouling factor at the heat removal zones.

Finally, the product quality (e.g., melt index) is tuned by calculating on-line the effective concentration of the chain transfer agent that controls the molecular weight developments of the product through the transfer to the CTA reaction.

On the issue of the adjustable model parameters selection, a final comment is in order. The mathematical model of a process is an artefact that can be manipulated according to its intended use. The parameters that are to be adjusted can be seen as part of the model development and not as part of a posterior selection procedure. Most of the parameters chosen to be adjusted in the present work were not even part of the initial cast of the reactor's model and were actually implanted in order to project the process variability on the model.

Problem Decomposition

The different time scales of the changes in the states of the process suggest a decomposition of the overall on-line parameter estimation problem. This decomposition can easily be accomplished since the adjustable model parameters are each affected by different reactor disturbances.

The estimation of the fouling factor and the overall initiator efficiency is required in accordance with the rate of the fouling of the inner wall of the reactor and the rate of the variability of the level of the impurities that affect the initiators. The measurements associated with these parameters are the light-off (inlet) and the peak temperature at each reaction zone, and the inlet and outlet temperatures at each coolant zone.

The lack of significant correlation between the two adjustable parameters is mainly substantiated on physical grounds. The polymerization of ethylene commonly occurs in a short section of a reaction zone, at conditions practically adiabatic, since only a small fraction (less than 10%) of the reaction heat is actually removed at this part. Subsequently, the reaction mixture is cooled off in the remaining part of the reaction zone. The intermediate sections of the reactor zones, that is, the ones lying between reaction zones, are only functioning as heat exchangers. This distinct spatial functionality of the reactor, and consequently of the reactor model, disentangles the correlation of the two parameters, assigning implicitly the monitoring of the ascending part of the temperature profile to the overall initiator efficiency and the descending part of it to the fouling factor.

The estimation of the effective chain transfer agent concentration is required in accordance with the rate of the chain transfer agents' buildup. The measurement that is associated with this parameter is the melt flow index measured at the reactor exit.

The order in which the parameters are evaluated is important. The initiator efficiency affects the polymerization rate and the molecular developments; thus, any revaluation of the initiator efficiency changes significantly the molecular weight, and thus the melt index has to be matched again. On the other hand, the CTA concentration does not affect the temperature profile and, as a result, there is no need for iterative calculation of the apparent CTA concentration.

A final comment is due on the spatial decomposition of the problem that is substantiated on the flow model of the reactor. The physical and operational separation of the reactor into zones, categorized as reaction and coolant zones, is adopted in the model and its parameter estimation procedures. Thus, the estimation of the fouling factor and the initiator efficiency are localized at a zone level (Figure 3). This is of course supported by the availability of temperature readings along the whole length of the tubular reactor. On the other hand, as there is just one melt flow index measurement at the reactor exit, the estimation of the solvent concentration efficiency has a global scope and, thus, its evaluation involves the whole reactor (Figure 4).

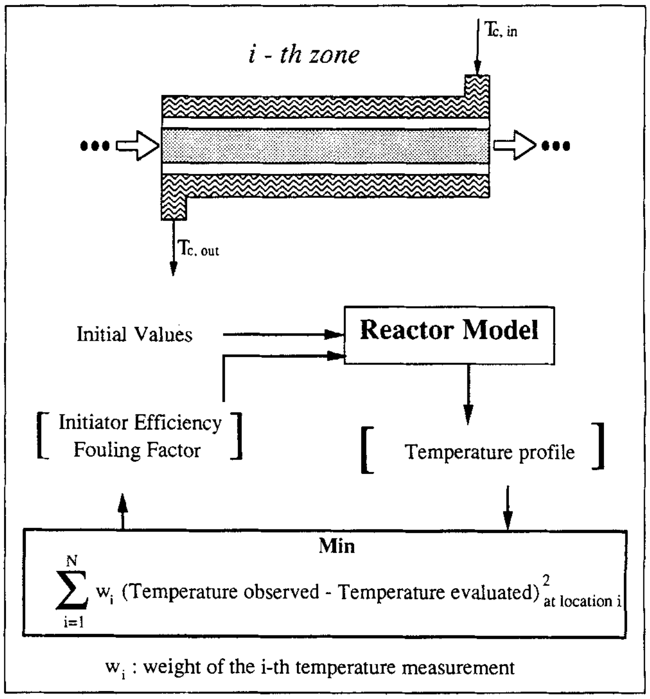

Figure 3. Evaluation of the fouling factor and the overall initiator efficiency.

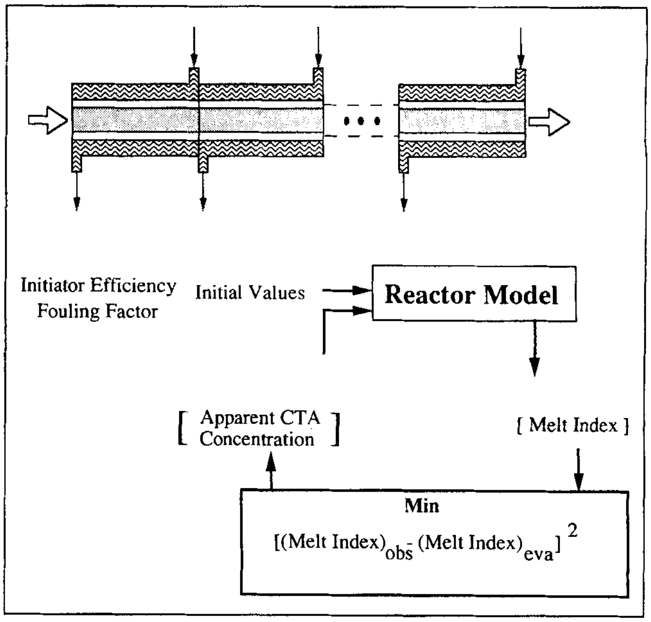

Figure 4. Evaluation of the apparent CTA concentration.

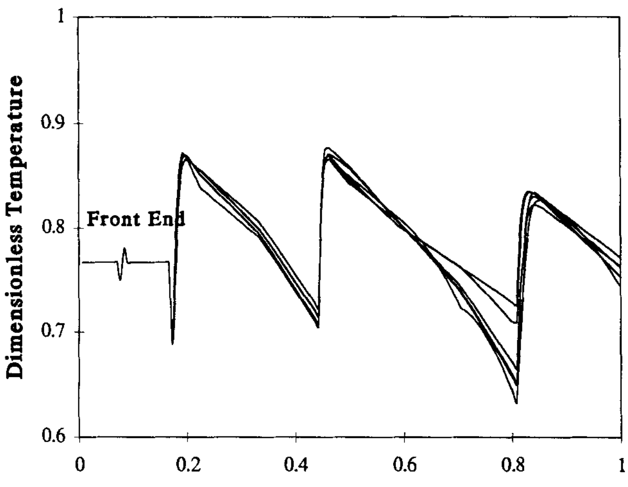

Figure 5. Overlay of the estimated temperature profiles at various instances of a defouling cycle.

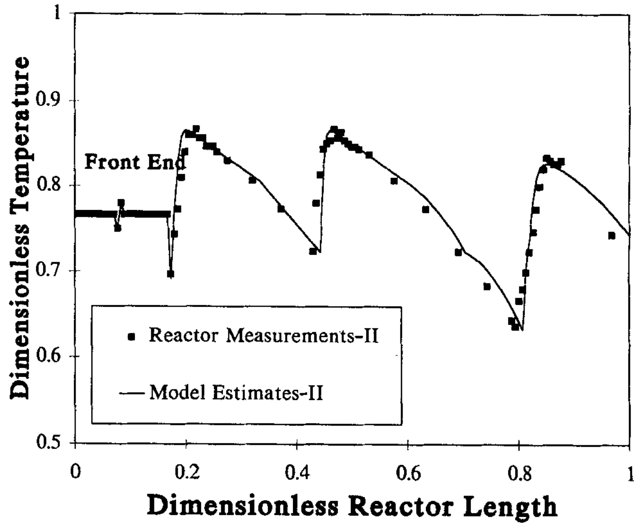

Figure 7. Estimated vs. measured temperature profiles at an instance of a defouling cycle-II.

Implementation and Presentation of Results

The capability of the on-line parameter estimator to capture the time-varying characteristics of an industrial LDPE reactor is demonstrated by simulating the performance of the reactor during a defouling cycle. Figure 5 shows a series of scaled temperature profiles at various instances of such a defouling cycle of an industrial LDPE reactor. The change in the heat removal capacity of the reactor is clearly manifested by the decrease of the light-off temperatures in the various reactor zones. On the other hand, the sustaining of the peak temperatures is an imperative task for both the safety of the reactor and the polymer production, which is accomplished by the proper manipulation of the initiator and coolant flowrates.

The parameter estimation programs described in this article are capable of reproducing the varying temperature profiles through the estimation of the fouling factor and the initiator efficiency (Figure 3). Snapshots of the off-line parameter estimation testing are illustrated in Figures 6, 7, and 8 for three instances of the defouling cycle. It is apparent that the model predictions are in excellent agreement with the measured temperatures (discrete points). It should be pointed out that the simulated temperature profiles correspond to significantly different operating conditions (initiator flows, coolant flows, and temperatures). Nevertheless, the parameter estimation program (local estimation) has successfully discerned the fouling effect and estimated realistic values for the fouling factor. It is important to note that in all three cases the melt index has been exactly matched (global estimation), as there is a dedicated adjustable parameter, the apparent CTA concentration that exclusively undertakes this task.

What makes the difference in using a parameter estimator based on a comprehensive reactor model, however, is that all the other output variables, including ethylene conversion,

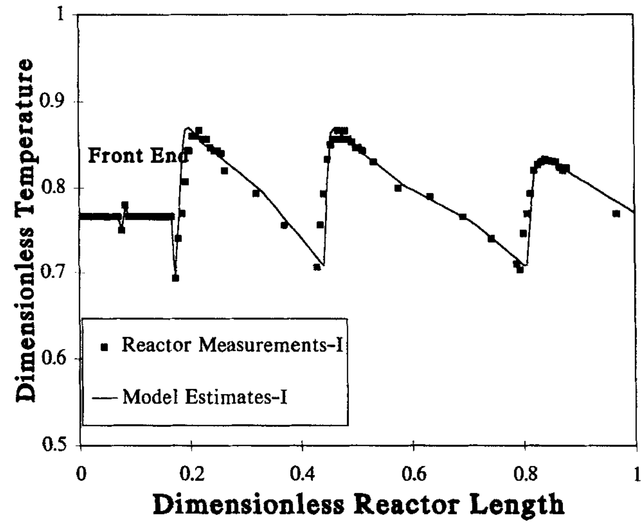

Figure 6. Estimated vs. measured temperature profiles at an instance of a defouling cycle-I.

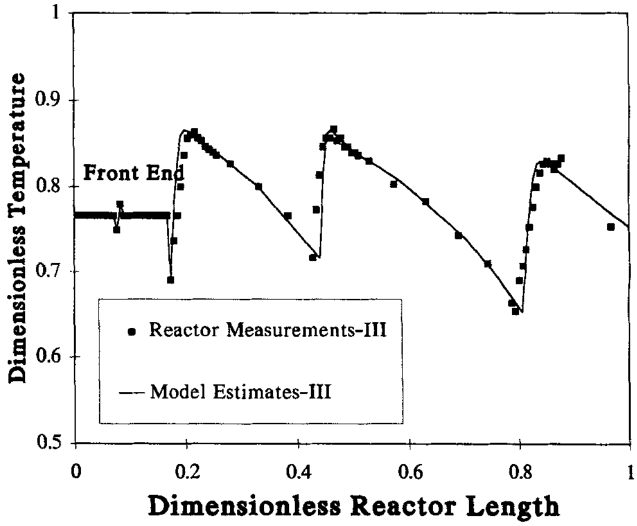

Figure 8. Estimated vs. measured temperature profiles at an instance of a defouling cycle-III.

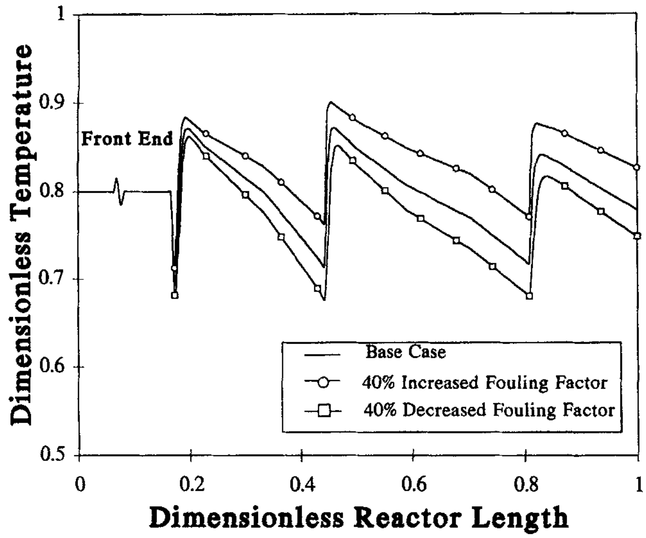

Figure 9. Temperature profiles: base case vs. a 40% increase/decrease in the fouling factors along the reactor.

number and weight average molecular weights, density, LCB, and SCB, can be predicted correctly up to the degree that the temperature profile and the melt index at the reactor exit have been accurately matched.

There is, however, a subtle point in the preceding statement that has to be further discussed. In order to address this issue in some detail, the effect of the fouling factor and the initiator efficiency variation on the temperature profile and the polymer properties is demonstrated in four numerical experiments. In the first two simulations, the fouling factor was varied by ±40% over its nominal value corresponding to an intermediate fouling state. In the latter two simulations, the initiator efficiency was varied likewise over its respective nominal value.

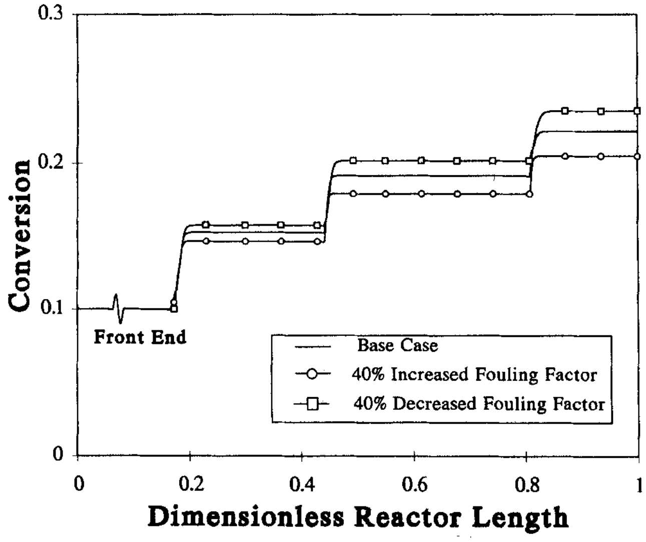

Figure 10. Conversion profiles: base case vs. a 40% increase/decrease in the fouling factors along the reactor.

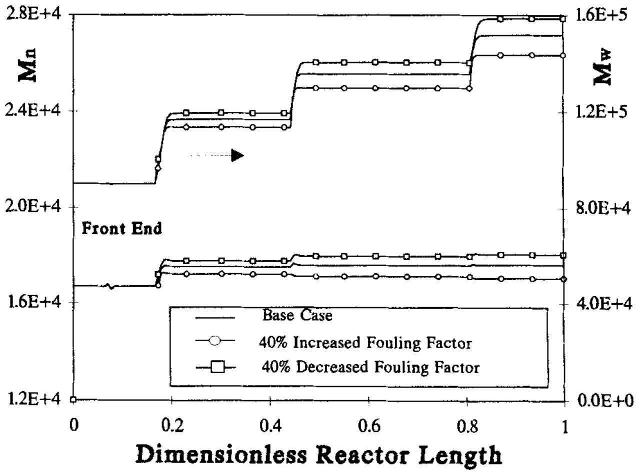

Figure 11. M_n, M_w profiles: base case vs. a 40% increase/decrease in the fouling factors along the reactor.

Figure 9 shows the temperature profile shift that resulted from the fouling factor variation. It is interesting to note that a significant nonlinearity in the temperature shift is observed (the upward temperature shift is visibly larger than the downward one), although the fouling factor has been varied by the same percentage in the two directions. Figures 10, 11, 12, and 13 show how these temperature variations affect, in turn, the other output variables of interest. Specifically, it can be seen that the ethylene conversion, M_n, M_w, LCB, and density decrease while the SCB and the melt index increase as the fouling factor increases.

Similarly, Figures 14, 15, 16, 17, and 18 illustrate the effect of the initiator efficiency variation on the temperature profile and the polymer properties. It is apparent that as the initiator efficiency increases the temperature, conversion, M_w, LCB, and SCB increase, while the M_n, the melt index, and the density decrease.

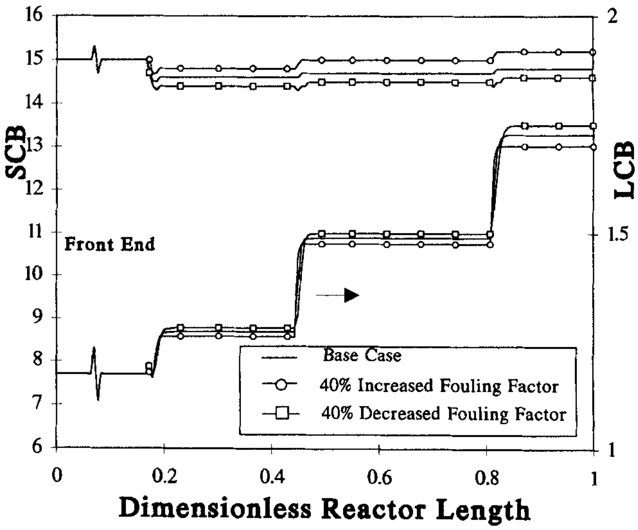

Figure 12. SCB, LCB profiles: base case vs. a 40% increase/decrease in the fouling factors along the reactor.

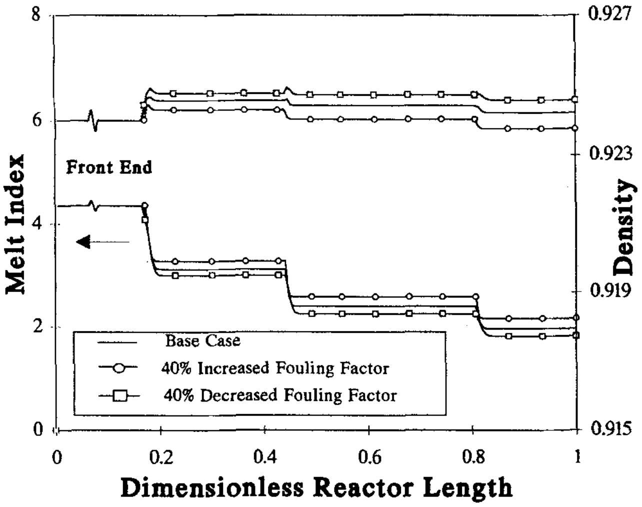

Figure 13. Melt index, density profiles: base case vs. a 40% increase/decrease in the fouling factors along the reactor.

In the on-line implementation of the parameter estimator the problem is stated inversely since the starting point is the measured temperature profile and the parameters to be estimated are the fouling factor and the initiator efficiency. In Figure 19, the temperature profiles calculated from the four numerical experiments are plotted together. It can be seen that the temperature profiles corresponding to a 40% decrease in either the fouling factor or the initiator efficiency are quite similar. This means that it is not always trivial to identify the exact cause for the observed downward shift of the temperature profile. Furthermore, it has to be pointed out that conversion, M_w, LCB, and the melt index change in opposite directions when the same temperature profile shift is affected by a different cause (e.g., decrease of the reactor wall fouling vs. decrease of the initiator efficiency). Therefore, it becomes apparent that assigning a temperature downward shift to the wrong cause would result in a grossly erroneous estimate of the output variables.

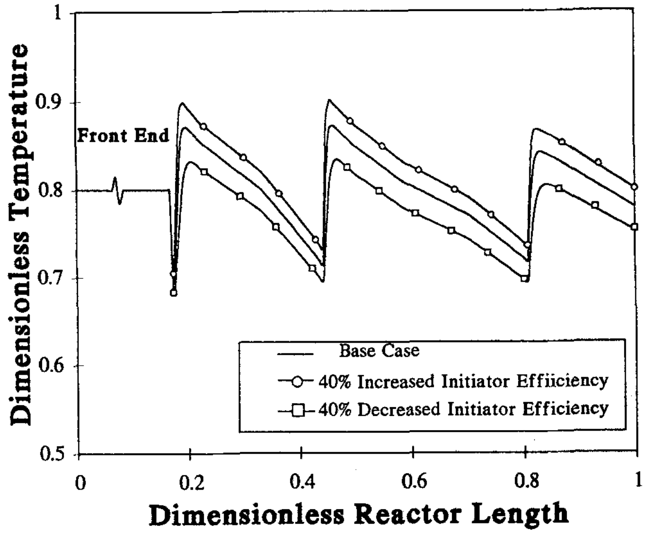

Figure 14. Temperature profiles: base case vs. a 40% increase/decrease in the initiator efficiencies along the reactor.

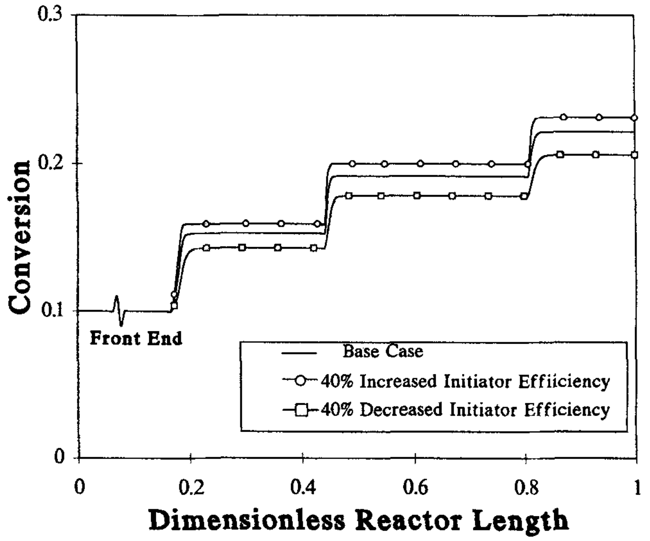

Figure 15. Conversion profiles: base case vs. a 40% increase/decrease in the initiator efficiencies along the reactor.

Facing this problem from a purely numerical point of view it appears to be quite an impossible task to discriminate between the two alternative solutions. The correct solution, though, can be found if the physical situation reflected in the alternative solutions is properly taken into account.

Part of the solution lies on the temperature profile itself. It should be noted that a fouled temperature profile has generally flatter cooling sections and more rounded peaks. This feature may be exploited by weighing the temperature measurements heavier in the vicinity of the peak and the light-off in the objective function of the parameter estimation problem (Figure 3). Furthermore, the fouling factor has a unique and clearly identifiable physical base. As a consequence, good

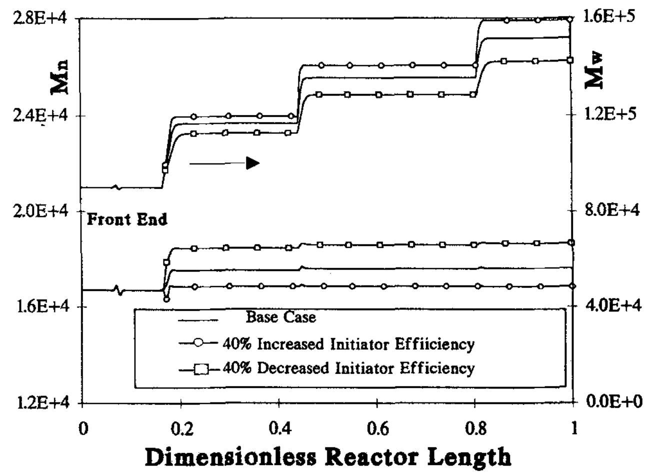

Figure 16. M_w, M_n profiles: base case vs. a 40% increase/decrease in the initiator efficiencies along the reactor.

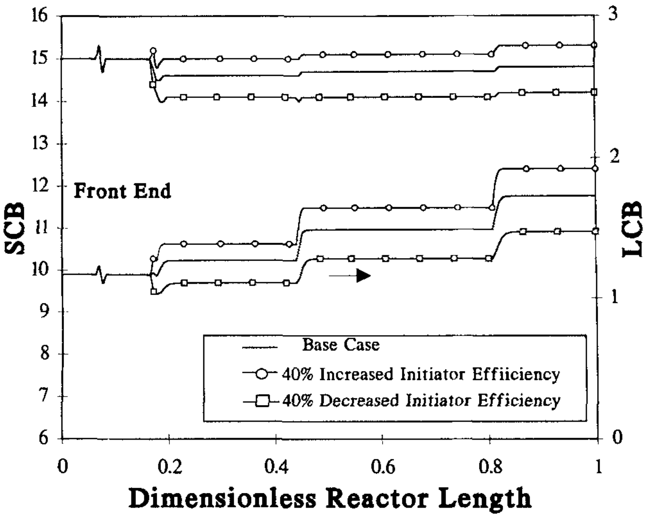

Figure 17. SCB, LCB profiles: base case vs. a 40% increase/decrease in the initiator efficiencies along the reactor.

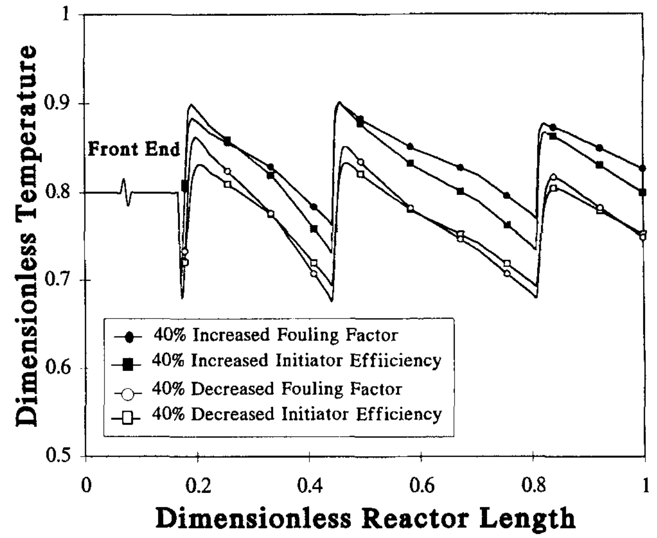

Figure 19. Overlay of the temperature profiles for a 40% increase/decrease in the fouling factors/initiators efficiencies.

initial values for the fouling factor are generally available, and thus the parameter estimator is assisted to converge to the correct values. Finally, the heat duty of the coolant can be used to resolve the discrimination problem. Actually the coolant flowrates, if available, can be used together with the coolant inlet and outlet temperatures to infer the ethylene conversion, providing still another means of directing the parameter estimator in identifying the correct solutions. Overall, the preceding features, put to work synergetically, have proved adequate in making the parameter estimator perform robustly.

Conclusions

The parameter estimation scheme that has been presented in this work has been tested extensively for various reactor geometries and operating conditions, and in all cases it proved capable of capturing the status of the reactor operation. Thus, it can be safely concluded that the operation of a high-pressure LDPE reactor can be simulated on-line if the initiator efficiencies, the fouling factors, and the apparent CTA concentration are properly tuned within a comprehensive reactor model.

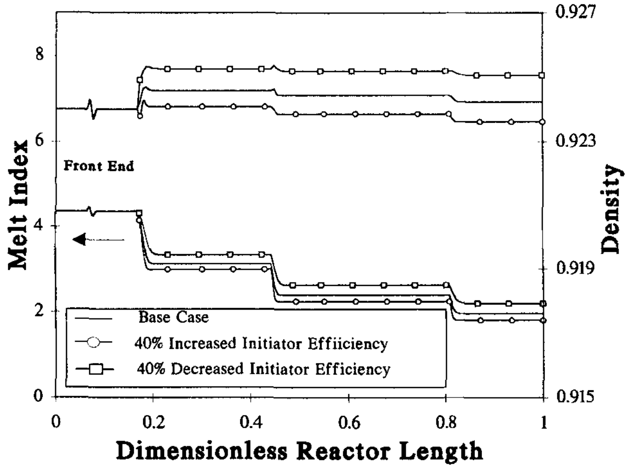

Figure 18. Melt index, density profiles: base case vs. a 40% increase/decrease in the initiator efficiencies along the reactor.

The fact that such a complex reacting system has been successfully reproduced by fitting a limited number of adjustable parameters, based on a limited number of on-line measurements (the temperature profile and the melt index at the exit of the reactor), is considered to be the major accomplishment of this work. The key to this accomplishment is the comprehensiveness of the model used and the knowledgable selection of the tuning parameters. Furthermore, the computational time requirements of the parameter estimation programs are not prohibitive for their on-line implementation.

Considering the continuous new arrivals in the software and hardware technology, a gradual shift in the paradigm for the management of the operation of the processes in the chemical industry is prescribed, if not already witnessed. As additional CPU capabilities are downloaded on the process lines, the potential of a much more intelligent perception and consequently management of the functions performed by the process can be assessed. The present work serves as an example of such an endeavor.

Acknowledgment

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Notation

A_i = inside area of the tube wall
A_o = outside area of the tube wall
f_r = friction factor
h_i = inside fluid film heat transfer coefficient
h_o = outside water heat transfer coefficient
k_b = rate constant for intramolecular transfer, s^{-1}
k_β = rate constant for β-scission of radicals, s^{-1}
k_d = rate constant for initiator decomposition, s^{-1}

k_p = propagation rate constant, m^3/kmol/s
k_{tc} = termination by combination rate constant, m^3/kmol/s
k_{td} = termination by disproportionation rate constant, m^3/kmol/s
k_{tm} = rate constant for transfer to monomer, m^3/kmol/s
k_{tp} = rate constant for transfer to polymer, m^3/kmol/s
k_{ts} = rate constant for transfer to chain transfer agent, m^3/kmol/s
k_w = thermal conductivity of the tube wall
L = length of the reactor
L_c = length of a cooling zone
$[R^{\cdot}]$ = primary radical concentration, kmol/m^3
R_f = fouling factor
υ = dimensionless fluid velocity
y_i = fractional conversion of the i component
z = dimensionless axial distance

Greek letters

θ = dimensionless reactor temperature, defined as $(T - T_o)/T_o$, where T_o is the inlet temperature
θ_c = dimensionless reactor temperature, defined as $(T_c - T_o)/T_o$
λ_i^j = ith order moment of "live" polymer chains ending at jth molecule, kmol/m^3
μ_i = ith order moment of "dead" polymer chains, kmol/m^3
ρ = reaction mixture density, kg/m^3

Subscripts

o = conditions at the inlet of the reaction zone
di = ith initiator
mi = ith monomer
si = ith chain transfer agent

Literature Cited

Achilias, D. S., and C. Kiparissides, "Towards the Development of a General Framework for Modeling Molecular Weight and Compositional Changes in Free Radical Copolymerization Reactions," *J.M.S.-Rev. Macromol. Chem. Phys.*, **C32**, 183 (1992).

Bard, Y. A., *Nonlinear Parameter Estimation*, Academic Press, New York (1974).

Biegler, L. T., J. J. Damaino, and G. E. Blau, "Nonlinear Parameter Estimation: A Case Study Comparison," *AIChE J.*, **32**(1), 29 (1986).

Biradello, P., X. Joulia, J. M. Le Mann, H. Delmas, and B. Koehret, "A General Strategy for Parameter Estimation in Differential-Algebraic Systems," *Comput. Chem. Eng.*, **17**(5/6), 517 (1993).

Brenan, K. E., S. L. Campbell, and L. R. Petzold, *Numerical Solution of Initial-Value Problem in Differential-Algebraic Equations*, Elsevier Science, New York (1989).

Byrne, G. D., and P. R. Ponzi, "Differential Algebraic Systems, Their Applications and Solutions," *Comput. Chem. Eng.*, **12**, 377 (1988).

Cutler, C. R., and R. T. Perry, "Real Time Optimization with Multivariable Control is Required to Maximize Profits," *Comput. Chem. Eng.*, **7**(5), 663 (1983).

Dovi, V. G., and A. P. Reverberi, "Optimal Solution of Processes Described by Systems of Differential-Algebraic Equations," *Chem. Eng. Sci.*, **48**(14), 2609 (1993).

Hulburt, H. M., and S. Katz, "Problems in Particle Technology," *Chem. Eng. Sci.*, **19**, 555 (1964).

Hwu, M. C., and R. D. Foster, "Detection of Fouling in a Tubular Reactor," *Chem. Eng. Prog.*, **7**, 62 (1982).

Jang, S. S., B. Joseph, and H. Mukai, "Comparison of Two Approaches to On-Line Parameter and State Estimation of Nonlinear Systems," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 809 (1986).

Jang, S. S., B. Joseph, and H. Mukai, "On-Line Optimization of Constrained Multivariable Chemical Process," *AIChE J.*, **33**(1), 26 (1987).

Kiparissides, C., and S. R. Ponnuswamy, "Hierarchical Control of a Train of Continuous Polymerization Reactors," *Can. J. Chem. Eng.*, **59**, 752 (1981).

Kiparissides, C., G. Verros, and J. F. MacGregor, "Mathematical Modeling, Optimization, and Quality Control of High Pressure Ethylene Polymerization Reactors," *J.M.S.-Rev. Macromol. Chem. Phys.*, **C33**(4), 437 (1993).

Krishnan, S., G. W. Barton, and J. D. Perkins, "Robust Parameter Estimation in On-Line Optimization—Part I. Methodology and Simulated Case Study," *Comput. Chem. Eng.*, **16**(6), 545 (1992).

Krishnan, S., G. W. Barton, and J. D. Perkins, "Robust Parameter Estimation in On-Line Optimization: 2. Application to an Industrial Reactor," *Comput. Chem. Eng.*, **17**(7), 663 (1993).

Mavridis, H., and C. Kiparissides, "Optimization of a High-Pressure Polyethylene Tubular Reactor," *Polym. Process Eng.*, **3**(3), 263 (1985).

McAuley, K. B., and J. F. MacGregor, "On-Line Inference of Polymer Properties in an Industrial Polyethylene Reactor," *AIChE J.*, **37**(6), 825 (1991).

Morari, M., and G. Stephanopoulos, "Part II: Structural Aspects and the Synthesis of Alternative Feasible Control Schemes," *AIChE J.*, **26**(2), 232 (1980).

Pantelides, C. C., and P. I. Barton, "Equation-Oriented Dynamic Simulation-Current Status and Future Developments," in *European Symposium on Computer Aided Process Engineering*: *2*, D. Depeyre, X. Joulia, B. Koehret, and J.-M., and Le Lann, eds., Pergamon Press, Oxford, pp. S263–S285 (1992).

Pantelides, C. C., Gritsis, K. R. Morison, and R. W. H. Sargent, "The Mathematical Modelling of Transient Systems Using Differential-Algebraic Equations," *Comput. Chem. Eng.*, **12**, 449 (1988).

Perregaard, J., B. S. Pedersen, and R. Gani, "Steady State and Dynamic Simulation of Complex Chemical Processes," *Chem. Eng. Res. Des.*, **70**(A), 99 (1992).

Pontor, J. W., and P. J. Gawthrop, "Systematic Construction of Dynamic Models for Phase Equilibrium," *Comput. Chem. Eng.*, **15**, 803 (1991).

Renfro, J. G., A. M. Morshedi, and O. A. Absjornsen, "Simultaneous Optimization and Solution of Systemas Described by Differential/Algebraic Equations," *Comput. Chem. Eng.*, **11**(5), 503 (1987).

Rhinehart, R. R., and J. B. Riggs, "Two Simple Methods for On-Line Incremental Model Parameterization," *Comput. Chem. Eng.*, **15**(3), 181 (1991).

Roberts, P. D., and T. W. C. Williams, "On an Algorithm for Continued System Optimization and Parameter Estimation," *Automatica*, **17**(1), 199 (1981).

Schbib, S., S. Tonelli, E. Brignole, and J. Romagnoli, "Linearized Dynamic Model of an Industrial Low Density Polyethylene Plant," *European Symposium on Computer Aided Process Engineering*: *2*, D. Depeyre, X. Joulia, B. Koehret, J.-M. and Le Lann, eds., Pergamon Press, Oxford, p. S323 (1992).

Schuler, H., and U. Schmidt, "Automated Operation of Polymerization Reactors," *4th Int. Workshop on Polymer Reaction Engineering*, K. H. Reichert and H. U. Moritz, eds., DECHEMA, VCH Publishers, Frankfurt, **127**, p. 235 (1992).

Sperati, C. A., Franta, Starkweather, "Structure of Polyethylene. V. The Effect of Chain Branching and Molecular Weight on Physical Properties," *J. Amer. Chem. Soc.*, **75**, 6127 (1953).

Tjoa, I.-B., and L. T. Biegler, "Simultaneous Solution and Optimization Strategies for Parameter Estimation of Differential-Algebraic Equation Systems," *Ind. Eng. Chem. Res.*, **30**, 376 (1991).

Verros, G., M. Papadakis, and C. Kiparissides, "Mathematical Modeling of High Pressure Tubular LDPE Copolymerization Reactors," *Polym. React. Eng.*, **1**(3), 427 (1993).

Appendix

A detailed review of the various approaches in the modeling of high-pressure LDPE reactors can be found in Kiparissides et al. (1993). In the present work the mathematical model of Verros et al. (1993) has been adopted. The kinetic mechanism includes the following elementary reactions:

Decomposition of the Initiators:

$$I_i \xrightarrow{k_{di}} 2R; \qquad i = 1, N$$

Chain Initiation:

$$\dot{R} + M_1 \overset{k_{I1}}{\rightarrow} P_{1,0,0}$$

$$\dot{R} + M_2 \overset{k_{I2}}{\rightarrow} Q_{0,1,0}$$

Propagation:

$$P_{r,s,t} + M_1 \overset{k_{p11}}{\rightarrow} P_{r+1,s,t}$$

$$P_{r,s,t} + M_2 \overset{k_{p12}}{\rightarrow} Q_{r,s+1,t}$$

$$Q_{r,s,t} + M_1 \overset{k_{p21}}{\rightarrow} P_{r+1,s,t}$$

$$Q_{r,s,t} + M_2 \overset{k_{p22}}{\rightarrow} Q_{r,s+1,t}$$

Chain Transfer to Monomer:

$$P_{r,s,t} + M_1 \overset{k_{fm11}}{\rightarrow} P_{1,0,0} + M_{r,s,t}$$

$$P_{r,s,t} + M_2 \overset{k_{fm12}}{\rightarrow} Q_{0,1,0} + M_{r,s,t}$$

$$Q_{r,s,t} + M_1 \overset{k_{fm21}}{\rightarrow} P_{1,0,0} + M_{r,s,t}$$

$$Q_{r,s,t} + M_2 \overset{k_{fm22}}{\rightarrow} Q_{0,1,0} + M_{r,s,t}$$

Chain Transfer to Polymer:

$$P_{r,s,t} + M_{x,y,z} \overset{k_{fp11}}{\rightarrow} P_{x,y,z+1} + M_{r,s,t}$$

$$P_{r,s,t} + M_{x,y,z} \overset{k_{fp12}}{\rightarrow} Q_{x,y,z+1} + M_{r,s,t}$$

$$Q_{r,s,t} + M_{x,y,z} \overset{k_{fp21}}{\rightarrow} P_{x,y,z+1} + M_{r,s,t}$$

$$Q_{r,s,t} + M_{x,y,z} \overset{k_{fp22}}{\rightarrow} Q_{x,y,z+1} + M_{r,s,t}$$

Chain Transfer to Solvent:

$$P_{r,s,t} + S \overset{k_{S1}}{\rightarrow} P_{1,0,0} + M_{r,s,t}$$

$$Q_{r,s,t} + S \overset{k_{S2}}{\rightarrow} Q_{0,1,0} + M_{r,s,t}$$

Termination by Combination:

$$P_{r,s,t} + P_{x,y,z} \overset{k_{tc11}}{\rightarrow} M_{r+x,s+y,t+z}$$

$$P_{r,s,t} + Q_{x,y,z} \overset{k_{tc12}=k_{tc21}}{\rightarrow} M_{r+x,s+y,t+z}$$

$$Q_{r,s,t} + Q_{x,y,z} \overset{k_{tc22}}{\rightarrow} M_{r+x,s+y,t+z}$$

Termination by Disproportionation:

$$P_{r,s,t} + P_{x,y,z} \overset{k_{td11}}{\rightarrow} M_{r,s,t} + M_{x,y,z}$$

$$P_{r,s,t} + Q_{x,y,z} \overset{k_{td12}=k_{td21}}{\rightarrow} M_{r,s,t} + M_{x,y,z}$$

$$Q_{r,s,t} + Q_{x,y,z} \overset{k_{td22}}{\rightarrow} M_{r,s,t} + M_{x,y,z}$$

Intramolecular Transfer (Backbitting):

$$P_{r,s,t} \overset{k_{b1}}{\rightarrow} P_{r,s,t} \quad \text{or} \quad Q_{r,s,t}$$

$$Q_{r,s,t} \overset{k_{b2}}{\rightarrow} Q_{r,s,t} \quad \text{or} \quad P_{r,s,t}$$

β-Scission of Radicals:

$$P_{r,s,t} \overset{k_{\beta 1}}{\rightarrow} M^{=}_{r,s,t} + \dot{R}$$

$$Q_{r,s,t} \overset{k_{\beta 2}}{\rightarrow} M^{=}_{r,s,t} + \dot{R}$$

Based on the assumptions discussed in the fourth section of the article and the preceding elementary reactions, the differential equations describing the mass balances of the various "live" and "dead" polymer species, the monomers, the initiators, and solvents, the energy balances, the molecular properties of the polymer, and the velocity along the reactor can be derived. To reduce the infinite system of molar balance equations into a lower order system of differential equations, the method of moments has been employed. Accordingly, one can represent the average molecular properties of a polymer (M_n, M_w) in terms of the leading moments of the dead polymer molecular weight distribution. Following the developments of Achilias and Kiparissides (1992) and Verros et al. (1993) the moments of the univariate number chain length distributions of live and dead macromolecular chains are defined as

$$\lambda_n^i = \sum_{k=1}^{\infty} \sum_{m=1}^{\infty} (k+m)^n R^i(k,m) \qquad \text{for} \quad i = 1,2 \quad \text{(A1)}$$

$$\mu_n = \sum_{k=1}^{\infty} \sum_{m=1}^{\infty} (k+m)^n D(k,m), \qquad \text{(A2)}$$

where $R^1(k,m) \equiv [P_{k,m,x}]$, $R^2(k,m) \equiv [Q_{k,m,x}]$, and $D(k,m) \equiv [M_{k,m,x}]$ for any number of long chain branches x.

Introducing the dimensionless quantities z, θ, θ_c, and y_i for the length, reactor, and jacket temperature and fractional conversion of the various species, defined in the nomenclature, the mathematical model for a high-pressure LDPE reactor can be written as follows:

Continuity Equation:.

$$\frac{dv}{dz} = -\frac{v}{\rho}\left[T_0 \frac{\partial \rho}{\partial T}\frac{d\theta}{dz} + \sum_{i=1}^{2} \frac{\partial \rho}{\partial y_{mi}}\frac{dy_{mi}}{dz}\right]. \qquad \text{(A3)}$$

Species balances for initiators, primary radicals, monomers, and solvents:

$$\frac{dy_{di}}{dz}=\frac{L}{v}k_{di}(1-y_{di})\qquad i=1,N_i \tag{A4}$$

$$\begin{aligned}\frac{d[\mathrm{R}^{\cdot}]}{dz}=\frac{Lv_0}{v^2}\Bigg[&\sum_{i=1}^{N_i}2fk_{di}c_{I0i}(1-y_{di})\\&-\sum_{i=1}^{2}k_{Ii}c_{m0i}(1-y_{mi})[\mathrm{R}^{\cdot}]\Bigg]-\frac{[\mathrm{R}^{\cdot}]}{v}\frac{dv}{dz}\end{aligned} \tag{A5}$$

$$\frac{dy_{mi}}{dz}=\frac{L(1-y_{mi})}{v}\left[k_{Ii}[\mathrm{R}^{\cdot}]+\sum_{j=1}^{2}(k_{pji}+k_{fmji})\lambda_0^j\right]\qquad i=1,2 \tag{A6}$$

$$\frac{dy_s}{dz}=\frac{L(1-y_s)}{v}\sum_{i=1}^{2}k_{si}\lambda_0^i. \tag{A7}$$

Live Polymer Moment Equations: $k=0,\ 1,\ 2-I=1,\ 2$:

$$\begin{aligned}\frac{d\lambda_k^i}{dz}=\frac{L}{v}\Bigg\{&\frac{v_0}{v}\Bigg[\Bigg(k_{Ii}[\mathrm{R}^{\cdot}]+\sum_{j=1}^{2}k_{fmji}\lambda_o^j+\sum_{j=1}^{2}k_{pji}\sum_{r=0}^{k}\binom{k}{r}\lambda_r^j\Bigg)\\&\times c_{moi}(1-y_{mi})+k_{si}\lambda_o^i c_{so}(1-y_s)\Bigg]\\&-\frac{v_o}{v}\sum_{j=1}^{2}k_{pij}\lambda_k^i c_{moj}(1-y_{mj})\\&-\Bigg(A_i+\sum_{j=1}^{2}k_{tcij}\lambda_o^j\Bigg)\lambda_k^i+\mu_{k+1}\sum_{j=1}^{2}k_{fpji}\lambda_o^j\Bigg\}-\frac{\lambda_k^i}{v}\frac{dv}{dz}.\end{aligned} \tag{A8}$$

Dead Polymer Moment Equations: $k=0,\ 1,\ 2$:

$$\begin{aligned}\frac{d\mu_k}{dz}=\frac{L}{v}\Bigg\{&\sum_{j=1}^{2}A_j\lambda_k^j+\frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}k_{tcij}\sum_{r=0}^{k}\binom{k}{r}\lambda_r^i\lambda_{k-r}^j\\&-\mu_{k+1}\sum_{i=1}^{2}\sum_{j=1}^{2}k_{fpij}\lambda_o^i\Bigg\}-\frac{\mu_k}{v}\frac{dv}{dz},\end{aligned} \tag{A9}$$

where

$$\begin{aligned}A_j=\frac{v_o}{v}\Bigg(&\sum_{i=1}^{2}k_{fmji}c_{moi}(1-y_{mi})+k_{sj}c_{so}(1-y_s)\Bigg)\\&+\sum_{i=1}^{2}k_{tdji}\lambda_o^i+\sum_{i=1}^{2}k_{fpji}\mu_1+k_{\beta j}.\end{aligned} \tag{A10}$$

Using the closure method of Hulburt and Katz (Hulburt and Katz, 1964), μ_3 is expressed as

$$\mu_3=\frac{\mu_2}{\mu_0\mu_1}(2\mu_0\mu_2-\mu_1^2) \tag{A11}$$

Molecular Properties:

$$\frac{dc_{\mathrm{LCB}}}{dz}=\frac{L}{v}\left(\mu_1\sum_{i=1}^{2}\sum_{j=1}^{2}k_{fpij}\lambda_o^i-\frac{c_{\mathrm{LCB}}}{L}\frac{dv}{dz}\right) \tag{A12}$$

$$\frac{dc_{\mathrm{SCB}}}{dz}=\frac{L}{v}\left(\sum_{i=1}^{2}k_{bi}\lambda_o^i-\frac{c_{\mathrm{SCB}}}{L}\frac{dv}{dz}\right) \tag{A13}$$

$$\frac{dc_{\mathrm{VNL}}}{dz}=\frac{L}{v}\left(\sum_{i=1}^{2}k_{\beta i}\lambda_o^i-\frac{c_{\mathrm{VNL}}}{L}\frac{dv}{dz}\right). \tag{A14}$$

Number Average Molecular Weight:

$$M_n=M_o\frac{\mu_1+\lambda_1^1+\lambda_1^2}{\mu_o+\lambda_o^1+\lambda_o^2} \tag{A15}$$

Weight Average Molecular Weight:

$$M_w=M_o\frac{\mu_2+\lambda_2^1+\lambda_2^2}{\mu_1+\lambda_1^1+\lambda_1^2}. \tag{A16}$$

Long-Chain Branches per 1,000 Carbon Atoms:

$$\mathrm{LCB}/1{,}000\ \mathrm{C-C}=500\,\frac{c_{\mathrm{LCB}}}{\mu_1+\lambda_1^1+\lambda_1^2}. \tag{A17}$$

Short-Chain Branches per 1,000 Carbon Atoms:

$$\mathrm{SCB}/1{,}000\ \mathrm{C-C}=\frac{500\,c_{\mathrm{SCB}}}{\mu_1+\lambda_1^1+\lambda_1^2}. \tag{A18}$$

Vinylene Double Bonds:.

$$\mathrm{VNL}/1{,}000\ \mathrm{C-C}=\frac{500\,c_{\mathrm{VNL}}}{\mu_1}. \tag{A19}$$

The melt index and the density of the PE product are generally evaluated by empirical formulas. The ones used in this work are (Sperati et al., 1953):

$$\log MI=a+b\,\mathrm{LCB}+c\log M_w \tag{A20}$$

$$Den=\alpha+\beta\,\mathrm{SCB}, \tag{A21}$$

where the coefficients a, b, c, and α, β were estimated by fitting pertinent measurements from the plant.

Energy Balances:

$$\begin{aligned}\frac{d\theta}{dz}=\frac{L}{\rho_o v T_o c_p}\Bigg(&\sum_{i=1}^{2}(-\Delta H_{ri})\sum_{j=1}^{2}k_{pij}\lambda_o^i c_{moj}(1-y_{mj})\\&+\frac{4UvT_o}{D_i v_o}(\theta_c-\theta)+\frac{v^2}{Lv_o}\left(\frac{d\ln V}{d\ln T}\right)_p\frac{dp}{dz}\Bigg)\end{aligned} \tag{A22}$$

$$\frac{d\theta_c}{dz}=\frac{\pi\,\mathrm{LUD}_0}{m_c c_{pc}}(\theta_c-\theta), \tag{A23}$$

where

$$\frac{1}{U_i} = \frac{1}{h_i} + \frac{A_i}{2\pi k_w L_c} \ln \frac{r_o}{r_i} + \frac{A_i}{A_o} \frac{1}{h_o} + R_f. \tag{A24}$$

Pressure Drop:

$$\frac{dp}{dz} = -2 f_r \frac{L}{D_i} \rho v^2. \tag{A25}$$

Application of the QSSA to the primary radicals $R^{\cdot}$ and the moments of the live polymer chain moments λ_k^i, elimination of the velocity gradient terms in Eqs. A5 and A8, and assuming that the reaction rate of a P radical chain with an M_2 monomer is approximately equal to the reaction rate of a Q radical with an M_1 monomer, the moments of the live polymer chains can be evaluated analytically as follows:

$$\lambda_o^1 = \frac{\sqrt{2 \frac{v_o}{v} \sum_{i=1}^{N_i} k_{di} c_{Ioi} (1 - y_{di}) G}}{G}, \tag{A26}$$

$$\lambda_o^2 = a \lambda_o^1 \tag{A27}$$

where

$$a = \frac{(k_{p12} + k_{fm12}) c_{mo1} (1 - y_{m1})}{(k_{p21} + k_{fm21}) c_{mo2} (1 - y_{m2})} \tag{A28}$$

and

$$G = (k_{tc11} + k_{td11}) + 2a(k_{tc12} + k_{td12}) + a^2 (k_{tc22} + k_{td22}). \tag{A29}$$

The higher order moments can then be estimated in pairs $(\lambda_k^1, \lambda_k^2)$ in terms of the zeroth moments by solving the following 2×2 linear system:

$$B_{i,k} + C_{i,k} \lambda_k^i + D_{i,k} \lambda_k^{f(i)} = 0 \qquad i = 1,2, \tag{A30}$$

where

$$f(i) = \begin{cases} 1 & \text{if } i = 2 \\ 2 & \text{if } i = 1 \end{cases}$$

and

$$B_{i,k} = \left(k_{Ii} [R^{\cdot}] + \sum_{j=1}^{2} k_{fmji} \lambda_0^j + \sum_{j=1}^{2} k_{pji} \sum_{r=0}^{k-1} \binom{k}{r} \lambda_r^j \right)$$

$$\times c_{m0i} (1 - y_{mi}) + k_{si} \lambda_o^i c_{so} (1 - y_s) + \mu_{k+1} \sum_{j=1}^{2} k_{fpji} \lambda_o^j \tag{A31}$$

$$C_{i,k} = -k_{pif(i)} c_{moi} (1 - y_{mi}) - A_i - \sum_{j=1}^{2} k_{tcij} \lambda_o^j \tag{A32}$$

$$D_{i,k} = k_{pf(i)i} c_{moi} (1 - y_{mi}). \tag{A33}$$

For a detailed account of the physicochemical properties variation and the numerical values of the kinetic parameters, the reader should see Kiparissides et al. (1993) and Verros et al. (1993).

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