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Modeling and Simulation of Liquid Phase Propylene Polymerizations in Industrial Loop Reactors

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Summary: Liquid phase tubular loop polymerization reactors are widely used in the polyolefin industries because of their capabilities to promote high mixing of reactants in the reaction vessel and to allow for high heat transfer rates with the cooling jacket due to their high aspect ratio. Previous works on this subject focused on the modeling of the polymerization system, but only a few compared their results with real industrial data. A literature review about the propylene production in loop reactors shows that the validation of a distributed model with actual industrial data is yet to be presented. A distributed mathematical model is presented for industrial liquid phase loop polypropylene reactors and validated with actual industrial data for the first time. The model is able to represent the dynamic trajectories of production rates, MFI and XS values during grade transitions within the experimental accuracy. The model indicates that the polymer quality can change significantly along the reactor train and that manipulation of feed flow rates can be successfully used for production of more homogeneous polymer products.

Keywords: liquid-pool; modeling; polymerization; propylene; Ziegler-Natta

Introduction

Liquid phase tubular loop polymerization reactors are widely used in the polyolefin industries because of their capabilities to promote high mixing of reactants in the reaction vessel and to allow for high heat transfer rates with the cooling jacket due to their high aspect ratio. The first mathematical models developed for the polymerization of propylene in loop reactors appeared in the 1970s[1,2] and used continuous stirred tanks to describe the mixing patterns in these systems. This approach was also used later by Ferrero and Chioveta.[3] Zacca and Ray[4] were the first to propose a distributed dynamic model to describe the polymerization of propylene in this process but, as in previous works, validation with industrial data was not presented. Recently, Reginato, Zacca and Secchi[5] used a nonideal continuous stirred tank model to describe this process and compared their simulation results with actual plant data. Production rates, slurry densities and melt flow indexes were used to validate the model developed.

This brief review shows that the validation of a distributed model for the propylene production in loop reactors with industrial data is yet to be presented. A distributed model may allow for a full analysis of the process behavior because it takes into account the distributed nature of the system, the possibility of using different levels of macromixing to describe the mixing patterns inside the reactor and the possibility of incorporating peculiar sedimentation, mass transfer and heat transfer aspects into the model formulation.[4]

This paper presents a distributed dynamic mathematical model for the polymerization of propylene in tubular loop

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reactors. The model aims at describing the main process variables related to the quality control of the industrial polymerization process, such as the production rate, the melt flow index (MFI) and the amount of xylene solubles (XS) in the final polymer resins. Hydrogen is used to control the average molecular weights (and, consequently, the MFI) of the polymer resin. The model implementation allows for the simulation of a train of loop reactors with multiple feeds. It is shown for the first time that a distributed model may be adequately tuned to describe grade transitions during industrial operation of polypropylene loop reactors. It is also shown that MFI and XS data may be properly simulated with the developed model. Therefore, the model can be used for interpretation of process operation data and for development of optimum operation strategies.

Mathematical Modeling

As discussed in the previous section, several models have been proposed to describe the polymerization of propylene in tubular loop reactors. The loop polymerization reactor investigated here consists of a pair of continuous tubular reactors whose ends are connected, at one side, to the inlet feed and, at the other side, to the exit stream and to a recycling pump, as presented in Figure 1.[6] It is important to emphasize that the recycling pump is not considered here as a zero-capacitance vessel but, instead, as a piece of equipment whose behavior may play a fundamental part on the overall process dynamics. In addition to that, the external thermal capacitance of both the reactor tubular sections and the recycling pump were also taken into account. These modifications were motivated by previous experimental and modeling results obtained in a lab-scale loop reactor[6,7] that emphasized the need of adding the recycling pump into the model in order to describe appropriately the macromixing behavior of the reactor as well as its thermal dynamics.

As depicted in Figure 1, the loop reactor considered here is composed of three distinct reaction sections, namely, the tubular section 1, that connects the inlet feed point to the exit stream and the recycling pump; the recycling pump, that recycles most part of the polymer slurry and is connected to the tubular section 2; and the tubular section 2, that connects the exit of the recycling pump to the inlet feed point. The tubular sections were described according to the axial dispersion model and the recycling pump is considered to be perfectly mixed. Other model assumptions may be found elsewhere.[8]

Thus, according to the axial dispersion model, a molar balance for a given species in a tubular section of the loop reactor results in:

$$\frac{\partial C_j^i(z,t)}{\partial t} + v_z^i \frac{\partial C_j^i(z,t)}{\partial z} = D_m \frac{\partial^2 C_j^i(z,t)}{\partial z^2} - R_j^i(z,t), \tag{1}$$

where C_j^i is the molar concentration of species j (monomer, catalyst, cocatalysts,

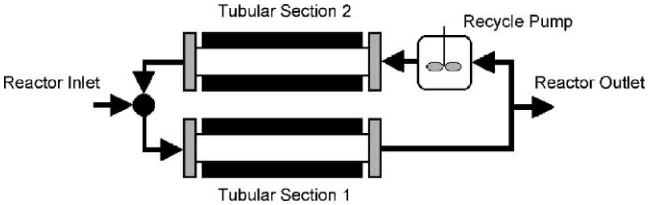

Figure 1.
Loop reactor diagram.[6,7]

hydrogen and moments of the polymer molar mass distribution) in tubular section i, v_z is the average flow velocity, D_m is the axial dispersion coefficient (assumed here to be the same for all species present in the tubular sections, which is equivalent to assuming that dispersion is determined by the internal flow patterns), R_j is the overall rate of consumption of species j, z and t are the space and time coordinates, respectively.

The energy balance is obtained by neglecting energy changes due to expansion work, viscous flow, external fields, radiation and heat of mixing. The energy balance for each tubular section can be given by[10]:

$$\begin{aligned}&\left[\rho C_p + \left(\rho C_p\right)_r\right]\frac{\partial T^j(t,z)}{\partial t}\\&\quad + \rho C_p v_z^i \frac{\partial T^j(t,z)}{\partial z_j}\\&= D_t \rho C_p \frac{\partial^2 T^j(t,z)}{\partial z_j^2} + (\Delta H_r) R_M(t,z)\\&\quad + \frac{4U_r}{d}\left[T_c - T^j(t,z)\right],\end{aligned} \tag{2}$$

where T^j is the reactor temperature in tubular section j. The term ρC_p in Equation (2) stands for the thermal capacitance of the polymer solution flowing through tubular section j, whereas the term $\left(\rho C_p\right)_r$ represents the overall thermal capacitance of the reactor externals (such as tube walls, fittings, valves, recycling pump etc). D_t is the thermal dispersion coefficient, ΔH_r is the reaction enthalpy and U_r is the reactor overall heat transfer coefficient.

The recycling pump is described as an ideal continuous stirred tank reactor. The mass balance for component j is given below.

$$\begin{aligned}V_p \frac{dC_j^p(t)}{dt} &= Q_2\left(C_j^1(t)\Big|_{exit}\right.\\&\quad \left. - C_j^p(t)\right) - V_p R_j(t),\end{aligned} \tag{3}$$

where C_j^p is the molar concentration of component j in the recycling pump, V_p is the internal volume of the recycling pump, and Q_2 is the volumetric flow rate in tubular section 2.

The energy balance for the recycling pump is given by

$$\begin{aligned}&\left[V_p \rho C_p + \left(V \rho C_P\right)_p\right]\frac{dT^p(t)}{dt}\\&\quad = \rho C_p Q_2\left(T^1(t)\big|_{exit} - T^p(t)\right)\\&\qquad + (\Delta H_r) V_p R_i(t)\\&\qquad + U_p\left(T_c - T^p(t)\right).\end{aligned} \tag{4}$$

For Equation (1)–(2), well-known Danckwerts boundary conditions have been applied. Equation (1)–(4) along with the boundary conditions constitute a set of coupled, non linear parabolic partial and ordinary differential equations. The axial coordinates of the tubular sections were discretized according to a polynomial approximation on finite elements. Convergence tests as well as other details regarding the numerical solution of the model equations may be found elsewhere.[6,11]

One important point regarding the reactor model developed in this work is that, in addition to the usual kinetic steps of site activation, chain initiation, propagation, transfer reactions, and deactivation (cf. Table 1 for the kinetic scheme and Table 2 for the kinetic parameters), the model also incorporates equations to account for the dynamic evolution of the melt flow index and amount of solubles in xylene in the polymer resins produced. Models for these properties are taken from Latado *et al.*[9] The method of moments is applied to population balances that describe live and dead polymer chains in order to allow for calculation of average molecular weights.

Table 1.
Kinetic mechanism for the polymerization reaction.

Site Activation:	Chain Transfer:
$S_p + A \xrightarrow{k_A} P_0$	$P_i + H_2 \xrightarrow{k_{TH}} P_0 + Q_i$
Chain Initiation:	$P_i + M \xrightarrow{k_{TM}} P_1 + Q_i$
$P_0 + M \xrightarrow{k_P} P_1$	$P_i \xrightarrow{k_{TS}} P_0 + Q_i$
Chain Propagation:	Site Deactivation:
$P_i + M \xrightarrow{k_P} P_{i+1}$	$P_i \xrightarrow{k_D} S_D + Q_i$
	$P_0 \xrightarrow{k_D} S_D$

Table 2.
Kinetic parameters for the liquid-phase polymerization of propylene with a fourth-generation Ziegler-Natta catalyst.

Parameter	Reference
$k_A = 7.04 \cdot 10^5\, e^{-12{,}000/R_gT}$ cm^3/gmol/s	[12]
$k_P = 6.3 \cdot 10^{11}\, e^{-10{,}000/R_gT}$ cm^3/gmol/s	[12]
$k_{TH} = 2.22 \cdot 10^{13}\, e^{-14{,}000/R_gT}$ cm^3/gmol/s	[12]
$k_{TM} = 2.76 \cdot 10^{10}\, e^{-14{,}000/R_gT}$ cm^3/gmol/s	[12]
$k_{TS} = 1.72 \cdot 10^6\, e^{14{,}000/R_gT}$ s^{-1}	[4]
$k_D = 7.93 \cdot 10^3\, e^{12{,}000/R_gT}$ s^{-1}	[4]

Results and Discussion

Model Validation

Case studies presented herein report data and simulations concerning a real industrial liquid phase propylene polymerization process using loop reactors. Due to confidentiality agreements, process operational parameters are not fully presented. Figure 2 illustrates typical grade transitions at plant site, during production of grades of very low to very high molar masses. Grade transition was performed through modification of the hydrogen feed concentrations according to the industrial practice. As observed, the model is able to describe appropriately the operation in the whole range of MFI values (within typical experimental errors), including the characteristic grade transition time, for multiple grade transitions performed sequentially.

In the industrial practice, grade transition zones should not be too long, as off-spec polymer resins are usually produced during these transitions. In order to minimize the impact of grade transitions on the process productivity, it is usually sought to depart from a low MFI operation (low hydrogen feed rates) and reach subsequent higher intermediate MFI plateaus (by increasing the hydrogen feed rates) until the attainment of the operation conditions required to produce the resin with the highest MFI. Figure 2 shows that model predictions can be regarded as very good, as deviations between predicted and measured values are smaller than 10%, which is the inherent experimental error. Similar results may be obtained for other process conditions.

For the case of the amount of solubles in xylene, XS, Figure 3 illustrates typical responses during MFI grade transitions. XS values are influenced mostly by the electron-donor concentrations (in this particular case, described as the ratio between TEA, tri-ethyl aluminum cocatalyst, and electron-donor). The higher the concentration of electron-donor, the lower is the expected XS level in the produced polymer. Regarding Figure 3, one may see that the model is capable of adequately reproducing the XS amounts in the polymer for the same operation conditions reported in Figure 2A. Again, model predictions can be regarded as very good, as deviations

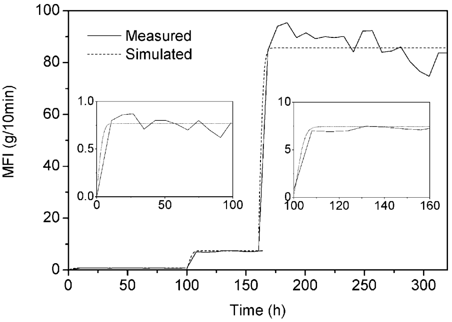

Figure 2.
Measured and simulated dynamic MFI profile during grade transitions.

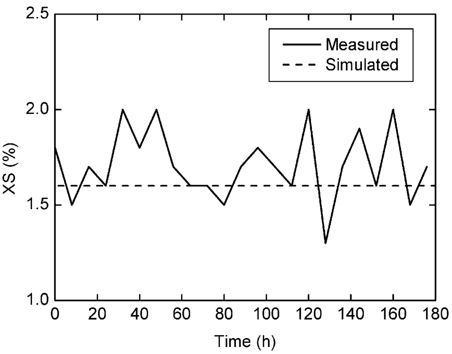

Figure 3.
Measured and simulated dynamic XS profiles.

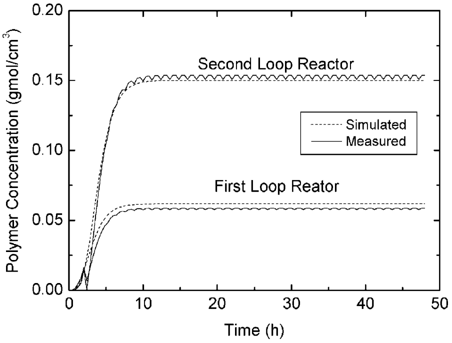

Figure 4.
Validation of productivity data during the production of polypropylene.

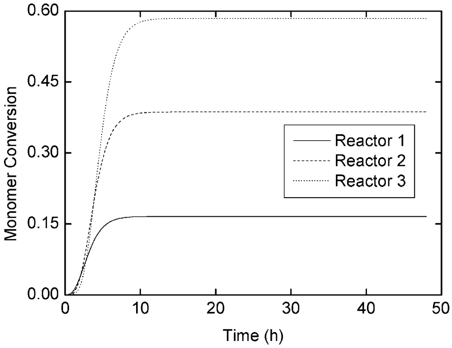

Figure 5.
Simulated monomer conversion dynamic profiles for a train of loop reactors.

between predicted and observed values are within the experimental accuracy (±0.3%). Similar results can be obtained in all other cases.

Figure 4 presents the model validation for the variable polypropylene production and considers the operation of two full-scale loop reactors in series. Operation conditions are similar to the ones reported in Figure 2 for low MFI during reactor start-up. It is possible to observe that model simulations provide a very fair prediction of the industrial process operation for both reactors. Low-amplitude measured data oscillations are due to the inherent fluctuations of the process instrumentation.

Process Simulation

The validated process model may now be used to simulate and investigate plant operation in order to increase process performance and polymer productivity. One possibility of increasing the polymer productivity is by adding another large-scale loop to the reactor train. Figure 5 explores this idea. Operation data refers to those used in Figure 2 during production of resins with low MFI. One may observe that conversions levels up to near 60% may be obtained, which can certainly be regarded as a significant improvement, considering the actual available process technology. If one assumes that the maximum allowed polymer concentration is equal to 55%, then the propylene feed flow rates can be increased to reduce the residence times and safely allow for significant increase (about 35%) of the polymer productivity.[13]

Other variables are also of practical interest. Simulated MFIs for the polymer produced in the reactor train are presented in Figure 6. As shown, the MFI of the polymer material can change quite considerably along the train when the monomer/hydrogen feed ratios are kept constant for all reactors. This can be explained in terms of the very distinct reaction conditions inside each of the reactors, due to varying polymer concentrations (which increase), catalyst concentrations (which decrease, due to catalyst decay) and monomer concentrations (which decrease, due to monomer consumption), which lead to distinct hydrogen concentrations and

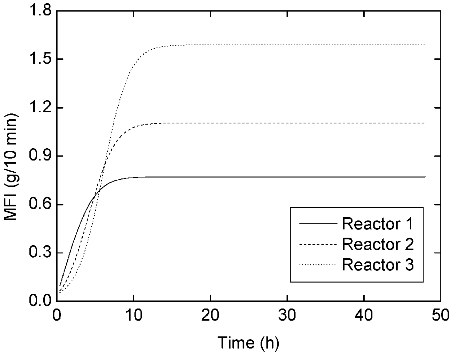

Figure 6.
MFI dynamic profiles along the reactor train during grade transition.

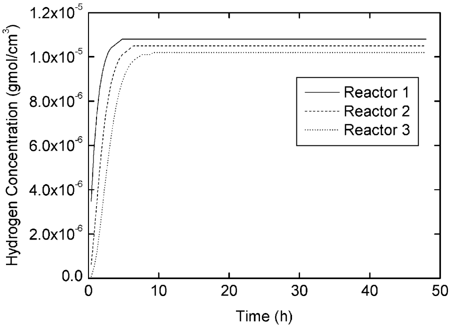

Figure 7.
Hydrogen dynamic profiles along the reactor train during grade transition.

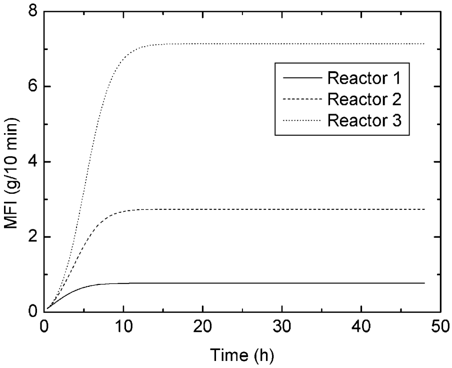

Figure 8.
MFI dynamic profiles along the reactor train when a multiple hydrogen feed is applied.

rates of chain transfer inside each of the reactors, as shown in Figure 7. Therefore, it sounds reasonable to propose the use of distinct monomer/hydrogen feed ratios (and also of hydrogen compositions) for each of the reactors, in order to allow for production of custom-designed polymer materials.

In order to explore this possibility, a more realistic process simulation may be performed in such a way that any reactor in the train may receive fresh monomer, catalyst, cocatalysts, and hydrogen. Usually, however, multiple feeds are restricted only to monomer and hydrogen, in order to modify both process productivity and the polymer grade. Besides, it is also known that, in a typical industrial site, the catalyst is firstly fed to a small size pre-polymerization vessel known as baby-loop. In this first reactor, catalyst particles are encapsulated by a growing polymer mass at mild reaction conditions. The control of the morphology of the polymer particles is basically performed in this step.[5] Pre-polymerization is used to produce spherical polymer particles in an early reaction stage, avoiding uncontrolled particle fragmentation in the large scale reactors.

Figure 8 and 9 present MFI and hydrogen concentration profiles, respectively, for the train of loop reactor composed by a baby-loop, whose total length is 1/58 of that of the other two full-scale loop reactors (although retaining the same length/diameter ratio). Monomer, catalyst, cocatalysts and hydrogen are fed to the baby-loop, but only hydrogen is also provided to the full-scale loop reactors. One may observe that very different polymer grades may be obtained in each reactor, thus reinforcing the fact that hydrogen is a crucial variable to determine the final product quality at plant site. For this reason, hydrogen feed rates should be manipulated independently at each reaction stage and properly designed with the help of validated simulation models.

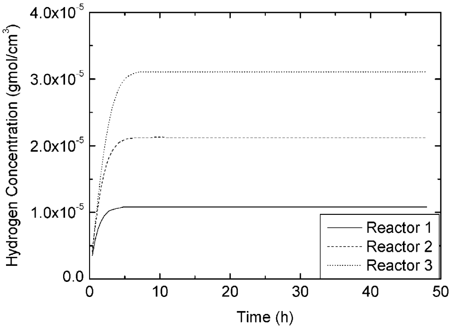

Figure 9.
Hydrogen concentration dynamic profiles along the reactor train when a multiple hydrogen feed is applied.

Conclusions

A distributed mathematical model is presented for industrial liquid phase loop polypropylene reactors and validated with actual industrial data for the first time. The model is able to represent the dynamic trajectories of production rates, MFI and XS values during grade transitions within the experimental accuracy. The model indicates that the polymer quality can change significantly along the reactor train and that manipulation of feed flow rates can be successfully used for production of more homogeneous polymer products.

Notation

C	molar concentration (gmol/cm^3)
C_p	heat capacity (cal/g/K)
D	Dipersion coefficient (cm^2/s)
d	reactor tubes internal diameter
Q	volumetric flow rate (cm^3/s)
R	reaction rate (gmol/cm^3/s)
t	time (s)
T	reactor temperature (K)
U_r	reactor overall heat transfer coefficient (cal/cm^2/s/K)
U_p	recycling pump overall heat transfer coefficient (cal/s/K)
v_z	axial flow velocity (cm/s)
V_p	volume of the recycling pump (cm^3)
z	reactor tubular section length (cm)

Greek characters

ΔH_r	reaction enthalpy (cal/gmole)
ρ	density (g/cm^3)

Superscripts characters

1	related to tubular section 1
2	related to tubular section 2

Subscripts characters

1	related to tubular section 1
p	related to the recycling pump

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