Rigorous Dynamic Model of the High-Pressure Polymerization of Ethylene in Tubular Reactors Able to Predict the Full Molecular Weight Distribution

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Introduction

High-pressure polymerization of ethylene in tubular reactors is a widely employed industrial process. It allows obtaining branched low density polyethylene (LDPE) with characteristics that have not been reproduced by the more modern low or medium pressure polymerizations. The process is carried out under rigorous conditions. For instance, the reactor is operated at very high pressure, between 1300 to 3000 bar at the inlet. The temperature rises from about 50 ºC at the reactor inlet to 330 ºC at the hottest points due to the exothermic polymerization. Axial velocities are also high, usually around 10 m/s. Besides, the reactor configuration is complex. The main feed usually consists of ethylene, inert components, transfer agents to control the molecular weight, and eventually oxygen as initiator. Most of the polymerization reaction, however, is initiated by peroxides that are fed to the reactor through lateral injections. Monomer and/or transfer agents can also be fed through side injections. The polymerization takes place in short reaction zones following the peroxides injections, exhibiting high heat generation and steep temperature profiles. The rest of the reactor is mainly used as a heat exchanger, heating or cooling the reaction mixture in order to reach appropriate temperatures for peroxides addition or for downstream units. The control of the reaction mixture temperature is achieved by circulating vapor or liquid water through different jacket zones, which may be interconnected or not. Moreover, some of these reactors are provided with a let-down valve located at the reactor exit that is periodically opened to produce a pressure pulse which sweeps out the polymer from the walls. Besides, the interaction between the different reacting species is very complex, and there is an intricate connection between polymer quality and process conditions.

In this context, a mathematical model is fundamental tool to study safely and economically the influence of the different design and operative variables on production performance and product quality, as well as for process optimization. In order to achieve high-quality results that could be useful for actual plants, comprehensive models with accurate predictive capabilities are required. In spite of mathematical modeling of industrial LDPE tubular reactors being a complex task, a considerable amount of research work has been devoted to this task. Rigorous steady state models of this process have been reported in the literature.[1-3] In general, these models consider realistic reactor configurations and include detailed predictions of physical and transport properties along the axial distance. Most of these models have focused on the polymer average molecular properties, like the average molecular weights or average degrees of branching. However, the prediction of their distributions, such as the full molecular weight distribution (MWD) or two-dimensional distributions in molecular weight and branching frequency have also been reported.[4-6]

On the other hand, less attention has been devoted to the dynamic operation of these reactors. Dynamics is an important component of the performance of this process. As is usual in continuous polymerization plants, different polymer grades are produced in the same equipment. Therefore, normal operation requires changes from one steady state to another in order to switch among different final products. In the transient states during these changes, off specification, low-value product is generally produced. Dynamic operation is also important in start-up or shut-down procedures. Although it has been stated that quasi-steady state can be assumed in this process,[7] recent works have shown that dynamics cannot be ignored under certain conditions, specially when material recycle is involved, because in this case time constants may change from minutes to hours.[8] There are few works dealing with the dynamic operation of this process available in the literature. In these, usually very simplified and small models have been used.[9,10] A few dynamic models involving a more detailed description of the process have been reported, [8,11] but they have not included prediction of distributions of molecular properties.

In previous works we developed a rigorous steady state model of a LDPE tubular reactor.[4,12] This model was validated against experimental data from an actual industrial reactor. In this work, we present an extension of that model consisting in the incorporation of the process dynamics. Comprehensiveness of the former model was kept. This involves employing rigorous correlations for the calculation of physical and transport properties, such as density, viscosity and heat capacity of the reaction mixture and coolant, and heat-transfer coefficient along the axial distance and time. Realistic reactor configuration is also considered. The resulting model is capable of predicting the full MWD, as well as average branching indexes, monomer conversion and average molecular weights along time and reactor length. This model is used for analyzing the influence of different dynamic scenarios on process and product quality variables. In particular, grade transition policies are studied.

Process Description and Mathematical Model

A simplified flow sheet of the LDPE process analyzed in this work is displayed in Figure 1. The polymer is produced by high-pressure polymerization of ethylene in a tubular reactor, using oxygen and peroxide mixtures as initiators. The make-up stream, consisting of ethylene, inert components, oxygen and transfer agents, is mixed with the low-pressure recycle stream, and then compressed to about 250 bars in a multi-stage primary compressor. This stream is mixed with the high-pressure recycle stream, and then compressed in a hyper-compressor up to the reaction pressure, which is usually around 2000-2800 bars. The compressor outcome is fed to the jacketed tubular reactor, where the ethylene is polymerized with a conversion per pass of approximately 25 – 30 %. Although the reaction is partially initiated by the oxygen, most of the polymerization is initiated by organic peroxide mixtures. These peroxides are added at additional feeds located at different axial positions, producing short reaction zones with sharp temperature and conversion increases. The reactor sections apart from these reaction zones are mainly used as heat exchangers in order to reach appropriate temperatures for peroxide addition or for downstream units. Monomer and/or transfer agents can also be fed through side feedings. The control of the reactor temperature is achieved by circulating vapor or liquid water through independent tube jackets. The reactor

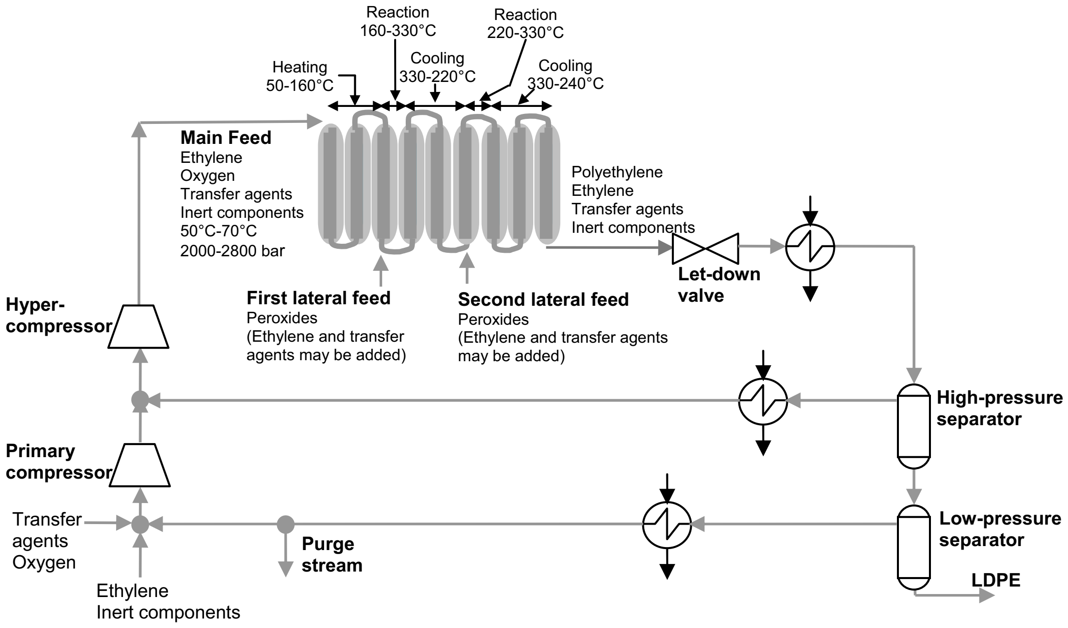

Figure 1. Simplified flow sheet of the LDPE production plant

output is expanded in a let-down valve, which produces a pressure pulse that travels back along the reactor removing polymer build ups from the reactor wall. The expanded reactor output is separated first in a high pressure and then in a low pressure separator. Unreacted ethylene and transfer agents, and inert components, are cooled and then recycled. The polymer is obtained from the low pressure separator. The particular configuration of the reactor analyzed in this work considers eight jacket zones and two lateral peroxide feeds.

This work is focused on the analysis of the tubular reactor unit. The mathematical model of the polymerization reactor is based on a previous, comprehensive steady state model developed by the authors, [4,12] which is extended by incorporating the process dynamics. The model assumes plug flow and supercritical reaction mixture. Besides, it considers variation of physical and transport properties (i.e. axial velocity, heat capacity, thermal conductivity, viscosity and density) along the axial distance, calculated with rigorous correlations. Detailed calculation of the heat-transfer coefficient along the axial distance is also included.[3] The kinetic mechanism considered in the reactor model is shown in Table 1. It includes all the kinetic steps commonly proposed in the literature for this process. In order to avoid iterative calculations that increase the computational burden, the jacket temperature at each one of the eight reaction zones is assumed uniform, and the pressure pulse is neglected. The peroxide mixtures are treated as single fictitious species. The same is done for the transfer agent mixtures. These simplifications were validated in a previous work by the authors[12] against several data sets from an industrial tubular reactor. The same transfer agent mixture, and therefore the same single fictitious transfer agent (S), that is employed for the main reactor feed is considered for possible lateral feeds. However, peroxide mixtures for the first and second lateral feeds are different in composition,[12] and hence they are represented in this model by two different fictitious peroxides (I_1 for the first lateral feed and I_2 for the second one).

The set of kinetic constants reported by Asteasuain et al.[12] is used here. The main model equations are outlined in Table 2. Reaction mixture physical and transport properties, such as density ($\rho(z,t)$), heat-capacity ($\mathrm{Cp}(z,t)$), heat-transfer coefficient ($U(z,t)$), and others like thermal conductivity and viscosity, are calculated along axial distance and time using rigorous correlations that are function of the reaction mixture composition, reactor temperature and pressure, and dimensionless numbers such as the Nusselt, Reynolds, Prandtl and Pecklet numbers. The well-known method of moments and the probability generating function (pgf) transformation technique[13,14] are employed for calculating the average molecular weights and the full MWD, respectively. Briefly, the pgf method is based on a transformation of the mass balances of macroradicals and dead polymer ($R(m)$ and $P(m)$, respectively, in Table 1) into the pgf domain. In this way, balances for the pgf transforms of the macroradicals and dead polymer number, weight and differential log distributions are obtained (see Eq. (20), with $\phi(a)$ and $\varphi(a)$ representing macroradicals and dead polymer transforms, respectively, and a = 0, 1, 2 standing for number, weight and differential log distributions, respectively). Pgf transforms obtained by solution of the pgf balances are inverted by an inversion algorithm (function f in Eq. (19)), to obtain the corresponding distributions. This technique allowed modeling the MWD easily and efficiently, in spite of the reactor model complexity. Expressions corresponding to the reaction rates $r_j(z,t)$ in Eq. (20) and the pgf inversion algorithm can be found elsewhere.[1,4]

Table 1. Kinetic mechanism

Peroxide initiation		*Oxygen initiation*	
$I_k \xrightarrow{k_{ik}} 2R(0) \quad k=1,2$	(1)	$O_2 + M \xrightarrow{k_o} 2R(0)$	(8)
Monomer thermal initiation		*Generation of inert*	
$3M \xrightarrow{k_{mi}} R(1) + R(2)$	(2)	$O_2 + R(m) \xrightarrow{f_o k_o} X$	(9)
Propagation		*Termination by combination*	
$R(m) + M \xrightarrow{k_p} R(m+1)$	(3)	$R(n) + R(m) \xrightarrow{k_{tc}} R(n+m)$	(10)
Thermal degradation		*Chain transfer to monomer*	
$R(m) \xrightarrow{k_{tdt}} P(m) + R(0)$	(4)	$R(m) + M \xrightarrow{k_{trm}} P(m) + R(1)$	(11)
Chain transfer to polymer		*Chain transfer to transfer agent*	
$R(n) + P(m) \xrightarrow{m\,k_{trp}} P(n) + R(m)$	(5)	$R(m) + S \xrightarrow{k_{trs}} R(m) + R(0)$	(12)
Backbiting		*β-Scission of secondary radical*	
$R(m) \xrightarrow{k_{bb}} R(m)$	(6)	$R(m) \xrightarrow{k_{\beta 1}} P(m) + R(0)$	(13)
β-Scission of tertiary radical			
$R(m) \xrightarrow{k_{\beta}} P(m) + R(0)$	(7)		

Peripheral units, such as compressors, separators and heat exchangers in the recycle section are not modeled, because this work focuses only on the qualitative effects of the material recycle on the reactor performance. Instead, a perfect separation of the polymer from the remaining components of the reactor output is assumed. The resulting recycle stream and the make-up stream are considered to be both at the reactor feed temperature when they mix with each other. However, an important aspect of this process is the presence of several time delays.[15] In this work, time delays are incorporated into the plant model as a pure delay in the recycle stream. Model implementation was carried out in the commercial software gPROMS (Process Systems Enterprise, Ltd.).

Table 2. Outline of the main model equations

Global mass balance $\frac{\partial\left(\rho(z,t)v(z,t)\right)}{\partial z}+\frac{\partial\rho(z,t)}{\partial t}=0 \qquad (14)$ *Pressure drop* $\frac{\partial P(z,t)}{\partial z}=c \qquad c:\text{constant parameter} \qquad (15)$ *Number average molecular weight* $\mathrm{Mn(z,t)}=\mathrm{Mw_M}\frac{\lambda_1(z,t)+\mu_1(z,t)}{\lambda_0(z,t)+\mu_0(z,t)} \qquad (16)$	*Mass balances of components, MWD moments and pgfs* $\frac{\partial C_j(z,t)}{\partial t}+\frac{\partial v(z,t)C_j(z,t)}{\partial z}=r_j(z,t)$ $j=O_2(\text{oxigen}),M(\text{ethylene}),I_k(k th\text{ initiator},k=1,2),$ $S(\text{transfer agent})$, Me (Methyl groups), Vi (vinyl groups), Vd (vinylidene groups),LCB (long chain branches), (20) λ_a(*ath* order moment of the macroradical MWD, *a*=0,1,2), μ_a(*ath* order moment of the dead polymer MWD, *a*=0,1,2), ϕ_a(*ath* pgf transform of the macroradical MWD, *a*=0,1,2), φ_a(*ath* pgf transform of the dead polymer MWD, *a*=0,1,2)
Weight average molecular weight $\mathrm{Mw(z,t)}=\mathrm{Mw_M}\frac{\lambda_2(z,t)+\mu_2(z,t)}{\lambda_1(z,t)+\mu_1(z,t)} \qquad (17)$ *Short chain branches / 1000 C* $\mathrm{SCB/1000C}\ (z,t)=500\frac{\mathrm{Me}(z,t)}{\lambda_1(z,t)+\mu_1(z,t)} \qquad (18)$	*Energy balance* $\rho(z,t)\mathrm{Cp}(z,t)\frac{\partial T(z,t)}{\partial t}+\rho(z,t)v(z,t)\mathrm{Cp}(z,t)\frac{\partial T(z,t)}{\partial z}=$ $-\frac{4U(z,t)(T(z,t)-T_j)}{D}+r_{\mathrm{pm}}(z,t)(-\Delta H) \qquad (21)$
Full MWDs $n(z,t)=f\left(\phi_0(z,t)+\varphi_0(z,t))/(\lambda_0(z,t)+\mu_0(z,t)\right)$ $w(z,t)=f\left(\phi_1(z,t)+\varphi_1(z,t))/(\lambda_1(z,t)+\mu_1(z,t)\right)$ $\frac{dW}{d(\log_{10}Mw)}(z,t)=f\left(\phi_2(z,t)+\varphi_2(z,t))/(\lambda_1(z,t)+\mu_1(z,t)\right)$ $n(z,t)$: number fraction distribution (19) $w(z,t)$: weight fraction distribution $dW/d\log_{10}Mw\,(z,t)$: differential log distribution $f(.)$: algebraic equations of the pgf inversion algorithm	*Vinyl groups / 1000 C* $\mathrm{Vi/1000C}\ (z,t)=500\frac{\mathrm{Vi}(z,t)}{\lambda_1(z,t)+\mu_1(z,t)} \qquad (22)$ *Vinylidene groups / 1000 C* $\mathrm{Vd/1000C}\ (z,t)=500\frac{\mathrm{Vd}(z,t)}{\lambda_1(z,t)+\mu_1(z,t)} \qquad (23)$ *Long chain branches / 1000 C* $\mathrm{LCB/1000C}\ (z,t)=500\frac{\mathrm{LCB}(z,t)}{\lambda_1(z,t)+\mu_1(z,t)} \qquad (24)$

Results and Discussion

In order to check the model validity, simulations were performed for different initial conditions. It was observed that model outputs evolved towards the expected steady state values. An example of this analysis is presented in Figure 2, which shows the evolution of the temperature profile during a reactor start-up. The reactor is considered to be initially filled with monomer at 76 ºC. The recycle stream is disconnected, and operating variables are set at their steady state values at time 0. It can be observed that the steady state temperature profile matches reasonable well the plant data. It is also interesting to note the extremely rapid increase of the reactor temperature. For instance, the steady state value of the first temperature peak is reached in less than 20 s, involving an increment of 255 ºC with respect to the initial value. At increasing times, steady state temperature values along the reactor are reached after an overshoot. However, it can be seen that the temperature value of 345 ºC, above which reactor runaway can occur, is never surpassed.

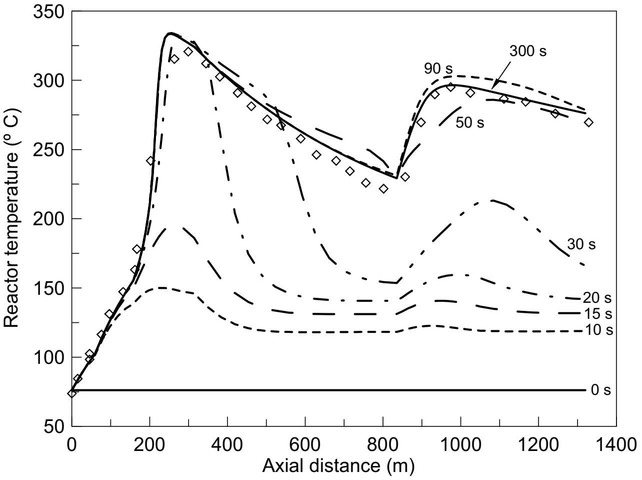

Figure 2. Axial temperature profiles calculated during a reactor start-up. Symbol: plant steady state values; lines: model

The model was used to asses the influences of different process perturbations, with and without recycle. Changes in the flow rates of monomer, initiators and transfer agents and in the feed temperature were analyzed. As an example, results for the flow rate of monomer are presented, which was the variable that most significantly affected the process for the same relative change in its original value. Figure 3 shows the time profiles of the position and temperature values of the temperature peaks after a step reduction of 30 % in the monomer feed rate, for the reactor without recycle. Temperature peaks are very important parameters for the operation of these reactors. It can be seen that the temperature of the first peak surpasses a dangerous value of 345 ºC before reaching its steady state value, and that its position moves towards the reactor entrance. The second peak shows larger differences between its transient and steady state values. This illustrates the importance of the capability of predicting the dynamic behavior of these reactors.

Figure 4 shows the time profiles of the temperature peaks for the same perturbation, but for the reactor with recycle. It can be seen, noting the different time scales of the graphics, that the behaviors of the second temperature peak with and without recycle are similar. However, dynamics for the first peak are slower for the reactor with recycle. The time profile of the position of this peak is similar to the one without recycle, but slightly delayed in time. On the contrary, the temperature value of this peak reaches a much higher value than in the previous case, showing a delay in reaching the new steady state more than ten times greater than before. This slower dynamics is an expected result of the influence of the recycle of material, since the recycle loop needs a time to settle down after the feed perturbation. Consistent results about the influence of the recycle loop on the reactor dynamics have been reported in the literature.[8]

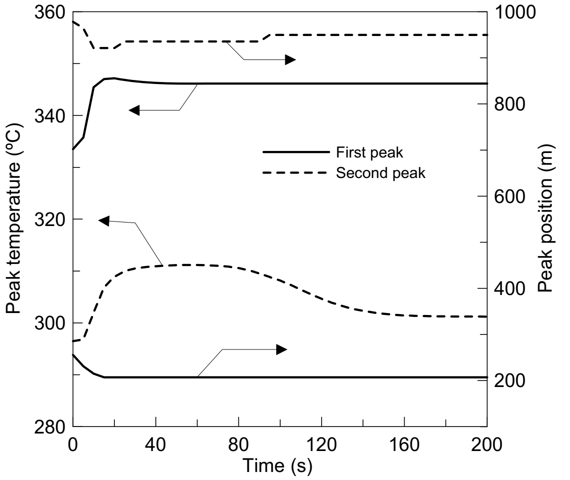

Figure 3. Position and temperature values of the temperature peaks after a step reduction of 30 % in the monomer feed rate without recycle

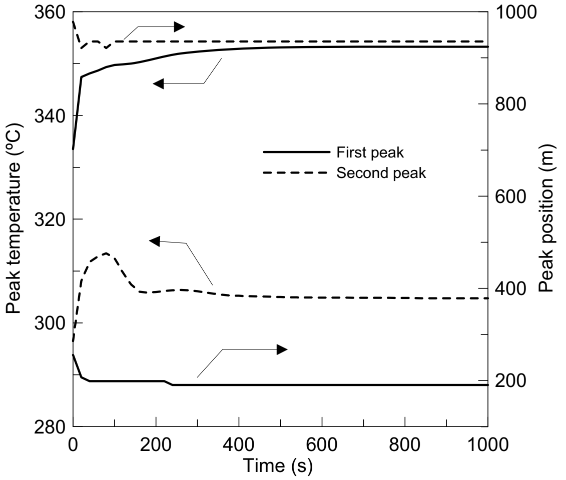

Figure 4. Position and temperature values of the temperature peaks after a step reduction of 30 % in the monomer feed rate with recycle

Transitions between the productions of different polymer grades are frequent and are an important component of the operation of this process. A usual method of achieving these transitions is to modify the transfer agent flow rate,[15] which directly affects the polymer molecular weights. Deviations of the monomer feed to the side feeds may also be applied.[4] Figure 5 shows the evolution of the MWD during a transition from a polyethylene grade of Mw = 140000 g/mol to a grade of Mw = 220000 g/mol, considering the reactor with recycle. The new operating scenario involves a reduction of the transfer agent flow rate at the reactor inlet from 0.27 kg/h to 0.23 kg/h, and a deviation of 7 % of the monomer feed to the second lateral feed. Also, a different jacket temperature profile is applied. The transition policy consists of a step change in each of these variables to the operating point value for the new grade. The shift of the MWD to higher molecular weights can be observed in Figure 5. It is interesting to note that the intermediate portion of the MWD partially shifts back to lower molecular weights after a certain time, while the high molecular weight tail of the distribution becomes more important towards the end of the transition with a marked formation of a shoulder. The grade transition finishes approximately 2.2 h after the change in operating conditions. The detailed tracking of the evolution of the MWD provided by the model has a great potential for a careful analysis of transition policies.

The transition time is markedly different for the same transition policy but without material recycle. In this case, the time needed to achieve the transition is only 0.08 h. This difference may be attributed to the fact that in the no-recycle case the transmission of the change in the make-up stream to the reactor inlet is instantaneous. On the contrary, when the recycle stream is mixed with the make-up stream, the changes in the latter are masked by the return of unreacted monomer and transfer agent. This is particularly important for the transfer agent, because the consumption per pass of this reactant is very small. Hence, a long time is needed before the excess of it is consumed through several passes through the reactor. This is illustrated in Figure 6, which shows the transfer agent flow rate at the reactor inlet and in the make-up stream for the grade transitions with and without recycle. A similar behavior is observed for the monomer flow rate, although the time delay is shorter.

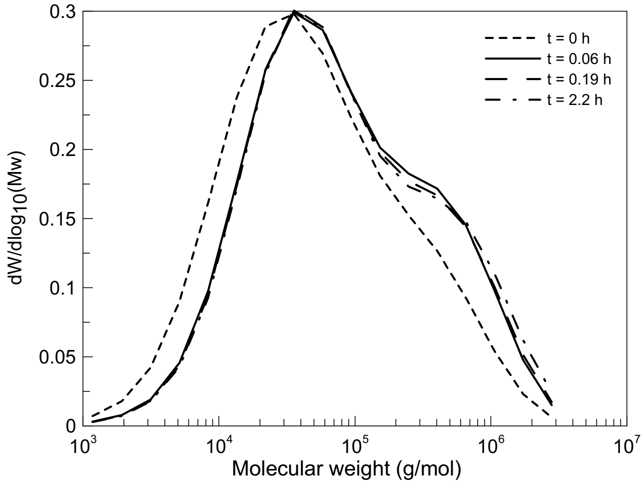

Figure 5. MWD at the reactor exit during grade transition

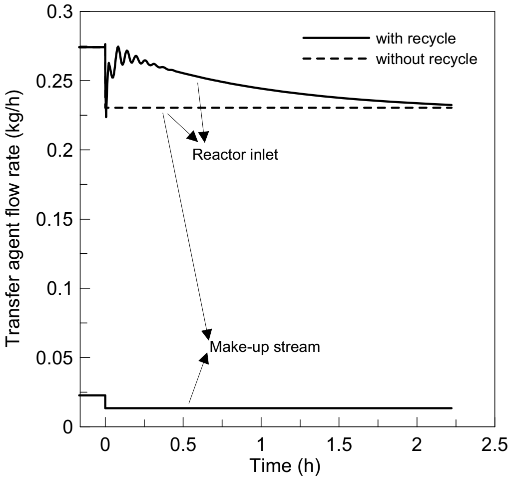

Figure 6. Transfer agent flow rates at the reactor inlet during grade transition. Make-up flow rates are switched to final values at t = 0

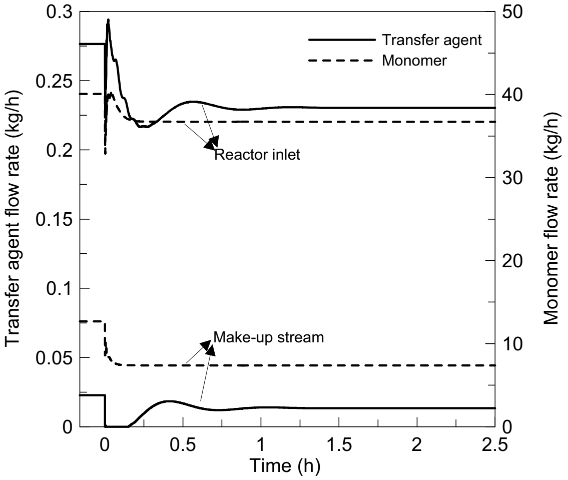

Figure 7. Monomer and transfer agent flow rates during grade transition. Make-up flow rates are manipulated by PI controllers

A corollary of these results is that an important benefit can be obtained by optimizing the transition policy. Figure 7 shows the flow rates of transfer agent and monomer at the reactor inlet and in the make-up stream, when the make-up flow rates are manipulated by PI controllers with the desired flow rates at the reactor inlet as set points. Although the PI controllers had only been roughly tuned by hand, the improvement in transition time is significant.

Conclusions

A comprehensive dynamic model of the high-pressure polymerization of ethylene in tubular reactors was developed. The model, which considers variable physical and transport properties calculated by means of rigorous correlations, can predict the full MWD, monomer conversion, reactants concentrations, average molecular weights and average degree of branching along the axial distance and time. In particular, the pgf technique allowed modeling the full MWD easily and efficiently in spite of the reactor model complexity. The results obtained show that the model has great potential for analyzing dynamic responses of MWD and other process variables under different transition policies, as well as to predict the influence of process perturbations and for studying start-up and shut-down operations. The influence of the material recycle on the process dynamics was assessed. In particular, it was shown that the recycle stream must be taken into account when analyzing transition policies. Besides, it was also shown that a significant improvement can be obtained by optimizing the transition procedure.

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