MODELING XS DYNAMICS IN LIQUID PROPYLENE PROCESS

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The present work illustrates the use of modeling and control strategies for evaluating the effects of changing operation conditions upon the xylene soluble (XS) trajectories in a real industrial propylene polymerization process. Special attention was given to the liquid bleed operation and to the XS dynamic responses. In order to evaluate the degree of coupling that may exist between the XS dynamics and the liquid bleed flow rate policy, a mass balance model was built and used to simulate the process behavior. It was observed that an eventual cocatalyst recirculation through the recycle stream may influence very significantly the dynamics of the cocatalyst/donor ratio and consequently the dynamics of XS during the polymerization. Simulation results indicated that the effect of the liquid bleed operation and the cocatalyst/donor ratio may be minimized if PI controllers are designed to control the propane concentration in the reactor and to increase the speed of the cocatalyst/donor transitions. Finally, the proposed model was able to reproduce the dynamic XS profile obtained during a large XS transition.

Keywords: Polypropylene, Bulk Polymerization, Dynamic Modeling, Process Control.

Introduction

The proper understanding of xylene soluble (XS) dynamic responses to changes of the operation conditions in the liquid pool process (LIPP) is very important because XS is a key property of the final polymer resin and defines the applicability of the polypropylene. Therefore, understanding of XS dynamics is important for the development of advanced control schemes and automation of the liquid pool process, whenever tight control of XS values is needed. In the bulk polypropylene technology universe, it is generically believed that it is difficult to model XS dynamics because of the sluggishness and strong nonlinear behavior of dynamic trajectories.

In LIPP processes, special attention should be given to liquid bleed operation and to XS dynamic responses. Depending on the liquid bleed operation, it may be observed that sometimes it...
is very difficult to specify the steady state operation conditions, as the liquid bleed stream is operated discontinuously. For this reason, all chemical species that recirculate through the recycle stream are allowed to fluctuate during actual plant operation. As liquid bleed flow rate cycles are usually very long and seemingly fluctuate at random, concentrations in the liquid pool are allowed to drift for long periods of time and dynamic trajectories appear to be sluggish and very complex. As the XS dynamic behavior seems to present similar dynamic characteristics, it is wondered whether the liquid bleed flow rate policy might exert any significant effect upon XS dynamic responses to process operation changes. For this reason, the dynamics of the liquid bleed operation should be well characterized.

The process studied here consists of a liquid-phase propylene polymerization with a single CSTR, using a commercial high-activity Ziegler-Natta catalyst. This process was extensively analyzed at steady-state by Mattos Neto and Pinto\textsuperscript{[1]}. A comprehensive steady-state mathematical model has been implemented as a commercial software named as SIMULPOL 3.0\textsuperscript{©, [2]} which can be used to simulate propylene polymerizations in both slurry and bulk processes, representing a very useful tool for description of reactor mass and energy inventories, particle size distribution, polymer molecular structure and end-use polymer properties.\textsuperscript{[1, 3]} Recently, Prata et al.\textsuperscript{[4, 5]} improved the original LIPP dynamic model\textsuperscript{[6, 7]} in order to study strategies for data reconciliation and parameter estimation of the process. The works developed by Prata et al account for the implementation of a methodology for dynamic data reconciliation and simultaneous estimation of quality and productivity parameters in real time, using industrial data from LIPP technology.

This work presents industrial operation and simulation data obtained with a simple process model, which seemingly indicate that the liquid bleed flow rate policy may be important for the proper modeling of the XS dynamics. The main conjecture is that part of the cocatalyst may recirculate through the propylene recycle stream and that, for this reason, the liquid bleed policy may cause drifts of the XS values during actual process operation. If this is true, the simultaneous modification of the cocatalyst / external electron donor feed ratio and of the liquid bleed flow rates may induce the appearance of different dynamic response patterns, including sluggishness, overshoots, etc.

**Process Modeling**

**Modeling Cocatalyst (COCAT) Recirculation**

Although liquid bleed flow rates must be manipulated to control the propane concentration in the liquid pool, it is expected that significant changes of the liquid bleed flow rates may occur during actual operation practice, independently from the values of measured propane concentrations in the liquid pool. In addition, if COCAT does recirculate in significant amounts (or if catalyst
contaminants present similar dynamic responses), then there may be important interactions between the dynamics of the liquid bleed operation and the dynamics of XS responses, which may potentially affect final polymer quality.

Based on the previous paragraph, it was decided to observe through simulation how the COCAT/DONOR ratio in the liquid pool might depend on the liquid bleed policy for different degrees of COCAT recirculation. A general scheme of the process flowsheet is depicted in Figure 1. Model equations may be written as:

\[ \frac{dP_e}{dt} = m_e - R_{pol} - \left( \frac{P_e}{P_e + P_a} \right) m_o \]  
\[ \frac{dP_a}{dt} = w_a m_e - \left( \frac{P_a}{P_e + P_a} \right) m_o \]  
\[ \frac{dPol}{dt} = R_{pol} - m_{pol} \]  
\[ \frac{dDONOR}{dt} = m_{DONOR} - \left( \frac{DONOR}{Pol} \right) m_{pol} \]  
\[ \frac{dCOCAT}{dt} = m_{COCAT} - \left( \frac{COCAT_{pol}}{Pol} \right) m_{pol} - \left( \frac{COCAT_{Rec}}{P_e + P_a} \right) m_o \]

where \( P_e \) is propylene in the reactor vessel; \( P_a \) is propane in the reactor vessel; \( Pol \) is polypropylene in the reactor vessel; \( DONOR \) is external electron donor in the reactor vessel; \( COCAT \) is cocatalyst in the reactor vessel; \( m_e \) is the fresh propylene feed rate; \( R_{pol} \) is the rate of polymerization; \( m_o \) is the liquid bleed flow rate; \( w_a \) is the propane concentration in the feed stream;
$m_{Pol}$ is the rate of polymer output; $m_{DONOR}$ is the external electron donor feed rate; $m_{COCAT}$ is the cocatalyst feed rate; and $COCAT_{Pol}$ and $COCAT_{Rec}$ are the amounts of cocatalyst in the solid polymer powder and in the liquid pool at the output respectively.

Assuming that polymer does not accumulate and that the solid concentration is constant and equal to 0.40 (polymer/ slurry ratio), it is possible to write:

$$R_{Pol} = m_{Pol}$$  \hspace{1cm} (6)

$$\frac{Pol}{Pol + Pe + Pa} = 0.40 \rightarrow Pol = 2 \left( \frac{Pe + Pa}{3} \right)$$  \hspace{1cm} (7)

Assuming additionally that the reactor level is controlled properly, then

$$(I + w_a)m_e = m_o + m_{Pol}$$  \hspace{1cm} (8)

Inserting Equations (6-8) into Equations (1-5)

$$\frac{dPe}{dt} = \left( \frac{1}{I + w_a} \right) \left( m_{Pol} + m_o \right) - m_{Pol} - \left( \frac{Pe}{Pe + Pa} \right) m_o$$  \hspace{1cm} (9)

$$\frac{dPa}{dt} = \left( \frac{w_a}{I + w_a} \right) \left( m_{Pol} + m_o \right) - \left( \frac{Pa}{Pe + Pa} \right) m_o$$  \hspace{1cm} (10)

$$\frac{dDONOR}{dt} = m_{DONOR} - 1.5 \left( \frac{DONOR}{Pe + Pa} \right) m_{Pol}$$  \hspace{1cm} (11)

$$\frac{dCOCAT}{dt} = m_{COCAT} - 1.5 \left( \frac{COCAT_{Pol}}{Pe + Pa} \right) m_{Pol} - \left( \frac{COCAT_{Rec}}{Pe + Pa} \right) m_o$$  \hspace{1cm} (12)

Finally, let us assume that a certain partition coefficient (K) defines the amount of COCAT that remains in the liquid pool and is recirculated through the recycle stream. In this case,

$$\frac{COCAT_{Rec}}{Pe + Pa} = K \frac{COCAT_{Pol}}{Pol} \rightarrow COCAT_{Rec} = 1.5 K COCAT_{Pol}$$  \hspace{1cm} (13)

As

$$COCAT_{Rec} + COCAT_{Pol} = COCAT \rightarrow \left\{ \begin{array}{l}
COCAT_{Rec} = \frac{1.5 K COCAT}{1 + 1.5K} \\
COCAT_{Pol} = \frac{COCAT}{1 + 1.5K}
\end{array} \right. $$  \hspace{1cm} (14)

Inserting Equation (14) into Equation (12)

$$\frac{dCOCAT}{dt} = m_{TEA} - (1 - \alpha) \left( \frac{COCAT}{Pol} \right) m_{Pol} - \alpha \left( \frac{COCAT}{Pe + Pa} \right) m_o$$  \hspace{1cm} (15)

where $\alpha$ is a recirculation factor, defined as
Modeling XS Dynamics

In order to investigate the main characteristics of the XS dynamic responses to changes of the COCAT/DONOR feed ratio, the XS balance is then written as:[6, 7]

\[
\frac{d(\text{Pol XS})}{dt} = -m_{\text{pol}} \times XS + R_{\text{pol}} \times XS^i
\]  

where \(XS^i\) is the instantaneous XS value of the polymer being produced inside the reactor vessel.

Equation 17 can be written as:

\[
\text{Pol} \frac{d(XS)}{dt} + XS \frac{d(\text{Pol})}{dt} = -m_{\text{pol}} \times XS + R_{\text{pol}} \times XS^i
\]

Inserting Equation 3 into Equation 18

\[
\text{Pol} \frac{d(XS)}{dt} + XS \left( R_{\text{pol}} - m_{\text{pol}} \right) = -m_{\text{pol}} \times XS + R_{\text{pol}} \times XS^i
\]

which leads to

\[
\frac{d(XS)}{dt} = \frac{R_{\text{pol}}}{\text{Pol}} \left( XS^i - XS \right)
\]

Finally, using data collected after the introduction of a sequence of small step changes of the COCAT/DONOR ratio during 5 days of continuous operation, it was possible to obtain a very good steady-state model for XS in the form:

\[
\frac{XS - XS^R}{\text{COCAT}/\text{DONOR} - 1} = 5.56
\]

where \(XS^R = 4.83\) is the reference value for a COCAT/DONOR feed ratio. Considering that Equation 1 is valid for the instantaneous polymer being produced, then

\[
\frac{d(XS)}{dt} = \frac{R_{\text{pol}}}{\text{Pol}} \left[ XS^R + K \left( \text{COCAT}/\text{DONOR} - 1 \right) - XS \right]
\]

which shows that the polymer production rate should also be expected to influence the dynamics of XS. The XS model, to be used comprises Equations 1-5, 22.

Controller Design

One question that remains unclear is the necessity to operate the liquid bleed stream discontinuously. In order to minimize possible undesired interactions between the liquid bleed policy and the remaining operation variables, control strategies were studied for regulatory control of propane concentration in the liquid pool and servo control of the COCAT/DONOR ratio in the
reactor vessel.\cite{6,7} It was shown that simple PI controllers are adequate for proper control of both variables, in the form:

**Propane Concentration Controller**

\[
m_o = m_{o}^{SS} + K_p (w - w^{\text{set}}) + \frac{1}{T_p} \int (w - w^{\text{set}}) \, dt
\]  

(23)

**COCAT/DONOR Ratio Controller**

\[
m_{\text{TEA}} = f(\alpha) + K_t (R - R^{\text{set}})
\]

(24)

where \(m_{o}^{SS}\) is the reference steady-state liquid bleed flow rate; \(K_p\) is the proportional gain for control of the propane concentration; \(w\) is the measured weight fraction of propane; \(w^{\text{set}}\) is the set-point value for the propane concentration; \(T_p\) is the integration time constant for control of the propane concentration; \(K_t\) is the proportional gain for control of the COCAT/DONOR ratio; \(R\) is the inferred COCAT/DONOR ratio in the reaction environment; \(R^{\text{set}}\) is the set-point value for the COCAT/DONOR ratio; and \(f(\alpha)\) is a reference value which depends on the recirculation factor as:

\[
f(\alpha) = R^{\text{set}} (a + b \alpha)
\]

(25)

where \(a\) and \(b\) are known parameters (parameters \(a\) and \(b\) may be obtained through simulation or may be identified at plant site, if necessary).

**Results and Discussion**

Equations (9-11, 15) constitute the dynamic model analyzed here. During the simulation \(m_o\) was allowed to vary at random, as observed in the plant procedure. \(\alpha\) was allowed to vary in the range \([0,1]\) in order to analyze the influence of the recirculation factor upon the COCAT/DONOR ratio in the reactor vessel during the simulations.

Figure 2 shows simulation results obtained for the propane concentration in the liquid pool when a random liquid bleed policy is performed. Both the range of variation of the propane concentration and the oscillatory pattern are very similar to the actual operation data displayed in Figure 2. \(\alpha\) is assumed to be equal to zero, in order to show that the liquid bleed policy does not affect the COCAT/DONOR ratio when no COCAT recirculation takes place.
Figure 2 - Propane Concentration in the Liquid Pool for Random Operation of the Liquid Bleed Stream. (A) Industrial Plant Data; (B) Simulation Data (COCAT recirculation is assumed to be equal to zero).

Figure 3 shows, however, that the COCAT/DONOR ratio in the reactor vessel oscillates with increasing amplitude as the recirculation factor increases. When the recirculation factor is equal to 0.2 ($K = 0.16$), the oscillatory response of the COCAT/DONOR ratio would probably cause observable XS fluctuations, given the high steady-state XS gain, as presented in Equation 21. The increase of $\alpha$ also shifts the steady-state COCAT/DONOR ratio to higher values. Therefore, it is clear that the liquid bleed flow rate policy may influence the XS dynamics if COCAT is partially recirculated through the recycle stream, even if the COCAT/DONOR feed ratio is kept constant.

Figure 4A shows dynamic responses of the COCAT/DONOR ratio when modifications of the COCAT/DONOR feed ratio and the liquid bleed flow rate occur simultaneously. Figure 4A also shows very clearly that the simultaneous modification of both operation variables may be synchronized to induce the development of apparent overshoots and apparent slow dynamic responses. Therefore, if partial COCAT recirculation does occur, then it is possible to interpret some dynamic responses as the execution of grade transitions without proper control of the liquid...
bleed flow rates. Figure 4B shows that the COCAT/DONOR ratio responds relatively fast to changes of the feed conditions when the liquid bleed operation is kept constant. Therefore, according to the model, sluggish and strong nonlinear dynamics should be expected only when simultaneous and uncontrolled variations of the bleed and feed operations take place.

Figure 4 - Dynamic Responses of the COCAT/DONOR Ratio to Simultaneous Changes of the Liquid Bleed Flow Rate and COCAT/DONOR Feed Ratio. (A) $\alpha = 0.4$; (B) $\alpha = 0.20$; initially, bleed flow rate is at maximum value.

Figure 5 shows simulation results obtained when the propane concentration in the feed stream is allowed to vary. Figure 6 shows simulation results obtained when a set-point change is introduced in the desired COCAT/DONOR ratio. In the first case, it may be observed that proper control of the propane composition is achieved without much difficulty for feasible values of the liquid bleed flow rate. In the second case, it may be observed that the controller allows much faster grade transition dynamics than the traditional open-loop grade transition strategy.

Figure 5 - Performance of the Control Scheme for Regulatory Control of Propane Concentration.
Figure 6 - Performance of the Control Scheme for Servo Control of the COCAT/DONOR Ratio (Linear Fit is the modification of the COCAT/DONOR feed ratio to attain the desired steady-state; Linear Fit + P is the modification of the COCAT/DONOR feed ratio to attain the desired steady-state (Linear gain) in minimum time (P is the proportional controller).

Figure 7 shows that XS dynamic responses may be very fast at certain operation conditions. Results were obtained during a large XS transition in industrial plant. Fast XS responses and fast stabilization of XS values can be observed. As samples were measured with a frequency of 1 h⁻¹, no more than a couple of hours are needed for XS values to reach the new steady-state conditions. It is also interesting to observe that XS values seem to oscillate after the final stabilization of the COCAT/DONOR feed ratio.

An example demonstrating that the model may be used to interpret dynamic experimental data available for large XS transitions was built. Equation 25 was applied to the data set displayed in Figure 7. Model predictions agree fairly well with the available XS data in this example. For this case, values estimated for the linear XS gain and for the recirculation factor were equal to 4.6 and 0.6 respectively. The first value is in good agreement with the previous result presented in Equation 21, which demonstrates the consistency of the parameter estimation procedure. The second value seems too high, and shows that there may occur a significant amount of TEA recirculation in the system.

Figure 7 - Model Predictions for XS Transition. (Vertical bars indicate the 95% range of experimental error).
Conclusions

It is then believed that the complex dynamic pattern of XS responses may be partially caused by fluctuation of the liquid bleed flow rate policy, which may provide a background signal for XS fluctuations, not analyzed so far. In order to evaluate the degree of coupling that may exist between the XS dynamics and the liquid bleed flow rate policy, a mass balance model was built and used to simulate the process behavior.

According to the model simulations results, it can be stated that the dynamics of propane concentration is sluggish and subject to huge oscillations. The dynamic responses of other chemical constituents that eventually recirculate through the recycle stream are expected to be similar to the dynamics of the propane concentration. If cocatalyst is allowed to partially recirculate through the recycle stream, then the liquid bleed policy may influence very significantly the dynamics of the cocatalyst/external electron donor ratio and consequently the dynamics of XS.

Simulation results indicate that if the recirculation factor is equal to or larger than 0.2, then the liquid bleed policy may be important to describe the XS dynamics and may induce sluggishness, overshoots, etc, observed at plant site. Simulation results also indicate that these effects may be minimized if PI controllers are designed to control the propane concentration in the liquid pool and to increase the speed of the cocatalyst/external electron donor transitions. The model was able to reproduce the dynamic XS profile obtained during a large XS transition and indicates that there may occur a significant amount of cocatalyst recirculation in the system.

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