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Control Heat Generation, Conversion Percentage and Effective Residence Time of Catalyst Via Hydrogen and Reaction Temperature in Propylene Polymerization by A Validated Mathematical Model

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Abstract: *Due to the unique complexity of the Ziegler-Natta catalyst, so far, the catalyst performance in the polypropylene polymerization is still ambiguous. Understanding the behavior of the catalyst is highly dependent on the reaction temperature and hydrogen amount as the process variables. Furthermore, knowing the proper reaction temperature control, heat generation amounts, the effective catalyst residence time and the conversion percent vs. the polymerization time are the remarkable gap issues in this field. Undoubted, the significance of these issues are multidiscipline for chemists, polymer scientists, process engineers, designers, and licensors. The main objective of the present work is to develop and propose a validated kinetics model to predict and reply to the aforementioned problems in a proper manner. The modeling approach is based on polymer moment balance technique and validated via experimental data from lab-scale reactor. The model has successfully shown that not only able to predict the vital indices of the final product properties but also able to cover the above gaps. In addition to the results which were the aims of this study, implicitly concluded that Hydrogen not only causes increases the rate of the polymerization but also gives rise to arising the deactivation constant and reducing the lifetime of the catalyst. Moreover, Hydrogen has no effect on the conversion percent and only increasing temperature has a significance effect on increasing the conversion percent.*

Keywords: *Mathematical Modeling, Propylene Polymerization, catalyst residence time, population balance, process variables, hydrogen effect.*

I. Introduction

Due to low costs and the interesting properties of polypropylene, an impressive growth of developing and demanding for the polymer is predicated and has been documented in the recent decade. The development of new technologies and the development of the used catalyst systems are the major reasons that have been given rise to remarkable development, lower production costs and high profitability in this field. Its application is strongly influenced by the final product properties, and also the final product properties strongly depend on the kinetics of the polymerization.

Despite a long history of the usage of Ziegler-Natta catalyst because the catalyst has unique complexity kinetic for producing the polymer, the nature and performance of the catalytic in the polymerization still remain ambiguous to us. A deep understanding of the behavior of the catalyst, which is highly dependent on the type of the used catalyst and operating conditions namely temperature and concentration of hydrogen in the system, which should be exactly evaluated as well.

Since the polymerization reaction is relatively exothermic; knowing the proper reaction temperature control, heat generation amounts, effective catalyst residence time, the conversion with polymerization time and the variation of process variable such as adjusting reaction temperature and hydrogen amount in polymerization system and also the effects of them on final product properties are the remarkable issues in view of the process and designer engineers and catalyst chemists. At present, these subjects are the existing unknowns and gaps in this field. In view of the significance of the matters, it seems that a mathematical model which is able to give a compelling answer to the problems is inevitable. To date, there has not been an adequate model to predict and clarify these gaps. Expected that if a validated mathematical model would be established in this regard definitely has a broad application in basic and applied research, and the main goal of this research is to propose an improved model to cover the existing gaps. We believe that it is the first kind research to accurately identify these issues in a proper way.

So far, to comprehend the behavior of the polymerization system, most studies have focused on an experimental approach, whereas this way is not reliable and applicable because of their results heavily dependent on test and laboratory conditions. The other constraint of the method is the type of the catalyst used [1-3]. Thus; their studies have not fulfilled the existing gap as defined earlier.

In regard to modeling, in 2018, Varshouee et al. focused on providing a validated model that able to predict and plot the polymerization profile [4-10]. Then they decided to expand their model to cover the above mentioned existing gap.

Reginato modeled an industrial-scale loop reactor by using a non-ideal continuous stirred tank model to explain the industrial process and compared their simulation results with commercial plant data [11]. Al-haj Ali proposed a generalized model for hydrogen response based on the dormant site theory in liquid propylene polymerization. His research work was only based on experimental data, and there was no validated mathematical model that might be capable of predicting the polymerization rate profile and the indices of final product properties simultaneously [1].

Although some other research has been carried out on the propylene polymerization modeling, there is still remaining the defined gap. Their models have been established on mathematical calculations without validation with experimental data. In this context, some studies have only tended to focus on a loop or fluidized-bed reactors (FBRs), namely bulk or gas phase polymerization [12-14]. Yang has modeled loop propylene polymerization reactors in bulk media. The model targeted at commercial reactor variables without being attentive to kinetics studies and final product properties [15]. Thereafter, another paper has been revealed by modeling of multi-scale polypropylene properties in the FBR reactor. They used the moment equations in their modeling [16].In 2016, likewise as previous work; Kim et al. attract their attention to the simulation of liquid polypropylene polymerization reactors based on Sheripol technology without attention to final product properties such as average molecular weight and polydispersity [17].

In view of the significance of the matters, this paper has been outlined a new way to reply to the gaps issues with the aid of providing a validated model as the best way. To clarify the aforementioned existing gap, these subjects could be classified to the following questions and by replying to them, the issues will be known which

1. What is the effect of the polymerization temperature changes on the variation of heat generation amount via the polymerization time? What is the modest temperature at the same condition?
2. What is the effect of hydrogen concentration changes on the variation of heat generation amount via the polymerization time and what is the modest temperature? What is the optimal hydrogen concentration at the modest temperature?
3. What are the effects of polymerization temperature and hydrogen concentration on the variation of reaction conversion via the polymerization time? In order to find out how long the useful life and yield of the catalyst in the polymerization system are, In other words, what is the behavior of the catalyst in the polymerization system?
4. From which model follows the variation of reaction conversion via the polymerization time in order to decision making to adjust the resident time of the used catalyst in the reactor?

After replying to the above questions, advantages and benefits of this work could be useful in the following area:

a. The chemist who working to improve their new catalyst generations, finding out the drawbacks and optimum conditions their catalyst as well.
b. The polymer scientist working to improve the final product properties as he knows that at the beginning of the polymerization if the monomer and catalyst encounter to excess heat, the runaway reactions would happen; then this event gives rise to undesired happenings on the polymer characteristic such as morphology, atactic polymer forming, average molecular weight, melting and crystalline temperature point and the melt flow index.
c. This model will be lucrative to the process engineers who operating industrial plant while desiring to replace new catalyst in specific purposes without risk and hazard. Other words, the industrial plant will be released from the specific catalyst monopoly. In addition, he can design a new recipe for new economical grades or a tailor-made of the polymer for a certain application by the handy catalyst.
d. Licensors and designer in order to improve their technology for avoiding hot spot and sticky polymer inside the reactor based on the used .a catalyst.

As above explaining, it seems that the benefit of this study belong to multidiscipline, then expected a wide application in this regard. The selected modeling approach is polymer moment balance method (population balance approach) in MATLAB/ SIMULINK software program then the model has been validated with the experimental data come from a lab scale reactor in slurry polymerization by the usage of the 4th generation of Ziegler-Natta catalysts with an acceptable margin of error. The model is able to predict and calculate the profile rate of the polymerization, then from the profiles rate, all the above targets will be obtained and clarified.

2. Experimental

2.1 Material specifications

The 4th generation of spherical $MgCl2$ supported Ziegler-Natta catalyst containing 3.6 wt% Ti and Di-isobutyl phthalate (DIBP) as internal donor supplied by Sudchemie, Germany. Tri-ethyl-aluminum (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 company in 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.

2.2 Experimental polymerization procedure

In this study, slurry homo-polymerization was carried out in heptane media. Polymerization reactor was a one-liter stainless steel vessel manufactured by Buchi Company; polymerization set-up was designed in order to conduct slurry polymerization in one vessel. A high-pressure N2 line was used to transfer the liquid monomer and catalytic system into the reactor.

The Catalyst system was injected into the reactor through a stainless steel cylinder under N2 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 Company.

Experimental the profile polymerization curve (Rpt) 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°C using 1,2,4-trichlorobenzene as a solvent. The GPC is calibrated with the narrow molecular weight distribution polystyrene standard as a reference. The melt flow index (MFI) of samples is evaluated according to ASTM 1238 at the temperature of 230ºC and load of 2.16kg.

A typical polymerization procedure exists for reactor preparation, polymerization, and discharge. The detailed procedure of the polymerization is as follows:

Firstly, the reactor was flushed with nitrogen gas during 1 hour at 90°C and was reduced reactor temperature until 20°C, then purged with propylene gas in 15 minutes. Afterward, 500 ml heptanes as a solvent were introduced to the reactor; next, all the inputs and outputs of the reactor were closed and were stirred at 200 rpm in 5 minutes for solvent degassing under a vacuum pump. Subsequently, hydrogen was entered into the reactor (based on recipe condition), then propylene was introduced to the reactor according to controller program, then the reactor was heated up until reach to equilibrium thermodynamic conditions (T=70°C, Pr = 7.5 bar), finally the reactor was ready to injecting catalyst for starting polymerization. Injecting the 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 a recipe in a glove box under a nitrogen atmosphere 20 minutes before injection to the reactor. After each experiment, the resulting polymer was dried under the ambient condition under Laboratory hood for 24 hours.

2.2 Mathematical modeling

2.2.1 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 polypropylene polymerization is at the thermodynamic equilibrium condition that Obeys from Sanchez and Lacombe Equation(SLE) for calculating the amount of X = CH/Cm, the hydrogen molar ratio[18]. (2) It was assumed that $\gamma 1 = \gamma 2 =.....= \gamma NC$. Where γ is equilibrium constant and NC is a number of solvent in slurry phase components[5]. (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[19].

2.2.2 Mathematical formulas and equations

As olefin polymerization kinetics with Ziegler-Natta catalysts might be fairly complicated[5]. To date, several reaction steps have been proposed in the open literature[5,6]. However, the most comprehensive steps were proposed by Zacca [5]. The ODE mass balance equations in the model are as follows:

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

Where

$$C_{j,R} = \frac{Mole \quad of \ j}{Total \quad Volume}$$

$$\eta_j = \frac{C_{j,a}}{C_{j,l}}$$

$$\zeta_j = \frac{C_{j,o}}{C_{j,R}} = \frac{\rho_0}{\rho_R} \cdot D_f$$

where

$$(\eta/\zeta) = \begin{cases} \eta \quad for \quad liquid \quad phase \quad components \\ \zeta \quad for \quad solid \quad phase \quad components \end{cases}$$

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 which V_R and Rj are defined as reactor volume and j component reaction rate in Eq. 1.

Since the model is a semi-batch process and assumed constant monomer concentration during the polymerization, the input and output terms are eliminated (Qf and Q0) then the terms of η and ζare 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:

$$C_j = C_H, C_A, C_E, C_{Mi}, C_B, C_S, C_{cat}, P_{\mathbf{0}}^k, \mu_{\mathbf{0}}^k, \mu_{\mathbf{1}}^k, \lambda_{\mathbf{0}}^k, \lambda_{\mathbf{1}}^k, \lambda_{\mathbf{2}}^k$$

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, Ccat, and P_0 is 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 is 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 (Mn), weight average molecular weight (Mw), melt flow index (MFI) and polydispersityindex(PDI). The relationship between the moment and these indices are defined by the following equations:

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

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

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

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[4].

Initial rate (Rp0), deactivation constant (Kd) and yield of catalyst (Y) easily obtain from profile rate of the polymerization, in this study listed them in Table 3, detailed procedure discussed in reference 4 and are not repeated here for the sake of brevity.

Table 1: the probable reactions and their rate equations in propylene polymerization used in the model[11].

Reaction Step	Component	Reaction	Rate Equation
Site activation	Hydrogen	$C_p + H_{\mathbf{2}} \rightarrow P_{\mathbf{0}}^{K}$	$R_{aH}^{K} = k_{aH}^{k} C_p C_{H,a}^{O_{aH}^{K}}$
	Al-alkyl	$C_p + A \rightarrow P_{\mathbf{0}}^{K} + B$	$R_{aA}^{K} = k_{aA}^{k} C_p C_{A,a}^{O_{aA}^{K}}$
	Monomer *i*	$C_p + M_i \rightarrow P_{\mathbf{0}}^{K} + M_i$	$R_{aMi}^{K} = k_{aMi}^{k} C_p C_{Mi}^{O_{aMi}^{K}}$
Chain initiation	Monomer *i*	$P_{\mathbf{0}}^{k} + M_i \rightarrow P_{\delta_i,i}^{K}$	$R_{P\mathbf{0}i}^{K} = k_{P\mathbf{0}i}^{k} P_{\mathbf{0}}^{K} C_{M_i,a}$
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	$P_{n,i}^{K} + H_{\mathbf{2}} \xrightarrow{Kh} P_{\mathbf{0}}^{K} + D_n^{k}$	$R_{cHi}^{K,n} = k_{cHi}^{k} P_{n,i}^{K} C_{H,a}^{O_{cHi}^{K}}$
	Monomer *j*	$P_{n,i}^{K} + M_j \xrightarrow{Km} P_{\delta_j,j}^{K} + D_n^{k}$	$R_{cM_{ji}}^{K,n} = k_{cM_{ji}}^{k} P_{n,i}^{K} C_{j,a}^{O_{cMj,i}^{K}}$
Site deactivation	Hydrogen	$P_{n,i}^{K} + H_{\mathbf{2}} \rightarrow C_d + D_n^{k}$	$R_{aHi}^{K,n} = k_{dH}^{k} P_{n,i}^{K} C_{H,a}^{O_{dH}^{K}}$
		$P_{\mathbf{0}}^{K} + H_{\mathbf{2}} \rightarrow C_d$	$R_{dH\mathbf{0}}^{K} = k_{dH}^{k} P_{\mathbf{0}}^{K} C_{H,a}^{O_{dH}^{K}}$
	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	$P_{n,i}^{K} \rightarrow C_d + D_n^{k}$	$R_{dSpi}^{K,n} = k_{dSp}^{k} P_{n,i}^{K}$
		$P_{\mathbf{0}}^{K} \rightarrow C_d$	$R_{dSp\mathbf{0}}^{K} = k_{dSp}^{k} P_{\mathbf{0}}^{K}$

Table 2: The component rate and moment equations used in the model[11].

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	$R_E = -\sum_{K=1}^{Ns}[R_{dE\mathbf{0}}^{k} + \sum_{\substack{l=1 \\ l\neq K}}^{Ns} R_{tE\mathbf{0}}^{kl} + \sum_{i=1}^{Nm}\sum_{n=\delta i}^{\infty}(\sum_{\substack{l=1 \\ l\neq K}}^{Ns}(R_{tEi}^{lk,n} + R_{dEi}^{k,n})] - R_{eE}$
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	$R_{Cp}=-\sum_{K=1}^{Ns}(R_{aH}^{k}+R_{aA}^{k}+R_{aSp}^{k}+\sum_{i=1}^{Nm}R_{aM_i}^{k})$
Dead sites	$\alpha_i^k = k_{cHi}^{k}C_{H,a}^{O_{cHi}^{k}} + k_{cSpi}^{k} + \sum_{j=1}^{Nm}k_{cMj,i}^{k}C_{Mj,a} + \sum_{\substack{l=1\\ l\neq K}}^{Ns}(k_{tEi}^{kl}C_{E,a}^{O_{tE}^{kl}} + k_{tSpi}^{kl}) + k_{dHi}^{k}C_{H,a}^{O_{dH}^{k}} + k_{dAi}^{k}C_{A,a}^{O_{dA}^{k}} + k_{dEi}^{k}C_{E,a}^{O_{dE}^{k}} + k_{dXi}^{k}C_{X,a}^{O_{dX}^{k}} + k_{dSpi}^{k}$
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	$R_{P_{n,i}^{k}}=\delta(n-\delta_i)[R_{P0i}^{k}+\sum_{j=1}^{Nm}\sum_{m=\delta i}^{\infty}R_{cMi,j}^{k,m}]+\sum_{j=1}^{Nm}k_{pij}^{k}C_{Mi,a}P_{n-\delta_i,j}^{k}-\sum_{j=1}^{Nm}k_{pij}^{k}C_{Mj,a}P_{n,i}^{k}-\alpha_i^kP_{n,i}^k$
Dead polymer	$R_{D_{n,}^{k}}=\sum_{i=1}^{Nm}\alpha_i^kP_{n,i}^{i}$ where $\alpha_i^k = k_{cHi}^{k}C_{H,a}^{O_{cHi}^{k}} + k_{cSpi}^{k} + \sum_{j=1}^{Nm}k_{cMj,i}^{k}C_{Mj,a} + \sum_{\substack{l=1\\ l\neq K}}^{Ns}(k_{tEi}^{kl}C_{E,a}^{O_{tE}^{kl}} + k_{tSpi}^{kl}) + k_{dHi}^{k}C_{H,a}^{O_{dH}^{k}} + k_{dAi}^{k}C_{A,a}^{O_{dA}^{k}} + k_{dEi}^{k}C_{E,a}^{O_{dE}^{k}} + k_{dXi}^{k}C_{X,a}^{O_{dX}^{k}} + k_{dSpi}^{k}$
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	$R_{\mu_{\delta_l}^{K}}=\sum_{i=1}^{Nm}\delta(i-l)[R_{P0i}^{k}+\sum_{j=1}^{Nm}k_{cM_i,j}^{k}C_{Mi,a}\mu_{0,J}^{k}]-\sum_{i=1}^{Nm}\alpha_i^k\mu_{\delta_l,i}^{k}+\sum_{i=1}^{Nm}\sum_{j=1}^{Nm}k_{pij}^{k}C_{Mi,a}\delta(i-1)\mu_{0,J}^{k}$
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 moment	$R_{\lambda_{\delta_l}^{K}}=\sum_{i=1}^{Nm}\delta(i-l)[R_{P0i}^{k}+\sum_{j=1}^{Nm}k_{cM_i,j}^{k}C_{Mi,a}\mu_{0,J}^{k}]+\sum_{i=1}^{Nm}\sum_{j=1}^{Nm}\delta(i-1)k_{pij}^{k}C_{Mi,a}\mu_{0,J}^{k}$
Second-order; bulk polymer moment	$R_{\lambda_2}=\sum_{K=1}^{Ns}\sum_{j=1}^{Nm}[R_{P0i}^{k}+\sum_{i=1}^{Nm}k_{cMj,i}^{k}C_{Mj,a}\mu_{0,i}^{k}]+\sum_{k=1}^{Ns}\sum_{i=1}^{Nm}\sum_{j=1}^{Nm}k_{pji}^{k}C_{Mj,a}(\mu_{0,i}^{k}+2\mu_{1,i}^{k})$

2.2.3 How to calculate the polymerization heat generation and the yield of the catalyst

The proposed model gives us the profile rate of the polymerization, as the amount of the catalyst yield (Y) is exactly equal to the area under the profile curve, then it could be calculated easily by integrating the rate as blow equation.

$$Y_{calc}=\int_0^t R_P\cdot dt \qquad (5)$$

.

If this value is multiplied by the amount by weight of the catalyst, produced the polymer (gr PP) would be obtained in each batch. In experimental, the yield is measured by weighing the dry product from batch polymerization. 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 of calculated yield and consumed monomer, directly.

By using the profile rate such as Fig. 3, It is possible to know at any time how is the rate of reaction, that is to say, the profile rate gives us the instantaneous rate of polymerization Rp(t), then instantaneous yield Y(t), conversion X(t) and heat generation Q(t) would be calculated by the following formulas:

$$Y(t) = \frac{R_p(t)}{Y_{total}} \quad (6)$$

$$X(t) = \sum_{0}^{t} Y(t) \quad (7)$$

.

$$Q(t) = Y_{total} \times \Delta H_{rxn} \times \frac{X(t)}{t} \quad (8)$$

Where ΔH_{rxn} =2.033 kJ/ kg for Polypropylene polymerization

2.2.4 Modelling Algorithm

In this study, we have outlined the algorithm for programming the mathematical model in a MATLAB/SIMULINK environment, as shown in Fig. 1A. 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 approach as iterative method algorithm by using consistency property of ODE's equation in Fig. 1B.

The advantage of the method is more easy and trustable rather than the conventional manners; i.e. using directly from open literature [11] or estimating by trial and error[5].

To use 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 the catalyst used by the algorithm.

In this study, From open literature[5,6], the initial guess of kinetic constants was estimated and applied to the model, next the constants were exactly adjusted and determined in accordance with the catalyst used in the Set-up (Experimental data) by the proposed algorithm in Fig. 1b. Comparing the polymerization profile rate of the model outputs and the

experimental data in Fig. 2A and 2B imply that the fairly accurate kinetic constants have been adjusted and applied in the model.

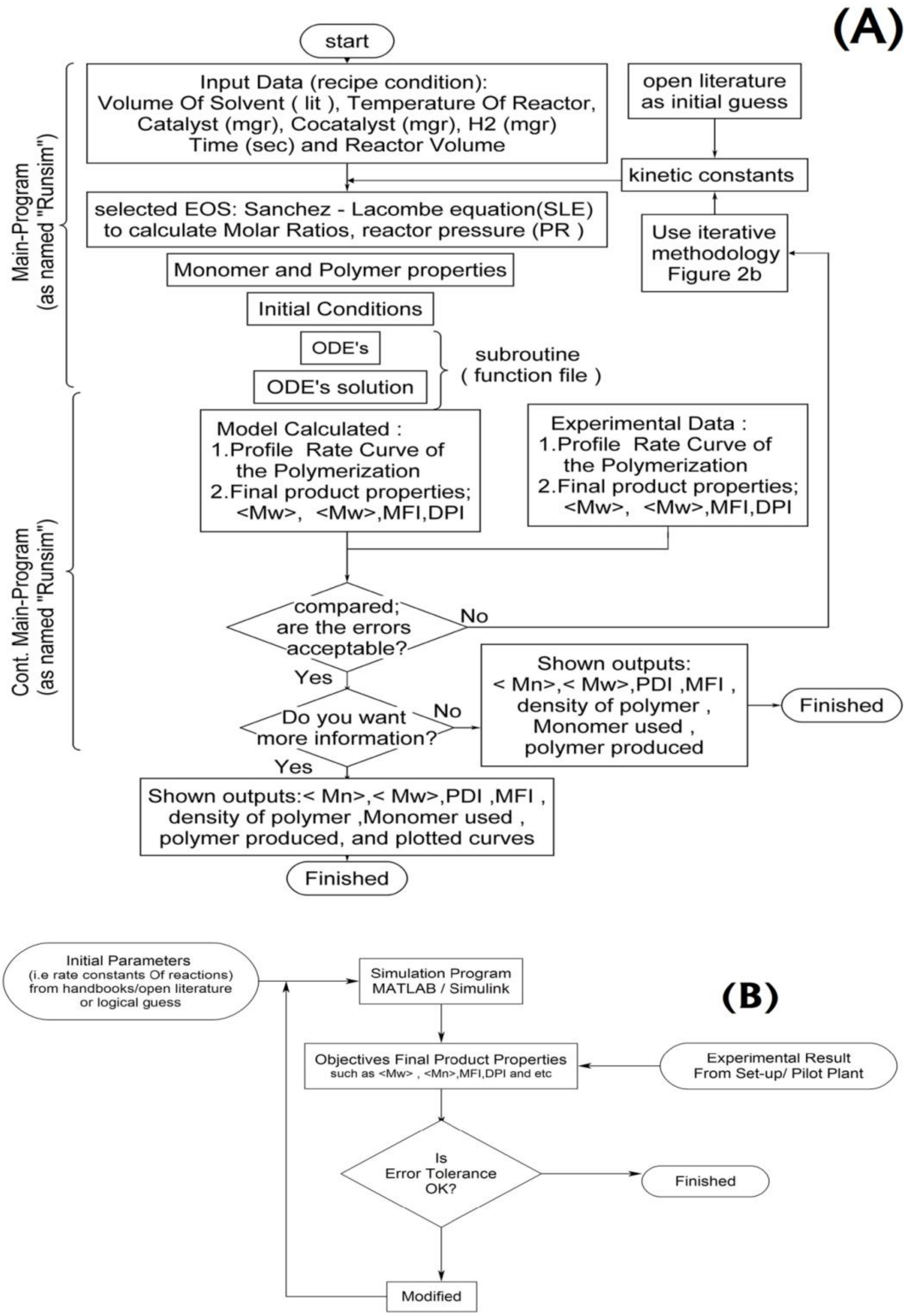

Fig. 1 :(A)The general algorithm modeling in this work; (B) The iterative methodology used for adjusting kinetic parameter (constants) in this work.

3 Results and discussion

Data obtained in our previous study [4], show that the model has been fairly acceptable validated. Fig. 3 and Table 3 are a comparison between the model outputs and the experimental results and illustrated the model trend is in line with the experimental profile rate in an acceptable error margin. Normally, the existing errors in modeling are inevitable by the following reasons:

1. The global error that is the summation of truncation, method, and rounds off error.
2. Personal and measurement Equipment errors.
3. The equation of state was selected.
4. The assumption errors.

As mentioned earlier in the introduction, on to the best our knowledge, up to now there has not been an adequate model to predict and display the mentioned existing gaps in this study or at least no pay a comprehensive attention as defined targets in this study for using in multi-discipline applications. These study attempts were to establish a comprehensive mathematical model to clarify the gaps by using population balance approach. The model was coded in MATLAB/ SIMULINK software program, exactly according to the proposed algorithm (Fig. 1A) along with using comprehensive possible reactions as listed in Table 1 and 2.

The instantaneous rate of polymerization Rp(t) could be determined by Fig. 3A and B, then by using Eqs. 6-8 the instantaneous yield Y(t), conversion X(t) and heat generation Q(t) would be obtained and next by plotting them Figs.3-4 would be displayed. As noted before, the amounts of Y_{calc} is exactly equal to the area under the profile curve. If this value is multiplied by the amount of the used catalyst, the produced polymer would be computed in each batch.

It can be seen from the Fig.3A that in the first half-hour of the polymerization time and in absence of hydrogen, increased about 50% heat generation in the peak of the curves by increasing 5ºC in reaction temperature. This event could be explained by Arrhenius' theory. Referring to Fig. 3B in presence of hydrogen at constant temperature 70ºC concluded that increasing hydrogen from 0 to 18 and 27 mg give rise to increase heat generation to 16.2% and 31.77% respectively (Table 4). This behavior easily could be justified by Dormant site theory, discussed in detail in our previous work [4]. We have already known qualitatively that increase reaction temperature and hydrogen amount leads to increase the rate of reaction, but the model outputs confirmed this issue properly in a quantitative way. The quantitative amount is most valuable for a process engineer to improve his design in order to heat removal from the reactor during polymerization. The other point is that we know that if the extra heat would be in reactor cause to increase the probability of runaway reaction and also we could roughly predict that this reaction has an adverse effect on the final product properties. Whereas the model is able to calculate exactly amount the vital indices as listed in Table 3. This issue is significant for the polymer scientist working to improve the final product properties and tailor-made products.

Table 3: The comparison of model output and experimental results in different conditions

Recipe					Results (Experimental / Model)							
Run No.	T (°C)	H2 (mg)	Catalyst (mg)		Y (gram)	Rp0	Kd (1/hr)	< Mn >	< Mw >	PDI	MFI	ρ (Kg/m^3)
1	65	0	20	Exp.R[1]	63.29	5.01	1.42	210259	863057	4.1	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	1134374	3.71	0.42	
				Mod.R	76.4	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	18[3]	10	Exp.R	81.33	11.24	2.27	29962	144192	4.81	37	
				Mod.R	88.4	11.43	2.3	32812.7	148874	4.54	36.9	637.11
5	70	27[4]	10	Exp.R	74.61	11.02	2.05	24016	116939	4.87	62	
				Mod.R	76.81	11.2	2.15	24981.1	123303	4.94	61.98	620.01

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

[1] Experimental Result

[2] Model Result

[3] 18mg H2 is equivalent to 0.00466 molar ratio X.

[4] 27mg H2 is equivalent to 0.00703 molar ratio X.

Fig. 4A displays the conversion percent of the polymerization in absence of hydrogen; the figure indicated that the variation of the conversion at the different temperature is unique because according to Arrhenius' theory, increasing temperature causes to raise the rate of reaction and consequently grow the conversion rate. The figure also gives an excellent fit to obtain the equation models i.e. the relationship between the time of the polymerization and the conversion percent of the polymerization with acceptable correlation (R^2), as inserted in table 4.

As shown in the Fig. 4B, the figure presents the conversion percent of the polymerization in presence of hydrogen at the constant temperature 70ºC; interestingly, we found that at the deferent hydrogen amounts at constant temperature only an equation model is fitted as inserted in table 4.here, One question is raised that hydrogen as increasing agent of the rate of the polymerization reaction, why the variation of the hydrogen amounts have no effect on the percentage of conversion.

In our opinion, hydrogen, as transfer agent, is able to react with activated sites and also react with the active chain of the polymer as termination agent because of hydrogen causes reduce average molecular weight and increase melt flow index(see table 3). In the other words, concluded that hydrogen leads increase the overall rate of the reaction and no effect on the conversion percent and only increasing temperature give rise to increase the conversion.

Table 4: Models for determining the conversion percent with polymerization time under different conditions

Temperature [ºC]	Hydrogen Amount [mg]	χ [-] The conversion percent	R^2 Fitting Correlation
65	0	$\chi = -0.1063\,t^2 + 0.7177\,t - 0.0229$ @t=0.6 hr $\chi = 0.369452 \equiv 37\%$ % Qtot (from Fig.3A)=48% ; Qtot (from Tab.3)=110.6 Kj	0.9988
70	0	$\chi = -0.1841\,t^2 + 0.8573\,t - 0.0216$ @t=0.6 hr $\chi = 0.426504 \equiv 43\%$ % Qtot (from Fig.3A)=57% ; Qtot (from Tab.3)=142.3 Kj	0.9953
75	0	$\chi = -0.1722\,t^2 + 0.787\,t + 0.0743$ @t=0.6 hr $\chi = 0.484508 \equiv 48\%$ % Qtot (from Fig.3A)=63% ; Qtot (from Tab.3)=189.7 Kj	0.9944
70	18	$\chi = -0.1828\,t^2 + 0.863\,t - 0.0095$ @t=0.6 hr $\chi = \ \equiv 37\%$ % Qtot (from Fig.3B)= 53% ; Qtot (from Tab.3)=165.1Kj	0.9953
70	27	$\chi = -0.1828\,t^2 + 0.863\,t - 0.0095$@ t=0.6 hr $\chi = \ \equiv 37\%$ % Qtot (from Fig.3B)= 67% ; Qtot (from Tab.3)=187.11 Kj	0.9953

χ : the conversion percent [-]   t: the polymerization time [hr]

In relevance to the useful residence time the catalyst in the reactor, From the Fig. 3A regarding the profiles rate at the different temperature in absence of hydrogen, it can be concluded that around 0.6 hours after starting the polymerization the curves trend to a plateau position. It means that the catalyst only 0.6 hour has sufficient power to continue the polymerization and after that, the catalyst reactivity is not noticeable. Referring to Fig 4A and Table 4, in regard to the reaction temperature of the overall conversion percent of the polymerization would be changed from 37% to 48.5% in the first 0.6 hours. From Fig. 3A, the area under the profile curve indicates the total heat generation during the polymerization time, in the first 0.6 hours after starting the polymerization 48%, 57% and 63% of the total heat generated belong to the reaction temperature at 65ºC, 70ºC, and 75ºC respectively. It can be concluded from this happening that about 50% of the catalyst activity has been lost after 30 minutes. Consequently, the useful resident time of the catalyst in the polymerization, in absence of hydrogen, would be kept until 0.5 hours and after adding 25% of the engineering factor, the maximum catalyst resident time would be 0.6 hours after starting the polymerization.

Concerning the useful resident time of the catalyst in the polymerization, in the presence of hydrogen, as Fig. 2c illustrates after 0.5 hours after starting the polymerization (point B in Fig.2 C) the profile rate curves gradually trend to a level out. It is concluded that the presence of hydrogen give rise to be increased the rate of the polymerization and declined the lifetime of the catalyst. Reduced the catalyst lifetime would be caused increase the deactivation constant (Kd) of the used catalyst (Table 3), detail discussed and how to calculate Kd was mentioned in our previous article and also the reason for this happening would be explained easily by the dormant site theory[4]. Fig. 2B could be considered as the other evidence in this regard. The figure illustrates that in the first 0.5 hours after starting the polymerization 53% and 67% of the total heat generated belong to 18mg and 27 mg of hydrogen amount in the polymerization system respectively, at the constant reaction temperature (70ºC). It means that a large percentage of the activated site on the catalyst in the first 0.5 hours have been deactivated and expected that the deactivation constant (Kd) would be increased; this prediction was investigated and confirmed (Table 3). As a result, the useful resident time of the catalyst in the polymerization in presence of hydrogen at the constant temperature (70ºC) would be kept until 0.5 hours and after adding 25% of the engineering factor, the maximum catalyst resident time would be 0.6 hours after beginning the polymerization. The significance conclusion in this regard is that hydrogen not only causes increases the rate of the polymerization but also could result in arising the deactivation constant (K_d).

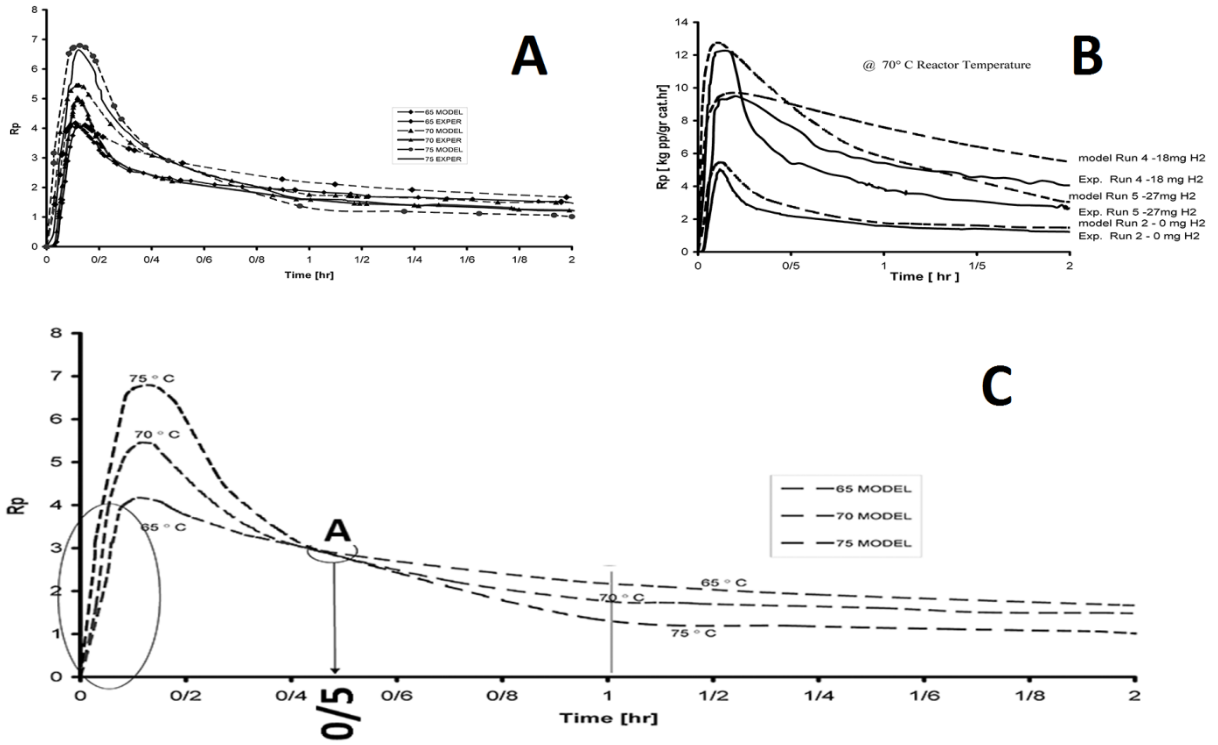

Figure 2: (A) The comparison of the experimental and model out of the profile rate in the absence of hydrogen at a different temperature. **(B)** The comparison of experimental and model profile rate in the presence of different hydrogen concentration at the constant temperature of 70°C. **(C):** The comparison of the model profile rates in the presence of different hydrogen concentration at the constant temperature of 70°C

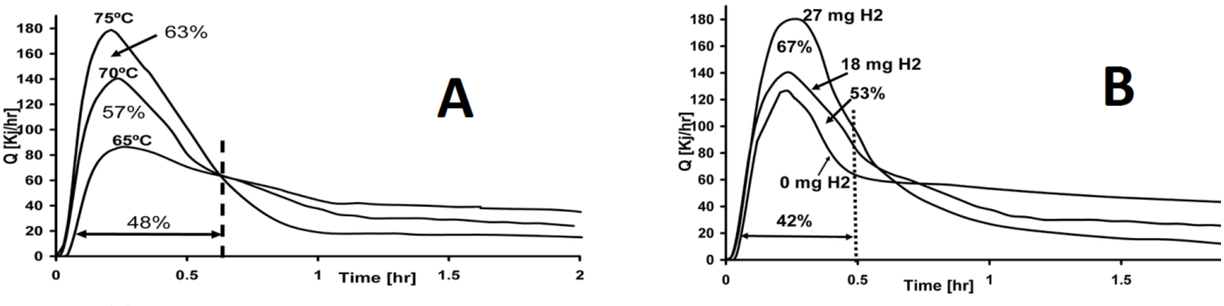

Figure 3: (a)Heat generation rate of polymerization at different temperatures in absence of hydrogen (0.0 mg H2; Run 1, 2, 3) (b) Heat generation rate of polymerization at different H2 amounts at 70 degree Celsius (run 2,5,7)

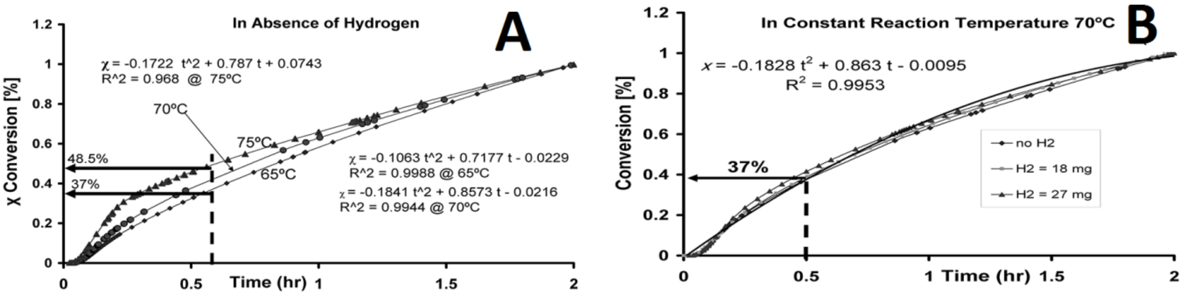

Figure 4: (a) Conversion rate polymerization at different temperatures (0.0 mg H2; Run1, 2, 3) (b) Conversion rate polymerization at different H2 amounts at 70 degree Celsius (run 2,5,7).

Conclusion

Ziegler-Natta catalyst is the most commonly used catalyst in production polypropylene. Due to having a unique complexity kinetic and high exothermic, the nature and performance of the catalytic in the polymerization still remain ambiguous to us. Understanding of the behavior of the catalyst is highly dependent on the type of the used catalyst and operating conditions namely temperature and concentration of hydrogen in the system, which should be exactly evaluated as well. Knowing the proper reaction temperature control, heat generation amounts, effective catalyst residence time, the conversion percent via the polymerization time and the variation of process variables such as adjusting reaction temperature and hydrogen amount in polymerization system are the remarkable gap issues in the field of the process and designer engineers and catalyst chemists. In view of the significance of the matters, a validated mathematical model which is able to reply to the problems is inevitable. Expected such model has a broad application in basic and applied research.

We attempted to propose a validated kinetic model which is able to reply to the existing gap. For this purpose, two algorithms were outlined; the first for the main program and the second for tuning and adjusting the constants of the kinetics equation based on the Ziegler-Natta catalysts used. The coded program of the model by using the polymer moment balance approach (population balance) was implemented in MATLAB/SIMULINK software program. The model was validated by experimental data. The conclusion of this study can be listed as the following:

1. This model was able to answer the whole research questions or the existing gap appropriately. It means that the selected methodology (population balance approach) and the proposed algorithms in this study were in a proper manner.
2. After investigating the results, resulted that 18 mg of hydrogen amount and 70 º C the reaction temperatures are the modest and reasonable recipe for the polymerization.
3. In this study, we proposed four model equations at the different condition to estimate the conversion percent via the time of polymerization.

In addition to the results which were the aims of this study; based on our knowledge, some other outcomes as the following were concluded in this study:

1. Hydrogen not only causes increases the rate of the polymerization but also could result in arising the deactivation

constant (Kd).

2. Hydrogen has no effect on the conversion percent and only increasing temperature give rise to increase the conversion.
3. Hydrogen gives rise to reduce the lifetime of the catalyst, in other words, causes to increase the deactivation constant (K_d).

It is suggested that recent results be reviewed by other researchers.

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