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HYDROGEN EFFECT MODELING ON ZIEGLER-NATTA CATALYST AND FINAL PRODUCT PROPERTIES IN PROPYLENE POLYMERIZATION

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ABSTRACT. Hydrogen, as chain transfer agent, effects on kinetic of propylene polymerization; consequently variation of hydrogen concentration leads to change final product properties and also activates site of used catalyst. This phenomenon is one of the most important process variables is to adjust the final product properties and optimize the operating conditions. This work has attempted to present a mathematical model that cable to calculate the most important indices of end used product, such as melt flow index, number and weight average molecular weight and poly dispersity index. The model can predict profile polymerization rates determining important kinetic parameters such as the activation energy, lumped deactivation reaction initial reaction rate and deactivation constant. The mathematical model was implemented in Matlab/Simulink environment for slurry polymerization in laboratory scale. The modeling approach is based on polymer moment balance method in the slurry semi-batch reactor. In addition, in this work have provided a model that calculating fraction activated sites catalyst via hydrogen concentration. The model was validated by experimental data from lab scale, reactor. The experimental and model outputs were compared; consequently, the errors were within acceptable range.

KEY WORDS: Mathematical modeling, Propylene polymerization, Kinetics study, Hydrogen response, population balance

INTRODUCTION

Polypropylene is one of the widest used polyolefin product and its application is strongly affected by the final product properties. It could be said that the most crucial indices of end used product of polypropylene are comprised of the melt flow index, number average molecular weight, weight average molecular weight, and polydispersity index. These indices depend heavily on independent operational variables such as temperature and hydrogen concentration, as well as the kinetics of polymerization. Hence, hydrogen as a chain transfer agent is one of the most vital affecting factors on the reaction kinetics and final product properties. On the other hand, the impact of hydrogen on catalyst activity in the course of olefin polymerization is less predictable and its effect depends on the type of catalyst and monomer. For instance, hydrogen generally reduces the polymerization rate of ethylene and increases the polymerization rate of propylene when high-activity $TiCl_4/MgCl_2$ catalysts are used [1]. As reported that hydrogen leads to extra activated sites and yield of the catalyst [1].

Despite sixty years of history of the use of Ziegler-Natta catalyst for manufacturing polypropylene, polymerization system performance it still remains as a black box [2]. However, it has been found that kinetics of polymerization with Ziegler-Natta catalysts is quite complicated [3]; particularly, when hydrogen exists in the polymerization reaction. So far, more research to understand the polymerization system has been carried out in a conventional manner based on trial and error or experimental approach; although this methodology isn't reliable and applicable because it's heavily dependent on test and laboratory conditions. Hence, a validated

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model that could be able to predict the impact of hydrogen of polymerization rate, final product properties, vital kinetics parameters and most of all calculating activated site percentage and yield of the catalyst by changing the concentration of hydrogen is inevitable. Up to now despite disputing on the role of hydrogen upon the polymerization, to the best of our knowledge there is no validated mathematical model presented that could be able to predict mentioned gaps simultaneously. In this study, we tried to propose a validated model to cover the gap.

To date, more articles published on the field of polypropylene polymerization modeling have been concerned with heat and mass transfer inside the catalyst particles the slurry polymer particles [4-5] or on the basis of the mechanism of reaction and how the particle increase regarding multigrain [6-8]. Their models have been focused on mathematical calculations without validation with experimental data. The other researchers were only targeted on loop reactors [2, 9] and fluidized-bed reactors (FBRs) [10], namely bulk and gas phase polymerization that they are not applicable to slurry reactor. In the regard to rate profiles of propylene polymerization, the first article in the liquid phase (i.e. bulk polymerization, no slurry) was issued by Samson *et al.* [11] and some authors investigated the hydrogen effect on kinetics experimentally without paying attention to polymerization rate and final product properties [12, 13].

Al-haj Ali *et al.* proposed a generalized model for hydrogen response based on the dormant site theory in liquid propylene polymerization [14]. His research work was based on experimental data, and there was no validated mathematical model that might be capable of predicting polymerization rate profile and indices final product properties simultaneously. Zacca *et al.* modeled industrial scale loop reactor by using non-ideal continuous stirred tank model to explain the industrial process and compared their simulation results with commercial plant data. The research targets defined to predict the macroscopic of the process, dynamics of the plant, advanced control strategies, grade transitions, and average polymer. In the paper, despite offering formulas for some important final properties such as number average molecular weight (M_n); weight averages molecular weight (M_w) and polydispersity index (PDI); no mentioned about validating the model with them. Furthermore, no considered concerning the effect of hydrogen on the vital indices of final production and kinetics and catalyst activation [3].

In relation to investigating hydrogen effect during propylene polymerization, many experimental studies have been carried out, but the results of these studies have been ambiguous and even contradictory. Guastalla and Gianinni experimentally concluded that when hydrogen exists in the system, the initial rate and activity of catalyst increase about 2.5 times than when not hydrogen in propylene polymerization reactor [15]. Spitz *et al.* described that low hydrogen concentrations in the reactor lead to causes of the enhancement of the rate profile, higher hydrogen levels increased lowered activity and increased deactivation [16]. Rishina *et al.* reported that in their study, there was a similar activation effect for hydrogen and they pointed out that such an effect is reversible and temporarily [17]. Some scholars confirmed a similar hydrogen activation effect for different catalyst types and polymerization media [10, 18]. Contrary to these findings, Soga and Siona obtained that propylene polymerization rate decreases with increasing hydrogen partial pressure. The authors justified their findings happened due to the slow addition of the monomer to the catalyst-hydrogen bond formed in the step of chain transfer to hydrogen [19]. Regardless of previous reports, Kahrman *et al.* achieved different conclusions and reported that hydrogen has not only an effect on the polymerization rate for low hydrogen concentrations but also the rate of polymerization decreases at high hydrogen concentration; the authors explained this phenomenon because of adsorbing hydrogen to activated sites of catalyst, amount of activated sites for polymerization are decreased, then the polymerization rate is reduced [20].

Nevertheless, up to now, these disputings have been continued. In 2013, Luo *et al.* modeled loop propylene polymerization reactors in bulk media. The model targeted on commercial reactor variables without paying attention to kinetics study and final product properties [21].

Next year, another paper published on modeling of multi-scale PP properties, but in FBR reactor [22]. Recently, in 2016, Song *et al.* drew their attention to a simulation of liquid polypropylene polymerization reactors based on Sheripol technology as well as preceding work. Although they paid attention to some final product properties such as average molecular weight and polydispersity, their simulation was not suitable for kinetics study and predicting final product properties [23].

On the whole, in regarding conflicting results reported, particularly while hydrogen exists in the reactor system; the effect of hydrogen on the reactor is still vague and unclear. Consequently, a validated model of profile polymerization rate that could be predicted correctly the system is inevitable. Despite the importance of the matter, a few investigators have been pied attention to this subject, however so far, no a comprehensive validated model to reply the existing gap has been presented. The aim of this work is to present a validated model to predicting profile polymerization rate, the effect of hydrogen concentration on profile rate, calculating the model of the fraction activated sites catalyst via hydrogen concentration and identifying vital kinetic parameters such as (E_a, E_p, Rp_0, K_d). In addition, the model is capable to calculate the most important final product index, such as melt flow index (MFI), number average molecular weight (M_n), weight average molecular weight (M_w) and poly dispersity index (PDI). In addition, another purpose of this paper is to reveal the impact of hydrogen content on the fraction of activated catalyst sites during polymerization. The model was carried out in a Matlab/Simulink environment and afterward, the model was validated with experimental data in slurry polymerization and investigated hydrogen response on the kinetic reaction. The global errors between the model outputs and experimental data are an acceptable margin of error.

EXPERIMENTAL

Materials

The 4th generation of spherical $MgCl_2$ supported Ziegler-Natta catalyst containing 3.6 wt% Ti and diisobutyl phthalate (DIBP) as internal donor supplied by Sudchemie, Germany. Triethylaluminium (TEA of 98% purity) from Merck, Germany, diluted in n-heptane was used as a cocatalyst and the so-called external donor (cyclohexyl methyl dimethoxy silane) were purchased from Merck and was used without further purification. Polymer-grade propylene was provided from Shazand Petrochemical, Iran and was used as received. Hydrogen and nitrogen used were of >99.999% purity. Nitrogen was further purified by passing over beds of absorbents.

Polymer synthesis

In this study, slurry homopolymerization was carried out in heptane media. Polymerization reactor was a one-liter stainless steel vessel manufactured by Buchi Co.; polymerization set-up was designed in order to conduct slurry polymerization in one vessel. A high-pressure N_2 line was used to transfer liquid monomer and catalytic system into the reactor. The catalyst system was injected into the reactor through a stainless steel cylinder under N_2 atmosphere. All gases were first purified online by passing through three purification trains (containing molecular sieves) in series. The individual gases were then filtered and flow of each reactant was measured and controlled with a mass flow controller manufactured by Brooks.

Experimental Rp-t curves come for setup monitor, then the molecular weight of products are measured by gel permeation chromatography (GPC), employing an Agilent PL-220 model with TSK columns at 155 ºC using 1,2,4-trichlorobenzene as a solvent. The GPC was calibrated with the narrow molecular weight distribution polystyrene standard as a reference. MFI of samples is evaluated according to ASTM 1238 at a temperature of 230 ºC and load of 2.16 kg.

Polymerization procedure

A typical polymerization procedure was consisting of reactor preparation, polymerization, and discharge. Details are as follows: Firstly, the reactor was flushed with nitrogen gas during 1 hour at 90 ºC and was reduced reactor temperature until 20 ºC, then purged with propylene gas in 15 min. Afterward, 500 mL heptane as a solvent was introduced to the reactor; next, all the inputs and outputs of the reactor were closed and were stirred at 200 rpm in 5 min for solvent degassing under a vacuum pump. Subsequently, hydrogen was entered to the reactor (based on recipe condition), then propylene was introduced to reactor according to controller program, then the reactor was heated up until reach to equilibrium thermodynamic conditions (T = 70 ºC, P = 7.5 bar), finally the reactor was ready to injecting catalyst for starting polymerization. Injecting catalyst to the reactor was carried out under pressure via an injection system during polymerization time (two hours) at the constant temperature and pressure, that is to say, the reactor was executed under isothermal and isobar reactor condition. Data were collected every five seconds.

It is worth mentioning that catalyst preparation should be done according to the recipe in a glove box under a nitrogen atmosphere 20 min before injection to the reactor. After each experiment, the resulting polymer was dried under an ambient condition under Laboratory hood for 24 hours.

Modeling

Assumptions

The following modeling assumptions are considered: (1) It was supposed that propylene polymerization was carried out in the amorphous phase and amorphous phase concentrations during the polypropylene polymerization are at the thermodynamic equilibrium condition that obeys from Sanchez and Lacombe Equation(SLE) [24] for calculating the amount of $X = C_H/C_m$, the hydrogen molar ratio. (2) It was assumed that $\gamma_1 = \gamma_2 = \cdots = \gamma_{NC}$. Where γ is equilibrium constant and NC is a number of solvent in slurry phase components [3]. (3) The reaction temperature, pressure, and monomer concentration were kept constant during the polymerization process. (4) The resistance of both mass and heat transfer and the diffusion effect of the reactants were ignored. (5) It was assumed that the propagation constant is independent of the length of the growing polymer chain. (6) Using "dormant sites theory" for activating catalyst by hydrogen concentration [14].

Formulation

As olefin polymerization kinetics with Ziegler-Natta catalysts might be fairly complicated [3]. To date, several reaction steps have been proposed in the literature [3, 9]. However, the most comprehensive steps were proposed by Zacca [3]. The ODE mass balance equations in the model are as follows:

$$\frac{dC_{j,R}}{dt} = [\frac{Q_f C_{j,f}}{V_R}]_{feed(input)} - [\frac{(\eta/\zeta)Q_0 C_{j,R}}{V_R}]_{output} + R_j \quad (1)$$

where $C_{j,R} = \frac{Mole \quad of\ j}{Total \quad Volume}$ for j = 1,2,....,NC

$\eta_j = \frac{C_{j,a}}{C_{j,l}}$ for j = 1,2,....,NC

$$\zeta_j = \frac{C_{j,o}}{C_{j,R}} = \frac{\rho_0}{\rho_R} \cdot D_f \qquad \text{where :} \qquad (\eta/\zeta) = \begin{cases} \eta & for \quad liquid \quad phase \quad components \\ \zeta & for \quad solid \quad phase \quad components \end{cases}$$

Q_f, Q_0, and Q_R are feed volumetric flow rate, reactor-output volumetric flow rate and volumetric recirculation flow rate in respectively. In addition to Eq. (1), V_R and R_j are defined as reactor volume and j component reaction rate.

Since the model is a semi-batch process and assumed constant monomer concentration during the polymerization, the input and output terms are eliminated (Q_f and Q_0) then the terms of η and ζ are meaningless for our study. Table 1 shows possible reactions with their rate equations in the polymerization reactor. The concentration variations with time used in modeling are as follows:

$$C_j = C_H, C_A, C_E, C_{Mi}, C_B, C_S, C_{cat}, P_0^k, \mu_0^k, \mu_1^k, \lambda_0^k, \lambda_1^k, \lambda_2^k$$

where k is site number of the catalyst. In this study, it is supposed that the catalyst has mono-site, and then k is equal to one. Here, C_H, C_A, C_E, C_{Mi}, C_B, C_S, C_{cat}, and P_0 are the concentration of hydrogen, co-catalyst (aluminum alkyl), electron donor, monomer, poison, site transfer, catalyst and potential site in the polymerization in respectively. Table 2 listed the component rate equations and moment equations have been used in the model. The final product properties of polypropylene can be estimated by the moment equations. The basic polymer properties, called as end-use properties, are four items; Number average molecular weight (M_n), weight average molecular weight (M_w), melt flow index (MFI) and polydispersity index (PDI). The relationship between the moment and these indices are defined by the following equations:

$$\overline{M_n} = \sum_{K=1}^{Ns} \sum_{i=1}^{Nm} \frac{\lambda_{\delta_i}^k}{\lambda_0^k} \cdot \overline{M_i} \tag{2}$$

$$\overline{M_w} = \lambda_2 \cdot \sum_{k=1}^{Ns} \lambda_0^k \overline{M_n} \Big/ \left(\sum_{K=1}^{Ns} \sum_{i=1}^{Nm} \lambda_{\delta_i}^k\right)^2 \tag{3}$$

Then : $$DPI = \frac{\overline{M_w}}{\overline{M_n}} \tag{4}$$

As melt flow index is a function of molecular weight through, the below power-law-type equation is suggested.

$$MFI = a \cdot (\overline{M_w})^b \tag{5}$$

a and b parameters are calculated by fitting proprietary experimental data. It will be discussed later in results and discussion.

Determination of the kinetic parameters

A typical polymerization rate profile is comprised of two following area; (I) initial polymerization start-up zone and (II) the quasi-steady-state zone [14]. Each zone has a significant meaning in the kinetic analysis; detailed discussions of these issues have a considerable debate and are not repeated here for the sake of brevity.

Pater *et al.* [12] and some other researchers [13, 14] have showed the rate of polymerization at isothermal conditions can be described as a first-order process in monomer concentration and the deactivation of the catalyst as a first-order process in the number of active sites, the following equations are used:

$$R_p = K_p C_m C \ = R_{p\mathbf{0}} \bullet \exp(-k_d \ \mathrm{o}t) = R_{p\mathbf{0}} \bullet \exp(-\frac{E_a}{R.T}) \tag{6}$$

$$\frac{dC^*}{dt} = -K_d C \ , where \mathrm{K} \ k_d = k_{d\mathbf{0}} \cdot \exp(\frac{-E_{a,d}}{RT}) \tag{7}$$

Here, Rp_0 is the initial reaction rate, k_d the deactivation constant, $E_{a,d}$ the activation energy for the lumped deactivation reaction, C activated site of the catalyst during polymerization, t shows time, and T indicates the temperature. So it could be calculation with profile rate curve of polymerization (t = 0).

Obviously, for finding Rp at the isothermal condition, two parameters namely Rp_0 and K_d should be obtained. The Rp_0 and K_d are determined graphically by plotting the natural logarithm of the reaction rate versus polymerization time, a linear fit can be made where the slope of the fit line is K_d, and the intercept is Rp_0. Due to the rate of polymerization has a dependency on temperature, with having Rp_0 at different temperatures by using Arrhenius Eq. (6), the activation energy of any type of catalyst is easily predictable.

Table 1. Possible reactions with their rate equations in the polymerization reactor.

Reaction step	Component	Reaction	Rate equation
Site activation	Hydrogen	$C_p + H_2 \rightarrow P_0^K$	$R_{aH}^K = k_{aH}^k C_p C_{H,a}^{O_{aH}^K}$
	Al-alkyl	$C_p + A \rightarrow P_0^K + B$	$R_{aA}^K = k_{aA}^k C_p C_{A,a}^{O_{aA}^K}$
	Monomer *i*	$C_p + M_i \rightarrow P_0^K + M_i$	$R_{aMi}^K = k_{aMi}^k C_p C_{Mi}^{O_{aMi}^K}$
Chain initiation	Monomer *i*	$P_0^k + M_i \rightarrow P_{\delta_i,i}^K$	$R_{P0i}^K = k_{P0i}^k P_0^K C_{M_i,a}$
Chain propagation	Monomer *j*	$P_{n,i}^K + M_j \xrightarrow{Kp} P_{n+\delta_j,j}^K$	$R_{Pji}^K = k_{Pji}^k P_{n,j}^K C_{M_j,a}$
Chain transfer	Hydrogen	$P_{n,i}^K + H_2 \xrightarrow{Kh} P_0^K + D_n^k$	$R_{cHi}^{K,n} = k_{cHi}^k P_{n,i}^K C_{H,a}^{O_{cHi}^K}$
	Monomer *j*	$P_{n,i}^K + M_j \xrightarrow{Km} P_{\delta_j,j}^K + D_n^k$	$R_{cM_{ji}}^{K,n} = k_{cM_{ji}}^k P_{n,i}^K C_{j,a}^{O_{cM_{ji}}^K}$
Site deactivation	Hydrogen	$P_{n,i}^K + H_2 \rightarrow C_d + D_n^k$	$R_{aHi}^{K,n} = k_{dH}^k P_{n,i}^K C_{H,a}^{O_{dH}^K}$
		$P_0^K + H_2 \rightarrow C_d$	$R_{dH0}^K = k_{dH}^k P_0^K C_{H,a}^{O_{dH}^K}$
	Al-alkyl	$P_{n,i}^K + A \rightarrow C_d + D_n^k$	$R_{dAi}^{K,n} = k_{dA}^k P_{n,i}^K C_{A,a}^{O_{dA}^K}$
	Spontaneous	$P_{n,i}^K \rightarrow C_d + D_n^k$	$R_{dSpi}^{K,n} = k_{dSp}^k P_{n,i}^K$
		$P_0^K \rightarrow C_d$	$R_{dSp0}^K = k_{dSp}^k P_0^K$
Using dormant sites theory [14]			
Dormant site formation		$C_j + M \xrightarrow{K_s} S_{j+1}$	
Dormant sites reactivation by H_2		$S_j + H_2 \xrightarrow{K_{reh}} C_0 + D_j$	
Reactivation of dormant sites by monomer		$S_j + M \xrightarrow{K_P} S_{j+1}$	
Deactivation		$C_j \xrightarrow{K_d} D_j$	

Table 2. The component rate and moment equations used in the model [3].

Hydrogen	$R_H = -\sum_{K=1}^{Ns}[R_{aH}^k + R_{rH}^k + R_{dH0}^k + \sum_{i=1}^{Nm}\sum_{n=\delta_i}^{\infty}(R_{cHi}^{k,n} + R_{dHi}^{k,n})]$
Cocatalyst	$R_A = -\sum_{K=1}^{Ns}[R_{aA}^k + R_{dA0}^k + \sum_{i=1}^{Nm}\sum_{n=\delta_i}^{\infty}R_{dAi}^{k,n}] - R_{eA}$
Electron donor	$R_E = -\sum_{K=1}^{Ns}[R_{dE0}^k + \sum_{\substack{l=1\\l\neq K}}^{Ns}R_{tE0}^{kl} + \sum_{i=1}^{Nm}\sum_{n=\delta i}^{\infty}(\sum_{\substack{l=1\\l\neq K}}^{Ns}(R_{tEi}^{lk,n} + R_{dEi}^{k,n})] - R_{eE}$
Poison	$R_X = -\sum_{K=1}^{Ns}[R_{dX0}^k + \sum_{i=1}^{Nm}\sum_{n=\delta_i}^{\infty}R_{dXi}^{k,n}] - R_{eE} - R_{eA}$
Potential sites	$R_{Cp} = -\sum_{K=1}^{Ns}(R_{aH}^k + R_{aA}^k + R_{aSp}^k + \sum_{i=1}^{Nm}R_{aM_i}^k)$
Vacant sites	$R_{P_0^k} = R_{aH}^k + R_{aA}^k + R_{aSp}^k + \sum_{i=1}^{Nm}R_{aMi}^k + R_{rH}^k - R_{dH0}^k - R_{dE0}^k - R_{dA0}^k - R_{dSp0}^k - R_{dX0}^k - \sum_{j=1}^{Nm}R_{p0j}^k + \sum_{i=1}^{Nm}\sum_{n=\delta i}^{\infty}(R_{cHi}^{k,n} + R_{cSpi}^{k,n})$ $+\sum_{i=1}^{Nm}\sum_{\substack{l=1\\l\neq K}}^{Ns}\sum_{n=\delta i}^{\infty}(R_{tEi}^{lk,n} + R_{tSpi}^{lk,n})] + \sum_{\substack{l=1\\l\neq K}}^{NS}(R_{tE0}^{lk} + R_{tSp0}^{lk} - R_{tE0}^{kl} - R_{tSp0}^{kl})$
Dead sites	$R_{Cd} = \sum_{K=1}^{Ns}[(R_{dH0}^k + R_{dE0}^k + R_{aA0}^k + R_{dX0}^k + R_{aSp0}^k - R_{rH}^k) + \sum_{i=1}^{Nm}\sum_{n=\delta i}^{\infty}(R_{dHi}^{k,n} + R_{dEi}^{k,n} + R_{dAi}^{k,n} + R_{dXi}^{k,n} + R_{dSpi}^{k,n})]$
Monomer	$R_{Mi} = -\sum_{K=1}^{Ns}[R_{P0i}^k + \sum_{j=1}^{Nm}\sum_{n=\delta i}^{\infty}(R_{Pij}^{k,n} + R_{cMi,j}^{k,n})]$
Moments equations	
Live polymer	$R_{P_{n,i}^k} = \delta(n-\delta_i)[R_{P0i}^k + \sum_{j=1}^{Nm}\sum_{m=\delta i}^{\infty}R_{cMi,j}^{k,m}] + \sum_{j=1}^{Nm}k_{pij}^k C_{Mi,a}P_{n-\delta_i,j}^k - \sum_{j=1}^{Nm}k_{pij}^k C_{Mj,a}P_{n,i}^k - \alpha_i^k P_{n,i}^k$
Dead polymer	$R_{D_{n,}^k} = \sum_{i=1}^{Nm}\alpha_i^k P_{n,i}^i$ where $\alpha_i^k = k_{cHi}^k C_{H,a}^{d_{Hi}} + k_{cSpi}^k + \sum_{j=1}^{Nm}k_{cMji}^k C_{Mja} + \sum_{\substack{l=1\\l\neq K}}^{Ns}(k_{tEi}^{kl}C_{E,a}^{d_E} + k_{tSpi}^{kl}) + k_{dHi}^k C_{H,a}^{d_{Hi}} + k_{dAi}^k C_{A,a}^{d_{Ai}} + k_{dEi}^k C_{E,a}^{d_E} + k_{dXi}^k C_{X,a}^{d_{Xi}} + k_{dSpi}^k$
Live moment	$\mu_{\delta_i,i}^k = \sum_{n=1}^{\infty}n^{\delta_i}P_{n,i}^k$
Bulk moment	$\lambda_{\delta_i}^k = \sum_{n=\delta_i}^{\infty}(\sum_{i=1}^{Nm}P_{n,i}^k + D_n^k)$
Zero-order live polymer moments	$R_{\mu_{0,i}^K} = R_{P0i}^k + \sum_{j=1}^{Nm}k_{cM_i,j}^k C_{Mi,a}\mu_{0,J}^k - \alpha_i^k\mu_{0,J}^k + \sum_{j=1}^{Nm}[k_{pij}^k C_{Mi,a}\mu_{0,J}^k - k_{pji}^k C_{Mj,a}\mu_{0,i}^k]$
First-order live polymer moments	$R_{\mu_{0i}^K} = \sum_{i=1}^{Nm}\delta(i-l)[R_{P0i}^k + \sum_{j=1}^{Nm}k_{cM_i,j}^k C_{Mi,a}\mu_{0,J}^k] - \sum_{i=1}^{Nm}\alpha_i^k\mu_{\delta_i,i}^k + \sum_{i=1}^{Nm}\sum_{j=1}^{Nm}k_{pij}^k C_{Mi,a}\delta(i-1)\mu_{0,J}^k$
Zero-order bulk polymer moments	$R_{\lambda_0^K} = \sum_{i=1}^{Nm}[R_{P0i}^k + \sum_{j=1}^{Nm}k_{cM_i,j}^k C_{Mi,a}\mu_{0,J}^k]$

First-order bulk polymer moments	$R_{\lambda_{0l}^k} = \sum_{i=1}^{Nm} \delta(i-l)[R_{P0i}^k + \sum_{j=1}^{Nm} k_{cM_i,j}^k C_{Mi,a} \mu_{0,J}^k] + \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} \delta(i-1) k_{pij}^k C_{Mi,a} \mu_{0,J}^k$
Second-order bulk polymer moments	$R_{\lambda_2} = \sum_{K=1}^{Ns} \sum_{j=1}^{Nm} [R_{P0i}^k + \sum_{i=1}^{Nm} k_{cMji}^k C_{Mj,a} \mu_{0,i}^k] + \sum_{k=1}^{Ns} \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} k_{pji}^k C_{Mj,a} (\mu_{0,i}^k + 2\mu_{1,i}^k)$

Two very important notes should be considered about activation energy of Ziegler-Natta catalyst. First, it is independent of the hydrogen concentration [14]. Secondly, this is an intrinsic property of any catalyst and thus can be expected to differ from one type to another. The yield of the polymerization can be calculated by integrating the rate.

$$Y_{calc} = \int_0^t R_P \cdot dt \tag{8}$$

Amount of Y_{calc} is exactly equal to the area under the profile curve. If this value is multiplied by the amount by weight of the catalyst, the produced polymer will be obtained in each batch. In experimental, the yield is measured by weighing the dry product from batch polymerization (as summarized in Table 1 for this study). But in fact, much more monomers are entered to the reactor, as called consumed monomer, that a part of them are reacted and the other part remains as an unconverted monomer in liquid and gas phases. The model is capable calculated yield and consumed monomer, directly.

Hydrogen effect and dormant sites theory to determining k_p

Propagation reaction is the most important reaction in the polymerization. Accordingly, determining the value of constant (K_P) and activation energy (E_p) are inevitable for modeling. We have used from the latest theory in regarding the effect of hydrogen on the catalyst sites. The theory is well-known to dormant sites theory. According to the theory, Since a propylene molecule is asymmetric with respect to the double bond, it has been suggested that monomers may insert at the catalyst site in four distinct arrangements (head to tail, tail to tail, tail to head and head to head). Growing chain has two positions of dealing with other monomers (position 1-2 and position 2-1). If growing chain reacts with position 2-1 of propylene, the dormant site will be created. Dormant sites are the drawback of propylene polymerization. Busico *et al.*, have measured the distributions of end groups in polypropylene in the presence of hydrogen and have suggested that if the propylene molecule inserts in the 2-1 mode, the rate of propagation is reduced due to steric hindrance by the Ti atom [25]. These results are supported by the end group analysis done by Chadwick *et al.* [26].

According to the dormant sites theory, increasing the hydrogen concentration decreases the concentration of the dormant sites. A series of general formulas in accordance with the dormant sites theory for modeling have been proposed by Weickert *et al.*, but the basis of their work was experimental and not attention to final product properties [14]. They are applied a "quasi-single-site" model to explain the average behavior of the active sites. In addition, it is assumed that all active sites have the same average rate constants. The chain transfer with co-catalysts is neglected and a quasi-steady state is assumed for dormant sites.

In reality, the active sites of the catalyst are more or less covered by the polymer produced. The actual catalyst site concentration is between the maximum concentration of active sites C_{max}, and the concentration of dormant sites C_s. Therefore C from Eq. (6) can be written as the following:

$$C = C_{max} - C_S \tag{9}$$

The concentration of the dormant sites can be calculated assuming the quasi-steady-state:

$$R_S = 0 = K_s.C.C_m - K_{reh}.C_s.C_{H2} - K_{rem}.C_s.C_m \rightarrow \therefore \quad C_s = \frac{K_s.C}{K_{reh}.X + K_{rem}} \tag{10}$$

with K_s, K_{reh} and K_{rem} are rate constants for dormant sites formation, dormant sites reactivation by hydrogen and monomer reactions respectively. Where X is the hydrogen molar ratio X = C_H/C_m. Combining equations (9) and (10) leads to:

$$C = \frac{C_{\max}.(1 + K_1.X)}{1 + K_2 + K_1 X} \quad \text{where} \quad K_1 = \frac{K_{reh}}{K_{rem}} \; ; \quad K_2 = \frac{K_s}{K_{rem}} \tag{11}$$

By inserting Eq. (11) in Eq. (6), we have the following equation.

$$R_p = \frac{K_p.C_m.C_{\max}.(K_1.X + 1)}{1 + K_1.X + K_2} \tag{12}$$

$$R_p = K_p.C_{\max}.C_m.f_{H_2}$$

Where:

$$f_{H_2} = \frac{1 + K_1.X}{1 + K_2 + K_1.X}$$

f_{H2} represents the fraction of active sites in the system. In the absence of hydrogen X = 0, f_{H2} has the minimum amount. It means active sites of catalyst are at a minimum level in the polymerization system. Consequently, if $f_{H2,max}$ = 1, namely 100% of catalyst sites are active in reaction.

Modeling algorithm

In this study, we have outlined the algorithm for programming the mathematical model in a Matlab/Simulink environment, as shown in Figure 1(a). It is composed of two part; main-program (as named "Runsim") and subroutine (function file). For obtaining kinetic constants in the model, we propose a new method as iterative method algorithm by using consistency property of ODE's equation in Figure 1(B). The advantage of the method is more easy and trustable rather than the conventional manners; i.e. using directly from open literature [9] or estimating by trial and error [3]. For using the iterative method algorithm; only the initial guess of kinetic constants should be estimated by referring to open literature, afterward, the kinetic constants are adjusted for used the catalyst by the algorithm.

In this study, from literature [3, 9], the initial guess of kinetic constants was estimated and applied to the model, next the constants were exactly adjusted and determined in accordance with used the commercial catalyst in the set-up (experimental data) by the proposed algorithm in Figure 1(B). Investigating Figure 1(A) and (B) implies that the fairly accurate kinetic constants have been applied in the model.

RESULTS AND DISCUSSION

Comparison of the model output and experimental results in different condition are summarized in Table 3. The model has been validated by experimental data (as shown in Figure 2; in the absence of hydrogen concentration with different temperature and Figure 3 at the constant reactor temperature (70 ºC) with different hydrogen concentration). As it can be seen the experimental results and model outputs had in an acceptable margin of error. The margin of errors might be justified for the following reasons: (i) the global error that is the summation of

truncation, method and round off error, (ii) personal and measurement equipment errors, (iii) selection of equation of state and (iv) errors resulting from assumptions.

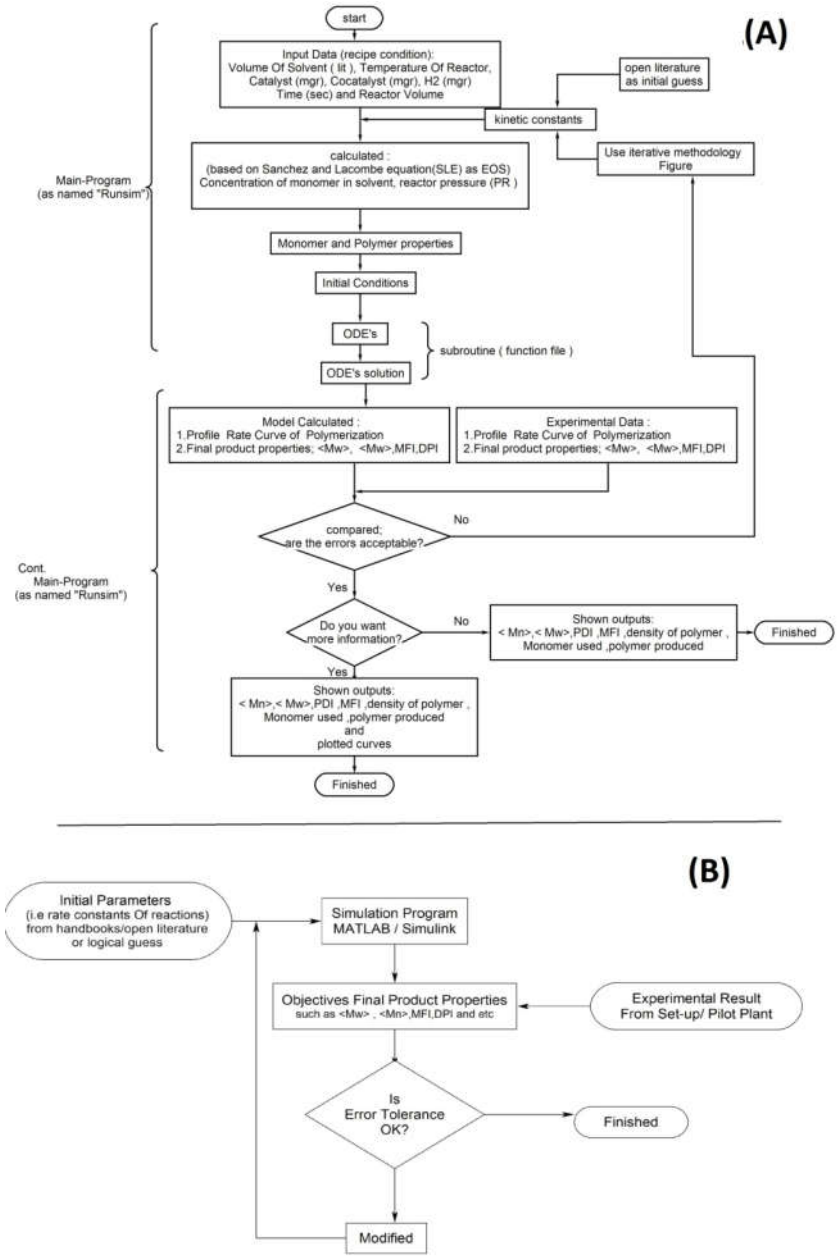

Figure 1. (A) The general algorithm modeling in this work and (B) the iterative methodology used to adjusting kinetic parameter (constants) in this work.

Table 3. Summarized recipe for polymerization; summarized polymerization recipe; model and experimental output results.

Recipe					Results (experimental/model)							
Run No.	T (°C)	H_2 (mg)	Cata-lyst		Y (g)	Rp_0	K_d (1/h)	M_n	M_w	PDI	MFI	ρ (kg/m)
1	65	0	20	Exp. R[1]	63.29	5.01	1.42	210259	863057	4.10	0.75	
				Mod. R[2]	65.13	5.19	1.42	205570	834523	4.06	0.81	589.44
2	70	0	20	Exp. R	72.66	6.5	1.95	304642	1104374	3.63	0.42	
				Mod. R	76.40	7.46	1.98	323780	1214440	3.75	0.33	619.37
3	75	0	20	Exp. R	63.07	8.85	2.04	236154	1124367	4.76	0.4	
				Mod. R	67.25	8.92	2.13	270243	1178300	4.36	0.36	614.62
4	70	183	10	Exp. R	81.33	11.2	2.27	29962	144192	4.81	37	
				Mod. R	88.40	11.4	2.30	32812.7	148874	4.54	36.99562	637.11
5	70	274	10	Exp. R	74.61	11.0	2.05	24016	116939	4.87	62	
				Mod. R	76.81	11.2	2.35	24981.1	123303	4.94	61.98627	620.01
6[6]	70	2000[5]	10	Exp. R								
				Mod. R	64.92	9.34	2.81	9952.25	70163.4	7.06		
7[7]	70	2500[8]	10	Exp. R								
				Mod. R	61.26	8.74	2.97	8353.86	61651.5	7.38		

X: Hydrogen molar ratio, it is calculated by Aspen Software polymer software based on SLE (SOE)

[1] Experimental result

[2] Model result

[3] 18 mg H_2 is equivalent to 0.00466 molar ratio X.

[4] 27 mg H_2 is equivalent to 0.00703 molar ratio X.

[5] 2000 mg H_2 is equivalent to 0.0206 molar ratio X.

[6] Mathematically calculated. But in fact, this product is off or wax grade.

[7] 2500 mg H_2 is equivalent to 0.0243 molar ratio X.

[8] Mathematically calculated. But in fact, this product is off or wax grade.

After validated model, the data run 6 and 7 come from the model. The results from Table 3 demonstrated that in the absence of hydrogen, the polymerization rate increased up to 70 °C and then decreased at 75 °C. This claim can be verified by investigating the yield amount of products. Because of the polymerization rate has a direct impact on the yield. Meanwhile, increasing reaction temperature leads to increasing deactivation constant (K_d) of the catalyst. This conclusion is one of the important constraints of the reaction.

By referring to Table 3, the other important conclusion is that increasing reaction temperature leads to decreasing yield of the catalyst. The reason for this phenomenon might be justified due to catalyst deactivation by over reduction of the catalyst sites or via alkylation process with the Lewis base [27].

In order to investigate the effect of varying the hydrogen concentration on the profile polymerization rate, Figure 3 has been plotted at 70 °C reactor temperature. Because it is concluded that 70 °C reactor temperature is the best condition with a maximum yield of catalyst (Table 3; comparing yield for run (1, 2 and 3)). To verify the performance of the model, Figure 3 is compared the experiment with the model profile polymerization rate. Figure 3 indicates that each of both profile rate in the same condition has a fairly good consistent with each other in an acceptable margin of error. On the other hand, the error margin of final product properties such as M_w, DPI, and MFI between model output results and experimental data is acceptable as well (Table 3). Accordingly, it is concluded that the model has been validated.

It is worth mentioning that according to Arrhenius equation, the overall activation energy for the polymerization (E_a) is dependent on temperature and independent on hydrogen concentrations [14]. The overall activation energy has been calculated by Eq. (6) and Figure 4(A). It is notable that the activation energy obtained in this work is in line with the literature data as shown in Table 4. From Figure 5(A), the constants of Eq. (5) could be estimated for predicting MFI by average M_W.

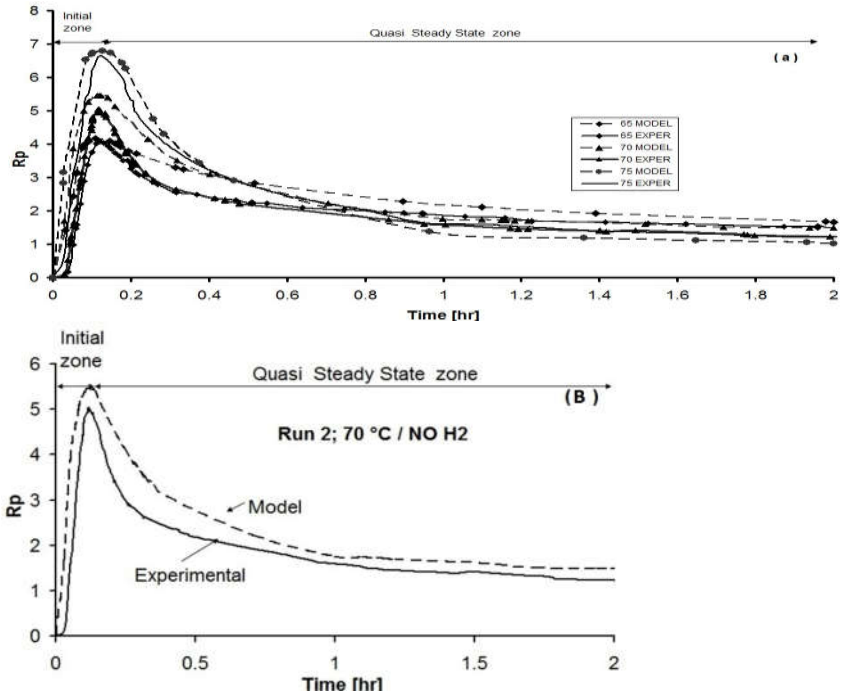

Figure 2. The comparison of experimental and model profile rate in the absence of hydrogen at a different temperature: (a) the comparison of the model and experimental altogether; run (1, 2, 3) and (b) the comparison of the model and experimental run 2.

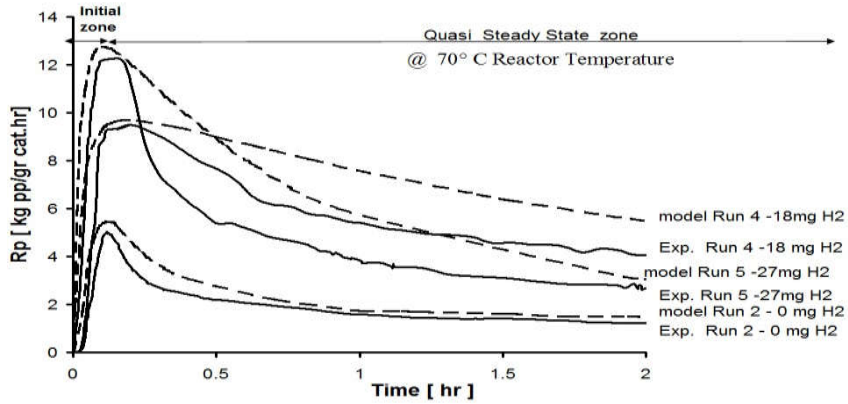

Figure 3. The comparison of experimental and model profile rate in the presence of different hydrogen concentration at the constant temperature 70 ºC.

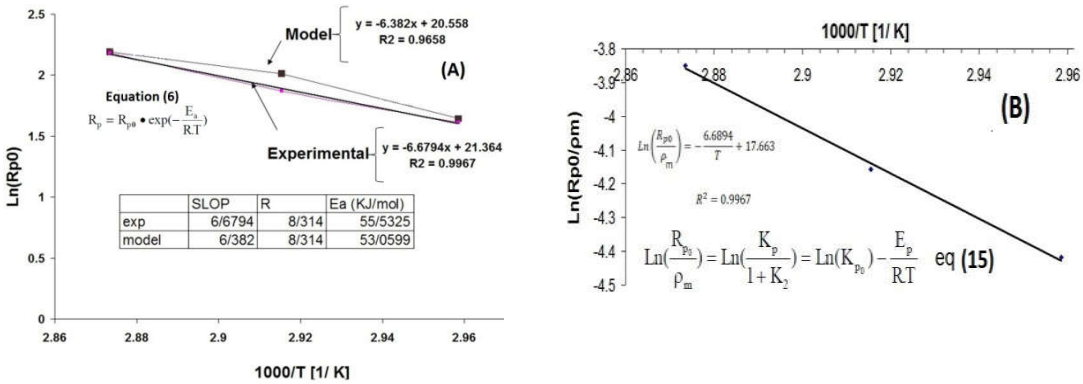

Figure 4. (A) obtaining E_a by Arrhenius plot of the initial polymerization rates Rp_0 at a different temperature; obtaining constants of Eq. (6), the relation of M_w with MFI and (B) calculation of propagation constant K_p and E_p by using Eq. (15).

Table 4. The compaction of reported activation energies (E_a) in propylene polymerization system.

Catalyst system	Phase	E_a (kJ/mol)	Reference
δ-$TiCl_3$ (1/3)$AlCl_3$/DEAC	Slurry	53.9	Yuan *et. al.* [28]
$TiCl_3$/DEAC	Slurry	57.7	Soares *et. al.* [18]
$MgCl_2$/$TiCl_4$/phthalate/silane/TEA	Liquid pool	58.6	Al-haj Ali *et al.* [14]
$MgCl_2$/$TiCl_4$/phthalate/silane/TEA	Slurry	55.53	This study (Exp.)
$MgCl_2$/$TiCl_4$/phthalate/silane/TEA	Slurry	53.05	This study (Model)

Equation (12) or polymerization rate has three parameters that should be determined (i.e. K_p, k_1, and k_2). The fit is done in two steps, in the first step the value of ($k_p/(1+k_2)$) is obtained by putting X = 0 (no hydrogen), then the values of k_1 and k_2 are estimated. The first step: as the active sites of catalyst are heterogeneity, the calculated value of K_P is an average amount. This value is determined using the experiments without hydrogen, run 1, 2 and 3. When no hydrogen is used, f_{H2} can be rewritten as:

If X = 0 (no hydrogen); Eq. (12) converts to the following equation:

$$R_{p_0} = \frac{R'_{p_0}}{\rho_m} = \frac{K_p'}{1+K_2} \tag{13}$$

where R'_{p_0} [mol/L.s] and R_{p_0} [kg/g_{cat}.h], and with rearrangement we have.

Here ρ_m is monomer density. The Arrhenius plot for ($K_P/1+k_2$), Figure 4(B), shows an excellent fit with a linear correlation coefficient (R^2) of 0.9967. Based on these results, the dependency of ($kp/1+k_2$) on reaction temperature has the following form:

$$K_p = K_{p_0}.(1+K_2).\exp(-\frac{E_p}{R.T}) \tag{14}$$

Then we have:

$$Ln(\frac{R_{p_0}}{\rho_m}) = Ln(\frac{K_p}{1+K_2}) = Ln(K_{p_0}) - \frac{E_p}{R.T} \tag{15}$$

From the slope of the fitted line in Figure 4(B), the activation energy of propagation reaction of the polymerization E_p is obtained. Table 5 shows the summarized results from this research (in the slurry process) and compared with the other researcher (in bulk process). The results of the model are in line with what was expected.

Since the most reactions in the polymerization belong to propagation reactions, as expected, the overall activation energy E_a should be very close to the propagation activation energy E_p. Therefore, with calculating and comparing of E_p with E_a at least error, it could be a criterion of the accuracy and validity of the model.

For calculating E_p is by means of dormant site generation theory by using Eq. (15) and plotting in Figure 4 (B). The figure shows an excellent fit with a linear correlation coefficient (R^2) of 0.9967. Then from the slop of the fitted line in Figure 4(B), E_p is obtained. It is interesting to note that with comparing E_a and E_p, the difference is only 4% error (Table 5). This is another reason that the model was well enough validated. In addition, the Dormant Site Generation Theory has accurately justified the profile curve rate of propylene polymerization.

In this respect, Al-haj Ali *et al.* [14], using the experimental method in liquid pool media, have been calculated E_a and E_p with approximately 12.8% error (Table 5). Therefore, this error difference has a significant effect on the subsequent calculations such as Rp_0, K_1, and K_2 (summarized in Table 5).

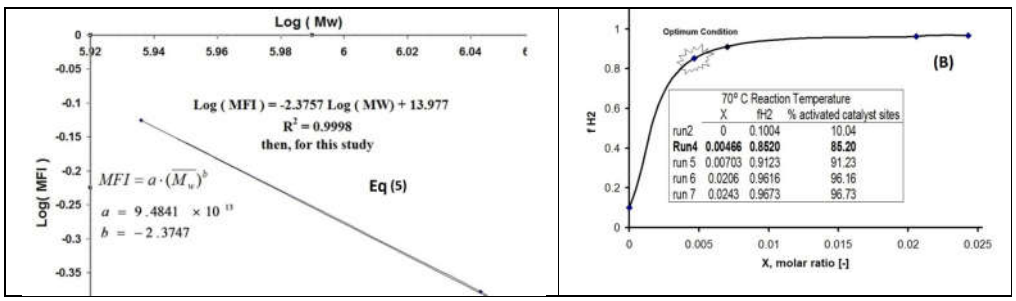

Figure 5. (a) Obtaining constants of Eq. (5), the relation of M_w with MFI and (b) the relation of the fraction of active sites by hydrogen concentration in system f_{H2}.

Table 5. The comparison of the kinetic constants obtained in this work with literature work.

	Condition	Overall E_a [kJ/mol]	E_p [kJ/mol]	Error %	K_{p_0} $[m^3/gr_{cat}.hr]$	K_2 [-]
Al-haj Ali *et al.* [14] slurry-bulk	Liquid pool	58.6	67.22	12.82	6.41×10^8	8.02
	Catalyst system: $MgCl_2/TiCl_4$/phthalate/silane/TEA	$K_1 = -32.2\cdot T^2 + 2.26\cdot T - 3.86\times10^6$				
This work	Slurry in heptane	53.0599	55.61	4.5	4.69×10^6	8.97
	Catalyst system: $MgCl_2/TiCl_4$/phthalate/silane/TEA	$K_1 = -1.529\cdot T^2 + 555.24\cdot T - 4.226\times10^6$				

By using the dormant theory, Eq. (12) is obtained. On the other hand, K_1 and K_2 can be estimated using the output of the model and Figure 4(a). The equation predicts the fraction of the catalyst active sites via hydrogen molar ratio (X). For instance, if there is no hydrogen in the

polymerization system (X = 0), only 10% of the potential of the catalytic is active, and about 90% of it is laid down and unused (Figure 5(B)). The impact of this issue on Y and Rp_0 is exactly clear and the model is able to predict that (Table 3). Then, by increasing very slightly hydrogen content such as X = 0.00466, speedily increasing fraction activated sites of the catalyst (85.5%) (Figure 5(B)). But the increasing hydrogen content caused to be increasing deactivation catalyst K_d (Table 3). It is not very desirable due to quickly deactivation of the catalyst. On the other side, the increased hydrogen content has an inverse effect on the Rp_0 and Y, in the other words; it may lead to changing final product properties and even producing off-grade or wax product.

CONCLUSION

In this paper, it has been presented a validated mathematical model based on moment approach for an isothermal slurry polymerization of propylene with Ziegler-Natta catalysts. that cable to calculate the most important indices of final product properties, such as melt flow index (MFI), number average molecular weight (M_n), weight average molecular weight (M_w) and poly dispersity index (PDI), and hydrogen response of propylene polymerization system. The model output was in good agreement with experimental results and revealed. At the 70 ^oC temperature, the PDI was a minimum amount, indicating optimum polydispersity of polymer chains. In absence of hydrogen, increase in temperature led to a reduction of molecular weight and enhancement of MFI. The activation energy did not depend on the presence and absence of hydrogen as well as hydrogen concentration. The model could be able to predict deactivation constant of unknown catalyst in the presence or absence of hydrogen in the polymerization system.

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