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# HYDROGEN EFFECT IN INDUSTRIAL LIQUID PHASE PROPYLENE POLYMERIZATION



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A continuous model for loop reactors used in liquid phase propylene polymerization (Spheripol Process) was developed to study the hydrogen effect on polymerization kinetics. Industrial data were used to investigate two possible mechanisms: the creation of new active sites and the reactivation of dormant sites. Comparing process production and polymer melt flow index predicted by the model with those obtained in the industrial process it was shown that both mechanisms are able to deal with hydrogen effect on propylene polymerization.

## Introduction

Polypropylene is one of the most important commodity polymers, and the Spheripol process is one of the most used in its production. Mathematical models of liquid phase propylene process, like Spheripol, should have a kinetic mechanism to account for hydrogen effect on the average molecular weight and in the rate of polymerization. Accounting for these effects is important to correctly predict the production and basic polymer properties like melt flow index (MFI), which are used in process control, process analysis and product development studies.

This paper presents a study of the hydrogen effect on the rate of propylene polymerization in a liquid phase industrial plant. Hydrogen acts mainly in two different ways: as a chain transfer agent and increasing the polymerization rate. Several researchers have studied the second effect. There is not a simple explanation about it. Some of them (Parson and Al-Turki, 1989; Rishina et al., 1993; Soares and Hamielec, 1996 a) showed that there is an increasing in the number of active sites when hydrogen is present in the reaction media. Sanson et al. (1999) and Mori et al. (1998) proposed that the dormant site reactivation should be responsible for the hydrogen effect on the rate of polymerization. A dormant site is an active site after a 2-1 propylene insertion that generates a secondary Ti-C bond. To model the creation of new active sites, two reactions were added into the kinetic

model: potential site activation and dead site reactivation by hydrogen. The dormant site reactivation mechanism was included in the kinetic model as an equilibrium between two site types, as explained later.

This paper is not aimed at fully explaining mechanism, but how this mechanism can be inserted into a mathematical model to predict hydrogen effect in an industrial process.

## Model Description

This work is based on data from an industrial Spheripol plant. Spheripol is a liquid phase propylene polymerization process that uses two loop reactors in series. Catalyst (4<sup>th</sup> generation supported Ziegler-Natta catalyst, previously activated by Al-alkyl and treated with an external electron donor), monomer and hydrogen are continuously fed to the first reactor, where polymerization starts. Between the two reactors there is an intermediate feed where monomer and hydrogen are also continuously fed.

The reactor model considers the loop reactor as a Continuous Stirred Tank Reactor (CSTR) to all effects (Zacca and Ray, 1993). The effective concentration is that in the amorphous polymer phase and this concentration is related to the liquid phase concentration by an equilibrium constant.

Table 1 shows the reactions considered in the reactor model (Zacca and Ray, 1993; Soares and Hamielec, 1996 b; Carvalho et al., 1989):

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Table 1. Reactions considered.

Potential site activation	$C_p + H_2 \xrightarrow{k_{aH}} P_0$
Chain initiation	$P_0 + M \xrightarrow{k_I} P_1$
Chain propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$
Chain transfer	$P_n + H_2 \xrightarrow{k_c} P_0 + D_n$
Catalyst deactivation	$P_n \xrightarrow{k_d} C_d + D_n$
	$P_0 \xrightarrow{k_d} C_d$
Dead site reactivation	$C_d + H_2 \xrightarrow{k_{rH}} P_0$

where  $C_p$  is a potential site,  $H_2$  is hydrogen (transfer agent),  $P_0$  is a vacant site,  $M$  is the monomer,  $P_n$  is a growing polymer molecule with  $n$  monomers,  $D_n$  is a dead polymer molecule with  $n$  monomers and  $C_d$  is a dead site.

The dormant site reactivation was modeled as an equilibrium between two site types. One of them ( $C_1$ ) polymerize propylene with a certain rate and the other one ( $C_2$ ) polymerize propylene with a higher rate. The interconversion between these two active species is supposed to follow an equilibrium mechanism as shown in Eq. (1).



With this assumption, it can be shown that the propagation rate constant ( $k_p$ ) may be substituted by Eq. (2) (Reginato, 2001):

$$k_p^1 (1 + rKC_H) (1 + KC_H)^{-1} \quad (2)$$

$$\text{where } r = \frac{k_p^2}{k_p^1} \text{ and } K = \frac{k_a}{k_{-a}}.$$

Considering this kinetic model, the following rate equations, in terms of the live polymer moments  $\mu_0$  and  $\mu_1$ , can be written:

$$R_{C_p} = k_{aH} C_p C_H \quad (3)$$

$$R_{P_0} = k_I P_0 C_M + k_d P_0 - k_{rH} C_d C_H - k_c m_0 C_H^{O_c} - k_{aH} C_p C_H \quad (4)$$

$$R_M = k_I P_0 C_M + k_p^1 (1 + rKC_H) (1 + KC_H)^{-1} m_0 C_M \quad (5)$$

$$R_H = k_{aH} C_p C_H + k_c m_0 C_H^{O_c} + k_{rH} C_d C_H \quad (6)$$

$$R_{C_d} = -k_d m_0 - k_d P_0 + k_{rH} C_d C_H \quad (7)$$

$$R_{m_0} = -k_I P_0 C_M + k_c C_H^{O_c} m_0 + k_d m_0 \quad (8)$$

$$R_{m_1} = -k_I C_M P_0 - k_p^1 (1 + KrC_H) (1 + KC_H)^{-1} C_M m_0 + k_c C_H^{O_c} m_1 + k_d m_1 \quad (9)$$

$$R_{I_0} = -k_I P_0 C_M \quad (10)$$

$$R_{I_1} = k_I P_0 C_M + k_p^1 (1 + KrC_H) (1 + KC_H)^{-1} C_M m_0 \quad (11)$$

$$R_{I_2} = k_I P_0 C_M + k_p^1 (1 + KrC_H) (1 + KC_H)^{-1} C_M (2m_1 + m_0) \quad (12)$$

where  $I_0$ ,  $I_1$  and  $I_2$  are the zero, first and second bulk (live + dead) polymer moments.

The mass average molecular weight can be obtained from the first and second bulk polymer moments:

$$M_w = M_M \cdot I_2 / I_1 \quad (13)$$

Bremner and Rudin (1990) present a correlation between mass average molecular weight and MFI for polypropylene resins:

$$MFI = 3.39 \cdot 10^{22} M_w^{-3.92} \quad (14)$$

The dynamic species balance can be generically written as (Q is volumetric flow rate):

$$\frac{dC_j}{dt} = \frac{Q_f C_{j,f}}{V} - \frac{Q_o C_j}{V} - R_j \quad (15)$$

The Ti content in the catalyst was considered to be 2 wt%, and 40% of the total titanium atoms is supposed to be active.

The effective concentration is related to liquid phase concentration by an equilibrium constant (Zacca, 1991):

$$\frac{C_{j,eff}}{C_{j,liq}} = g_j = 0.5, \quad j = 1, 2, \dots, NC \quad (16)$$

where  $NC$  is the number of liquid phase components.

The model described above was implemented as a S-function in MATLAB/Simulink® environment and solved with the BDF (*Backward Differentiation Formulas*) algorithm (Shampine and Reichelt, 1997).

### Experimental Data

It was selected a set of industrial data with changes in hydrogen concentration. Figure 1 shows the process inputs.

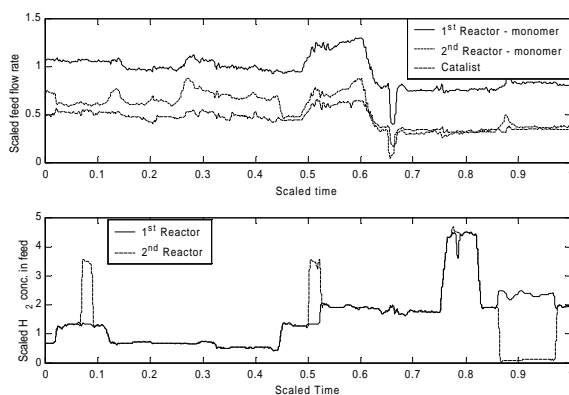


Fig. 1. Process inputs.

### Results and discussion

The results were obtained with the best-estimated parameter in each case. Fig. 1 shows the best results obtained without hydrogen effect on propagation reaction rate. The parameters related to hydrogen activation effect was set to zero and all sites are fed as active sites.

The parameter estimation was performed using the Nelder-Mead algorithm (Secchi and Bolsoni, 1998).

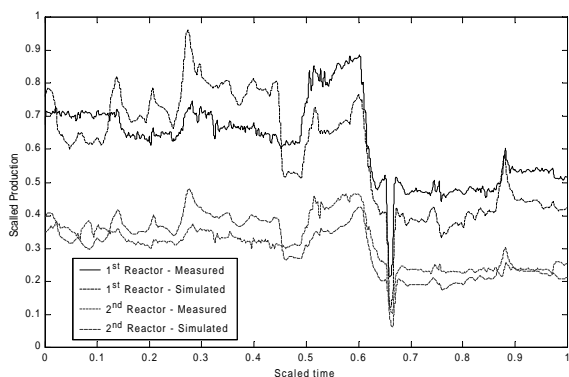


Fig. 2. Production prediction without hydrogen effect on rate of polymerization.

From Fig. 2 it can be noticed that for low hydrogen concentration the production prediction is higher than the measured, and for high hydrogen concentration, the predicted production is lower than the measured

production. So, it is possible to conclude that there is an increase in rate of polymerization due to hydrogen effect.

### Potential site activation mechanism (creating new active sites)

This mechanism is able to create new active sites due to hydrogen activation. To do so, a part of total site concentration (50%) was fed as potential sites. This mechanism was tested estimating the kinetic constants of the following reactions: site activation by hydrogen ( $k_{aH}$ ), chain propagation ( $k_p$ ), catalyst deactivation ( $k_d$ ) and chain transfer ( $k_c$ ). Figure 3 shows the best result obtained after a parameter estimation.

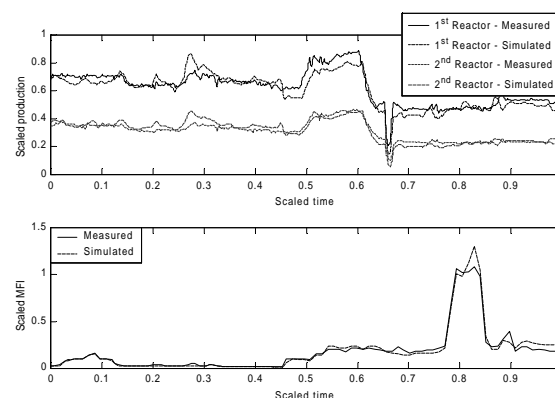


Fig. 3. Results obtained with the potential site activation mechanism.

### Dormant site reactivation mechanism (two site equilibrium)

The dormant site reactivation mechanism considers that after a 2-1 propylene insertion the site remains active, but with a lower propagation rate constant.

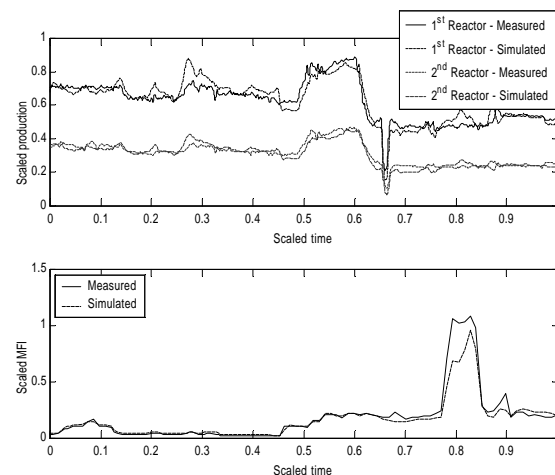


Fig. 4. Results obtained with the two-site equilibrium mechanism (dormant site reactivation).

This mechanism is different from that proposed in literature where a dormant site is not able to add new monomer units until a chain transfer reaction occurs. Figure 4 shows the results obtained after parameter estimation was performed. It was estimated the following kinetic constants: chain propagation ( $k_p^1$ ), catalyst deactivation, ( $k_d$ ) the parameters  $K$  and  $r$  from the two site equilibrium model and chain transfer ( $k_c$ ).

### Conclusions

In this work, two mechanisms for the hydrogen effect in propylene polymerization were analyzed: hydrogen creating new active sites from potential sites fed to the reactor, and a two-site equilibrium that aims to simulate the dormant site reactivation mechanism. Simulation results considering production and melt flow index was compared with industrial data. It was shown that a model without any mechanism to account for hydrogen activation effect generates poor simulation results. In the other hand, both mechanisms for the hydrogen activation effect investigated in this work (potential site activation and dormant site reactivation) proved to be useful to predict, in a quantitative way, the production and MFI in industrial liquid phase propylene polymerization using 4<sup>th</sup> generation supported Ziegler-Natta catalyst.

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