

Mathematical Modeling of Propylene Polymerization with Ziegler-Natta Catalyst and Hydrogen Response Validation

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ABSTRACT: *Hydrogen in spite of having a chain transfer agent role is one of the most important factors which directly affecting on kinetic of propylene polymerization. Hydrogen causes to dramatically increase the percentage of activated sites in proportion to being total potential sites on the catalyst surface. On the other hand, the chain transfer agent role of hydrogen gives rise to changing some vital indices of final product properties. This study has attempted to present a validated mathematical model that able to predicting profile polymerization rate and also calculating some of the vital indices of the final product, properties to be derived from kinetic equations. Furthermore, in this paper, we present a developed model that calculates fraction activated sites catalyst via hydrogen concentration based on dormant site theory and determining the best process condition. The modeling approach is based on the polymer moment balance method, i.e. population balance technique and validated by experimental works. The main aim of this study is assigned to investigate the behavior change of polymerization rate to hydrogen. The experimental data and model outputs were compared and concluded that the global errors were in the acceptable range.*

KEYWORDS: *Mathematical modeling; Propylene polymerization; Kinetics study; Hydrogen response; Population balance; Dormant site theory.*

INTRODUCTION

Polypropylene is one of the widely used polyolefin products, and its application is strongly affected by the final product properties. Despite the fact that Ziegler catalyst has been widely used in the production of this product for 60 years, its polymerization system performance still remains as a black box [1] and hydrogen has a key role in this matter. Hydrogen has two key effects on the polymerization. Firstly, hydrogen

as chain transfer agent has direct impact on the indices of final product properties including Number and Weight Average Molecular Weights (Mw&Mn), and Polydispersity Index (PDI) and secondly, secondly, it affects on changing the percentage of the activated sites which being on the surface of the catalyst. The impact of hydrogen on catalyst activity during olefin polymerization is less predictable and its effect depends on the type

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of catalyst and monomer. For instance, hydrogen generally reduces the polymerization rate of ethylene and increases the polymerization rate of propylene when high-activity $\text{TiCl}_4/\text{MgCl}_2$ catalysts are used [2]. On the other hand, as reported that hydrogen leads to extra activated sites and yield of the catalyst [3].

Regarding the complexity of the polymerization kinetics, particularly when hydrogen exists in the polymerization reaction, so far, most researchers in order to find out the polymerization performance have carried out their study based on trial and error or experimental approach; although this way is easy but it isn't reliable and applicable everywhere because the experimental results are heavily dependent on test and laboratory conditions. Hence, a validated model that could be able to evaluate the performance of the polymerization by changing the concentration of hydrogen is needed that can be considered as an existing gap in this field. In view of the significance of these matters, the defined aim of this study is to propose a validated model to cover the aforesaid gap.

Most modeling articles which published in this field have been focused on the subjects of heat and mass transfer inside the catalyst particles the slurry polymer particles [4-5] or concerned with studying of the mechanism of the reaction and how to grow the polymer particle according to multigrain method [6]. None of these models have been validated with actual reactor data.

The other modeling paper evaluated fluidized-bed reactors [7] and loop reactors [8, 9] or namely gas phase and bulk polymerization; however, the models are not applicable to the slurry reactor. On the other hand, the major drawbacks of their works are inattention to the effect of hydrogen on the rate profiles and final product properties. Reginato et al. have modeled industrial scale loop reactor by assuming non-ideal continuous stirred tank model in order to explain the industrial process and then claimed that their simulation results have been compared and validated with commercial plant data without addressing to the used condition. The targets research were defined to predict the macroscopic of the process, dynamics of the plant, advanced control strategies, grade transitions, and average polymer, despite offering formulas for some important indices of final properties such as number average molecular weight (M_n); weight averages Molecular weight (M_w) and

Polydispersity index (PDI); however, no mentioned about validating them in his work with actual reactor data. The main aim of the study was to justify and approve that non-ideal continuous stirred tank model could explain the performance of the loop reactor for propylene polymerization. Furthermore, the research was not considered the effect of hydrogen on the vital indices of final production and kinetics and catalyst activation [9].

The first time, Samson et al. paid attention to the rate profiles of propylene polymerization in the liquid phase experimentally without considering to final product properties. They have stated hydrogen as a chain transfer agent to be used to adjust to the polymer molecular weight [10]. *Al-haj Ali et al.* proposed a generalized model for hydrogen response according to the dormant site theory in Liquid propylene polymerization, the study was experimental data as well [11].

Concerning to investigating hydrogen effect during propylene polymerization, many experimental studies have been carried out, but their conclusions have been unclear and even contradictory. Guastalla concluded hydrogen causes to increase the initial rate and activity of catalyst about 2.5 times when not hydrogen exists in propylene polymerization reactor [12]. Contrary to these findings, Soga and Siona obtained that propylene polymerization rate decreases with increasing hydrogen partial pressure [13]. Regardless of the previous reports, *Kahrman et al.* achieved different conclusions and announced 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 [14].

On the whole, in regarding conflicting results reported, particularly while hydrogen exists in the reactor system; the effect of hydrogen on the reactor still remains ambiguous. Consequently, a validated model of profile polymerization rate that could be correctly predicted and computed the system is required. As mentioned above, despite the importance of the matter, a few investigators have been paid 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 the following our previous works [15-20] with aim of evaluating the effect of hydrogen on the profile polymerization rate and also investigation the existing theories in this regard.

Moreover, another purpose of this paper is to reveal the impact of hydrogen content on the fraction of activated catalyst sites during polymerization and is the initial reaction rate (R_{p0}), the deactivation constant (K_d) and the yield of the catalyst (Y). In addition, the model is able to calculate the most important final product index, such as Number average molecular weight (M_n), Weight average molecular weight (M_w) and Polydispersity Index (PDI) in absence or presence of hydrogen in the polymerization system.

One of the other advantages of this study is that the kinetic constants for each catalyst in the model can be easily estimated by proposed iterative method algorithm with acceptable accuracy. However, other researchers have applied the kinetic constants in their model either directly from open literature [8] or by trial and error method [9].

Because of polymerization conditions; type and nature of Ziegler – Natta catalyst and hydrogen impact are the vital factors on final product properties in polypropylene polymerization. In this research, these factors have been modeled and investigated in the absence and presence of hydrogen simultaneously

The model was carried out in a MATLAB/SIMULINK environment and afterward, it was validated with the experimental result; the global errors were in acceptable range.

EXPERIMENTAL SECTION

Materials

The materials used in this study are as follows: The catalyst used; the 4th generation of spherical $MgCl_2$ supported Ziegler-Natta catalyst containing 3.6 wt% Ti, Diisobutyl phthalate (DIBP) as internal donor supplied by Sudchemie, Germany. Triethylaluminium (TEAL of 98% purity) as a cocatalyst from Merck, Germany which diluted in n-heptane. Cyclohexyl Methyl Dimethoxy Silane (CMDS) as an external donor; from Merck, Germany. Polymer-grade propylene was provided from Shazand Petrochemical, Iran. Hydrogen and nitrogen with, >99.999% purity.

Polymer synthesis

In this study, slurry homo-polymerization was carried out in n-heptane media. Polymerization reactor was a one-liter stainless steel vessel manufactured by Buchi Company; polymerization set-up was designed in order to

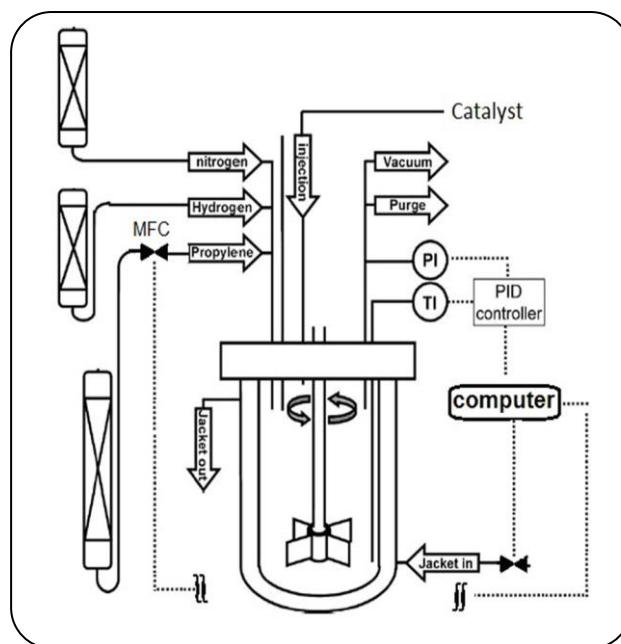


Fig. 1: Simplified schematic of the reactor system.

conduct slurry polymerization in one vessel. A schematic diagram of polymerization set-up is shown in Fig.1. 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 Company. Experimental the profile polymerization curve (R_{pt}) curves come from 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 $155^\circ C$ using 1,2,4-trichlorobenzene as a solvent. The GPC is calibrated with the narrow molecular weight distribution polystyrene standard as a reference.

A typical polymerization procedure exists for reactor preparation, polymerization, and discharge. The detailed procedure of the polymerization is according to Ref. [16].

THEORETICAL SECTION

Dormant sites theory and formulation

Here, it is necessary to understand dormant sites theory and the role of hydrogen in the polymerization.

As discussed earlier, Hydrogen always acts as a chain transfer agent to regulate the molecular weight of the olefin polymer; when the hydrogen concentration increases, the molecular weight of the polyolefin decreases. On the other hand, the effect of hydrogen on catalyst activity during olefin polymerization is less predictable and varies depending on the type of catalyst, monomer, and donor systems. Hence, it is concluded that the hydrogen effect depends on two factors: (i) nature of the catalyst system and (ii) monomer type.

Three theories have been suggested justifying the influence of the hydrogen on polypropylene polymerization rate as the following:

Theory 1: Increase in the number of active sites theory.

Theory 2: The change in oxidation states theory.

Theory 3: Dormant sites theory.

Detailed discussions of the first and second theories studies have been discussed and rejected in the open literature [13, 21]. For the sake of brevity, they are not repeated here.

So far, Dormant sites theory is the strongest theory in this issue. 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 have two positions of dealing with other monomers (position 1-2 and position 2-1). If Growing chain reacts with position 2-1 of propylene, "dormant site" will be created, as shown in Fig. 2. *Busico et al.* believe that the dormant sites on the catalyst are the defect of propylene polymerization. The researchers 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 [22]. These results are supported by the end group analysis done by *Chadwick et al.* [23]. Therefore, based on 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.* [11]. 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 cocatalysts is neglected and a quasi-steady state is assumed for dormant sites. This means that according to the dormant sites theory, the reactions R_6 and R_8 and also R_{11-14} from Table 1 are the more effective reactions for hydrogen response.

The lump propagation reactions have been considered a first order reaction; the rate of the polymerization can be described as a function of both monomer concentration, C_m , and the concentration of active sites, C and using a lumped constant as K_p .

$$R_p = K_p \cdot C \cdot C_m \quad (1)$$

In reality, the active sites 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 :

$$C = C_{max} - C_s \quad (2)$$

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

$$R_s = 0 = K_s \cdot C \cdot C_m - K_{reh} \cdot C_s \cdot C_{H_2} - K_{rem} \cdot C_s \cdot C_m \quad (3)$$

Where; K_s , K_{reh} , and K_{rem} are rate constants for dormant sites formation, dormant sites reactivation by hydrogen and monomer reactions respectively. So with the rearranging of these equations, it is concluded that:

$$C_s = \frac{K_s \cdot C}{K_{reh} \cdot X + K_{rem}} \quad (4)$$

where X is the hydrogen molar ratio defined as:

$$X = \frac{C_{H_2}}{C_m} \quad (5)$$

Combining Equations (4) and (5) leads to:

$$C = \frac{C_{max} (1 + K_1 \cdot X)}{1 + K_2 + K_1 X} \quad (6)$$

With

$$K_1 = \frac{K_{reh}}{K_{rem}}, \quad K_2 = \frac{K_s}{K_{rem}} \quad \text{dimensionless} \quad (7)$$

Consequently, Equation (6) can be described as a function of three parameters, K_1 , K_2 , and kp :

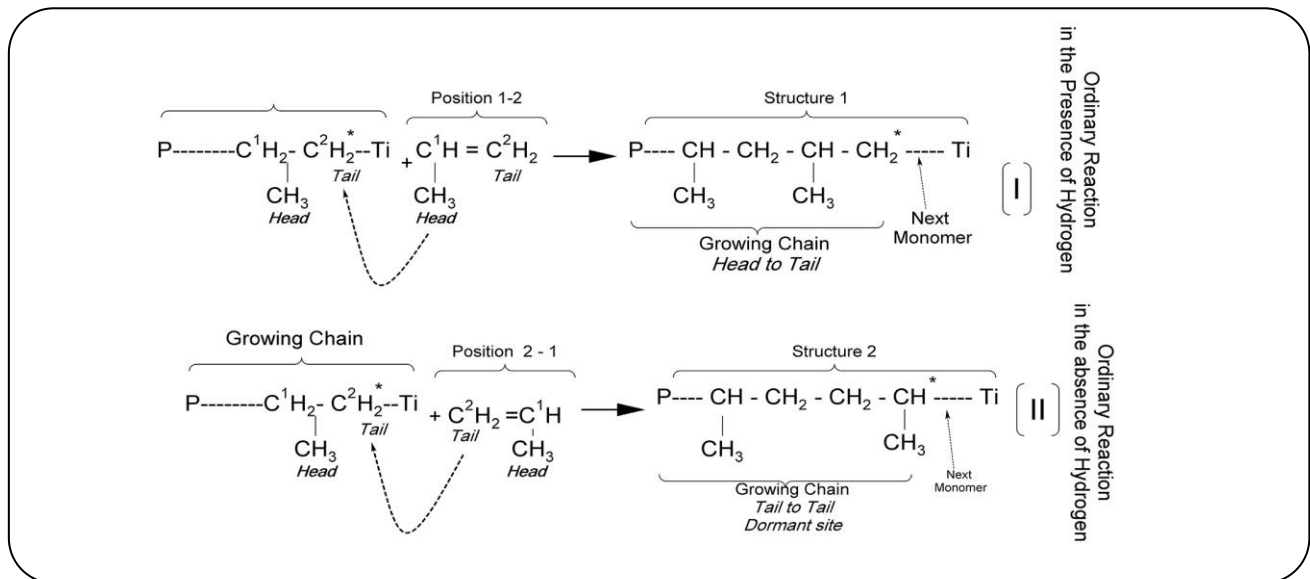


Fig. 2: Dormant site generation.

$$R_p = \frac{K_p \cdot C_m \cdot C_{max} (K_1 \cdot X + 1)}{1 + K_1 \cdot X + K_2} \quad (8)$$

This equation can be rewritten as:

$$R_p = K_p \cdot C_{max} \cdot C_m \cdot f_{H_2} \quad (9)$$

With the hydrogen dependent function f_{H_2} defined as:

$$f_{H_2} = \frac{1 + K_1 X}{1 + K_2 + K_1 X} \quad (10)$$

f_{H_2} represents the fraction of active sites in the system and dimensionless. In the absence of hydrogen $X = 0$, f_{H_2} has the minimum amount. It means active sites of catalyst are at a minimum level in the polymerization system. Consequently, if $f_{H_2, max} = 1$, namely 100 % of catalyst sites are active in reaction [15].

Equation (10) has three parameters to be determined, namely 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, then the values of k_1 and k_2 are estimated. In the first step: As the active sites of catalyst are heterogeneity, the calculated value of K_p is an average amount. When no hydrogen is used in the experiments, Eq (8) can be rewritten as:

If $X=0$ (no hydrogen)

$$R'_{p_0} = \frac{K'_p}{1 + K_2} \cdot \rho_m \quad (11)$$

Where R'_{p_0} [mol/lit.sec] and R_{p_0} , R_{p_0} [kg/gr_{cat} .hr], and with rearrangement we have:

$$R_{p_0} = \frac{R'_{p_0}}{\rho_m} = \frac{K'_p}{1 + K_2} \quad (12)$$

Here ρ_m is monomer density. In accordance with these results, the dependency of $(k_p/1 + k_2)$ on reaction temperature has the following form:

$$K_p = K_{p_0} (1 + K_2) \cdot \exp\left(-\frac{E_p}{R \cdot T}\right) \quad (13)$$

Then we have:

$$\ln\left(\frac{R_{p_0}}{\rho_m}\right) = \ln\left(\frac{K_p}{1 + K_2}\right) = \ln(K_{p_0}) - \frac{E_p}{R T} \quad (14)$$

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 [24,25]:

$$R_p = K_p C_m C = R_{p_0} \cdot \exp(-k_d t) = R_{p_0} \cdot \exp\left(\frac{E_a}{R T}\right) \quad (15)$$

$$\frac{dC^*}{dt} = -K_d C^*, \text{ where } k_d = k_{d_0} \cdot \exp\left(\frac{-E_{a,d}}{R T}\right) \quad (16)$$

Here, R_{p0} is the initial reaction rate, k_d the deactivation constant, E_a 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 R_p at the isothermal condition, two parameters namely R_{p0} and K_d should be obtained. The R_{p0} 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 R_{p0} .

Due to the rate of polymerization has a dependency on temperature, with having R_{p0} at different temperatures by using Arrhenius Eq.(15), the activation energy of any type of catalyst is easily predictable.

Two very important notes should be considered about the activation energy of Z.N catalyst; in the first, it is independent of the hydrogen concentration [11]. 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.

$$Y_{calc} = \int_0^t R_p \cdot dt \quad (17)$$

Amount of Y_{calc} is exactly equal to the area under the profile curve.

Due to olefin polymerization kinetics with Ziegler-Natta catalysts might be fairly complicated. To date, several reaction steps have been proposed in the open literature [8,9]. However, the most comprehensive steps were proposed by Zacca [9]. The ODE mass balance Equations used in the model are as follows:

$$\frac{dC_{j,R}}{dT} = \left[\frac{Q_f C_{j,f}}{V_R} \right]_{\text{feed(input)}} - \left[\frac{(\eta/\zeta) Q_o C_{j,R}}{V_R} \right]_{\text{output}} + R_j \quad (18)$$

$$C_{j,R} = \frac{\text{Mole of } j}{\text{Total Volume}} \quad \text{for } j = 1, 2, \dots, NC \quad (19)$$

$$\eta_j = \frac{C_{j,a}}{C_{j,i}} \quad \text{for } j = 1, 2, \dots, NC \quad (20)$$

$$\zeta_j = \frac{C_{j,o}}{C_{j,R}} = \frac{\rho_o}{\rho_R} \quad (21)$$

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

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_o) then the terms of η and ζ are meaningless for this 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:

$$C_j = C_H, C_A, C_E, C_{Mi}, C_B, C_S, C_T, C_{cat},$$

$$P_0^k, \mu_0^k, \mu_1^k, \lambda_0^k, \lambda_1^k, \lambda_2^k$$

Where: k is the site number of the catalyst.

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.

Modeling Description

Assumptions

The following modeling assumptions are considered:

1. It was supposed that propylene polymerization was carried out in the amorphous phase [9] and amorphous phase concentrations during the polypropylene Polymerization are at the thermodynamic equilibrium condition that obeys from Sanchez and Lacombe Equation (SLE) [26] for calculating the amount of X , the hydrogen molar ratio Eq (5)

2. It was assumed that $\gamma_1 = \gamma_2 = \dots = \gamma_{NC}$. Where γ is equilibrium constant and NC is the number of solvent in slurry phase components [9].

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 (as shown in Fig. 2) [11].

Modeling algorithm

This study has outlined the algorithm for programming the mathematical model in a MATLAB/SIMULINK

Table 1: The probable reactions and their rate equations in propylene polymerization used in the model [9].

Reaction Step	Component	Reaction	Rate Equation
Site activation	Hydrogen; R1	$C_p + H_2 \rightarrow P_0^K$	$R_{aH}^K = k_{aH}^k C_p C_{H,a}^{O,K}$
	Al-alkyl; R2	$C_p + A \rightarrow P_0^K + B$	$R_{aA}^K = k_{aA}^k C_p C_{A,a}^{O,K}$
	Monomer i ; R3	$C_p + M_i \rightarrow P_0^K + M_i$	$R_{aMi}^K = k_{aMi}^k C_p C_{Mi}^{O,K}$
Chain initiation	Monomer i ; R4	$P_0^K + M_i \rightarrow P_{\delta_i,i}^K$	$R_{P0i}^K = k_{P0i}^k P_0^K C_{M_i,a}$
Chain propagation	Monomer j ; R5	$P_{n,i}^K + M_j \xrightarrow{Kp} P_{n+\delta_j,j}^K$	$R_{Pji}^K = k_{Pji}^k P_{n,i}^K C_{M_j,a}$
Chain transfer	Hydrogen; R6	$P_{n,i}^K + H_2 \xrightarrow{Kh} P_0^K + D_n^k$	$R_{cHi}^{K,n} = k_{cHi}^k P_{n,i}^K C_{H,a}^{O,K}$
	Monomer j ; R7	$P_{n,i}^K + M_j \xrightarrow{Km} P_{\delta_j,j}^K + D_n^k$	$R_{cMji}^{K,n} = k_{cMji}^k P_{n,i}^K C_{M_j,a}^{O,K}$
Site deactivation	Hydrogen; R8	$P_{n,i}^K + H_2 \rightarrow C_d + D_n^k$	$R_{aHi}^{K,n} = k_{aHi}^k P_{n,i}^K C_{H,a}^{O,K}$
		$P_0^K + H_2 \rightarrow C_d$	$R_{dH0}^K = k_{dH0}^k P_0^K C_{H,a}^{O,K}$
	Al-alkyl; R9	$P_{n,i}^K + A \rightarrow C_d + D_n^k$	$R_{dAi}^{K,n} = k_{dAi}^k P_{n,i}^K C_{A,a}^{O,K}$
	Spontaneous; R10	$P_{n,i}^K \rightarrow C_d + D_n^k$	$R_{dSpi}^{K,n} = k_{dSpi}^k P_{n,i}^K$
		$P_0^K \rightarrow C_d$	$R_{dSp0}^K = k_{dSp0}^k P_0^K$
Using dormant sites theory[11]			
Dormant site formation; R11		$C_j + M \xrightarrow{K_s} S_{j+1}$	
Dormant sites reactivation by H ₂ ; R12		$S_j + H_2 \xrightarrow{K_{sh}} C_0 + D_j$	
Reactivation of dormant sites by monomer; R13		$S_j + M \xrightarrow{K_p} S_{j+1}$	
Deactivation; R14		$C_j \xrightarrow{K_d} D_j$	

environment, as shown in Fig.3a. It is composed of two part; main-program (as named "Runsirn") and subroutine (function file). For obtaining kinetic constants in the model, it is proposed a new approach as iterative method algorithm by using consistency property of ODE's equation in Fig.3b. The advantage of the method is more easy and trustable rather than conventional manners; i.e. using directly from open literature or estimating by trial and error [9].

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[8,9], the initial

guess of kinetic constants was estimated and applied to the model, next the constants were exactly adjusted and determined in accordance with the catalyst used in the Set-up (Experimental data) by the proposed algorithm in Fig. 3b.

RESULTS AND DISCUSSION

The recipe conditions for each of the runs and also the comparison of the model output and experimental results in different condition are summarized in Table 3 [15]. As can be seen, the model outputs are in line with the experimental results in an acceptable margin of error. The margin of errors might be justified for the following reasons:

1. The global error that is the summation of the truncation method and rounds off error.

Table 2: The component rate and moment equations used in the model [9].

Hydrogen	$R_H = - \sum_{K=1}^{Ns} [R_{aH}^k + R_{rH}^k + R_{dH}^k] + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} (R_{cHi}^{k,n} + R_{dHi}^{k,n})$
Cocatalyst	$R_A = - \sum_{K=1}^{Ns} [R_{aA}^k + R_{dA}^k] + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} R_{dAi}^{k,n} - R_{eA}$
Electron donor	$R_E = - \sum_{K=1}^{Ns} [R_{dE}^k] + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} \sum_{l \neq K} (R_{lEi}^{k,n} + R_{dEi}^{k,n}) - R_{eE}$
Poison	$R_X = - \sum_{K=1}^{Ns} [R_{dX}^k] + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} R_{dXi}^{k,n} - R_{eE} - R_{eA}$
Potential sites	$R_{Cp} = - \sum_{K=1}^{Ns} (R_{aH}^k + R_{aA}^k + R_{aSp}^k + \sum_{i=1}^{Nm} R_{aMi}^k)$
Dead sites	$\alpha_i^k = k_{cHi}^k C_{H,a}^{O_{in}^k} + k_{cSpi}^k + \sum_{j=1}^{Nm} k_{cMj,i}^k C_{Mj,a} + \sum_{l=1}^{Ns} (k_{dEl}^{kl} C_{E,a}^{O_{IE}^{kl}} + k_{dSpi}^{kl}) + k_{dHi}^k C_{H,a}^{O_{aH}^k} + k_{dAi}^k C_{A,a}^{O_{aA}^k} + k_{dEi}^k C_{E,a}^{O_{aE}^k} + k_{dXi}^k C_{X,a}^{O_{aX}^k} + k_{dSpi}^k$
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	$R_{P_{n,i}}^k = \delta(n - \delta_i) R_{p0i}^k + \sum_{j=1}^{Nm} \sum_{m=\delta_i}^{\infty} R_{cMi,j}^{k,m} + \sum_{j=1}^{Nm} k_{pij}^k C_{Mi,a} P_{n-\delta_i,j}^k - \sum_{j=1}^{Nm} k_{pij}^k C_{Mj,a} P_{n,i}^k - \alpha_i^k P_{n,i}^k$
Dead polymer	$R_{D_{n,i}}^k = \sum_{i=1}^{Nm} \alpha_i^k P_{n,i}^k$ where $\alpha_i^k = k_{cHi}^k C_{H,a}^{O_{in}^k} + k_{cSpi}^k + \sum_{j=1}^{Nm} k_{cMj,i}^k C_{Mj,a} + \sum_{l=1}^{Ns} (k_{dEl}^{kl} C_{E,a}^{O_{IE}^{kl}} + k_{dSpi}^{kl}) + k_{dHi}^k C_{H,a}^{O_{aH}^k} + k_{dAi}^k C_{A,a}^{O_{aA}^k} + k_{dEi}^k C_{E,a}^{O_{aE}^k} + k_{dXi}^k C_{X,a}^{O_{aX}^k} + k_{dSpi}^k$
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	$R_{\mu_{0,i}}^k = R_{p0i}^k + \sum_{j=1}^{Nm} k_{cMi,j}^k C_{Mi,a} \mu_{0,j}^k - \alpha_i^k \mu_{0,i}^k + \sum_{j=1}^{Nm} [k_{pij}^k C_{Mi,a} \mu_{0,j}^k - k_{pj}^k C_{Mj,a} \mu_{0,i}^k]$
First-order; live polymer moments	$R_{\mu_{\delta_i,i}^k} = \sum_{i=1}^{Nm} \delta(i-1) [R_{p0i}^k + \sum_{j=1}^{Nm} k_{cMi,j}^k C_{Mi,a} \mu_{0,j}^k] - \sum_{i=1}^{Nm} \alpha_i^k \mu_{\delta_i,i}^k + \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} k_{pij}^k C_{Mi,a} \delta(i-1) \mu_{0,j}^k$
Zero-order; bulk polymer moments	$R_{\lambda_{\delta_i}^k} = \sum_{i=1}^{Nm} [R_{p0i}^k + \sum_{j=1}^{Nm} k_{cMi,j}^k C_{Mi,a} \mu_{0,j}^k]$
First-order; bulk polymer moment	$R_{\lambda_{\delta_i}^k} = \sum_{i=1}^{Nm} \delta(i-1) [R_{p0i}^k + \sum_{j=1}^{Nm} k_{cMi,j}^k C_{Mi,a} \mu_{0,j}^k] + \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} \delta(i-1) k_{pij}^k C_{Mi,a} \mu_{0,j}^k$
Second-order; bulk polymer moment	$R_{\lambda_{\delta_i}^k} = \sum_{K=1}^{Ns} \sum_{j=1}^{Nm} [R_{p0i}^k + \sum_{i=1}^{Nm} k_{cMj,i}^k C_{Mj,a} \mu_{0,i}^k] + \sum_{k=1}^{Ns} \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} k_{pij}^k C_{Mj,a} (\mu_{0,i}^k + 2\mu_{1,i}^k)$

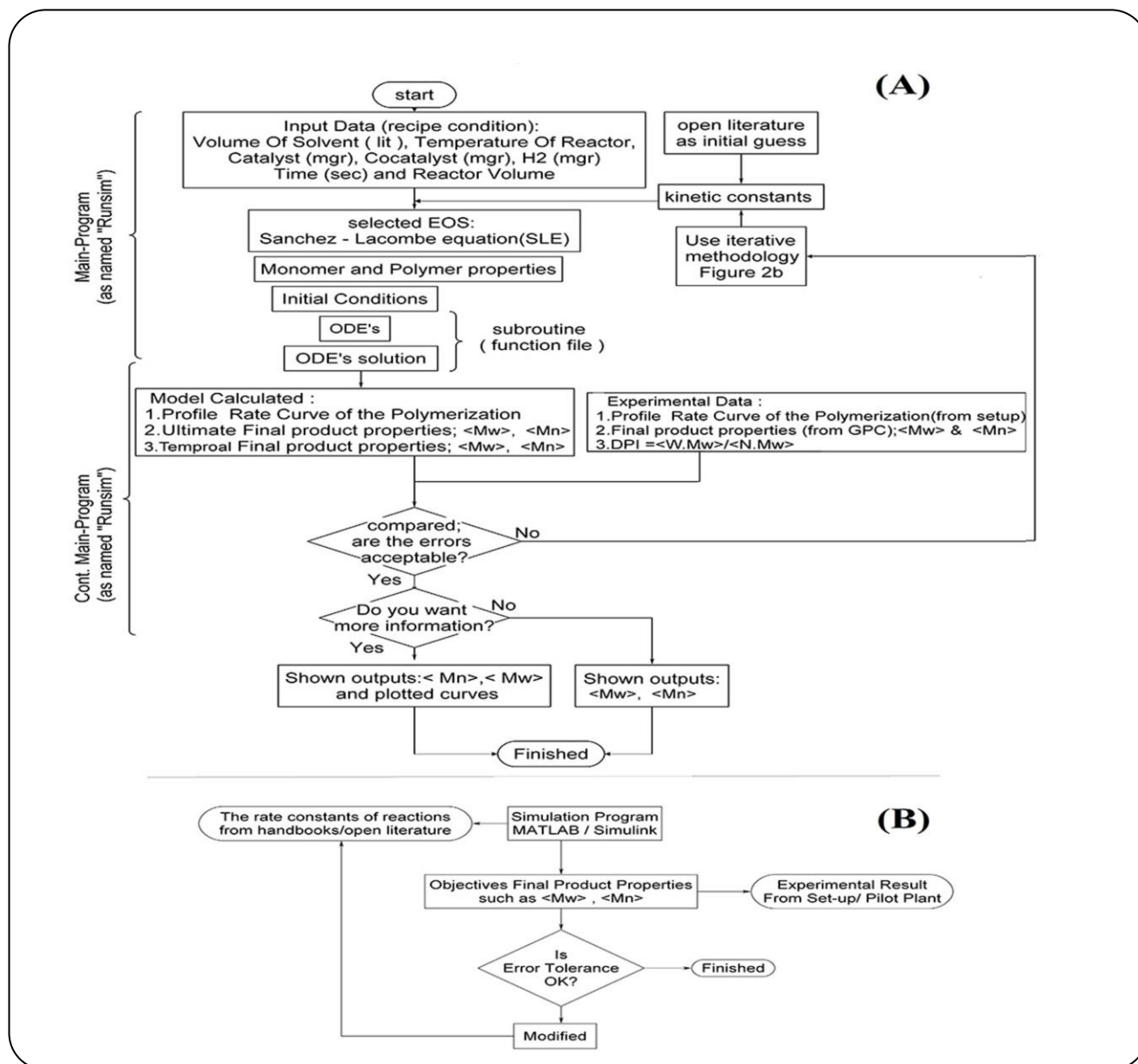


Fig. 3: (a) The general algorithm modeling in this work; (b) The iterative methodology used to adjust kinetic parameters.

2. Personal and measurement Equipment errors.
3. Selection of Equation of state.
4. Errors resulting from assumptions.

For the reason, that activation energy is an inherent property of the reaction, and also it is independent of any process variable. Accordingly, this subject could be considered as one of the important criteria which show whether the model is validated. A model is validated in a proper manner, provided that the calculated amount of activation energy from the model is equal or very close to the amount from experimental works and also this

amount should be in line with the other researchers' results. Table 4 is revealed this subject. On the other hand, the comparison of model output and experimental results at different conditions or recipe of the polymerization implies the model has been properly validated due to the model outputs are in line with the experimental results; as shown in Table 3. The acceptable error of these comparisons could be considered as the second reason for being validated the model. The third reason is the trend of being a remarkable conformity between the profile polymerization rate

Table 3: Summarized Polymerization Recipe; Model Output and Experimental Results.

Recipe				Results (Experimental / Model)						
Run No.	T (°C)	H2 (mg)	Catalyst (mg)		Y (gram)	Rp0	Kd (1/hr)	< Mn >	< Mw >	PDI
1	65	0	20	Exp.R ¹	63.29	5.01	1.42	210259	863057	4.1
				Mod.R ²	65.13	5.19	1.42	205570	834523	4.06
2	70	0	20	Exp.R	72.66	6.5	1.95	304642	1134374	3.71
				Mod.R	76.4	7.46	1.98	323780	1214440	3.75
3	75	0	20	Exp.R	63.07	8.85	2.04	236154	1124367	4.76
				Mod.R	67.25	8.92	2.13	270243	1178300	4.36
4	70	183	10	Exp.R	81.33	11.24	2.27	29962	144192	4.81
				Mod.R	88.4	11.43	2.3	32812.7	148874	4.54
5	70	274	10	Exp.R	74.61	11.02	2.05	24016	116939	4.87
				Mod.R	76.81	11.2	2.35	24981.1	123303	4.94

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.

Table 4: Reported activation energies (Ea) in propylene polymerization [16].

Worker	Catalyst System	Phase	Ea, (KJ/mol)
Yuan et. Al.[27]	δ -TiCl ₃ . 1/3 AlCl ₃ /DEAC	slurry	53.9
Soares et. al.[28]	TiCl ₃ /DEAC	slurry	57.7
<i>This work (ave)</i>	MgCl ₂ /TiCl ₄ /phthalate/silane/TEA	slurry	55.53
<i>This work (ave)</i>	MgCl ₂ /TiCl ₄ /phthalate/silane/TEA	slurry	53.05

from the model and from the experimental works could be the third reason in which the model is validated, as shown in Figs. 4 and 5.

The main conclusions which can be attained from these arguments are that the model is properly validated; it means the selected approach and the designed algorithms, i.e. Fig. 2 in this study are graceful and appropriate. Therefore, the model's results can be worthy and reliable for achieving the aim of this study. By plotting the natural logarithm of the reaction rate profiles versus polymerization time, a linear fit can be made for each run where the slope and y-intercept of the fitted line are the deactivation constants K_d and initial rate R_0 respectively; as listed in Table 3.

To be implied from Eq. 17, that the yield of the catalyst is the area under the profile curve.

In Fig. 5, we compare the comparison of experimental and model profile rate in the absence of hydrogen at a

different temperature, i.e. 65°C, 70°C and 75°C (Runs 1,2 and 3). It is apparent that increasing temperature causes to raise the rate of the polymerization (Fig. 5a) that can be explained by Arrhenius theory, but the most remarkable results to emerge from the data (Table 3) are as follows:

1- The yield of the catalyst (Y), average molecular weight (Mn and Mw) attain own maximum amount at 70°C reaction temperature in absence of hydrogen. Either model outputs or experimental results confirm this matter (i.e. Run 4 in comparing with Run 2,5). Maybe one of the reasons for decreasing polymer yield at the higher temperature might be justified due to catalyst deactivation by over reduction of the catalyst sites or via alkylation process with the Lewis base [29].

2- Poly Dispersity Index (PDI) as an indicator of the molecular weight distribution (MWD) obtains its minimum amount at 70°C reaction temperature in

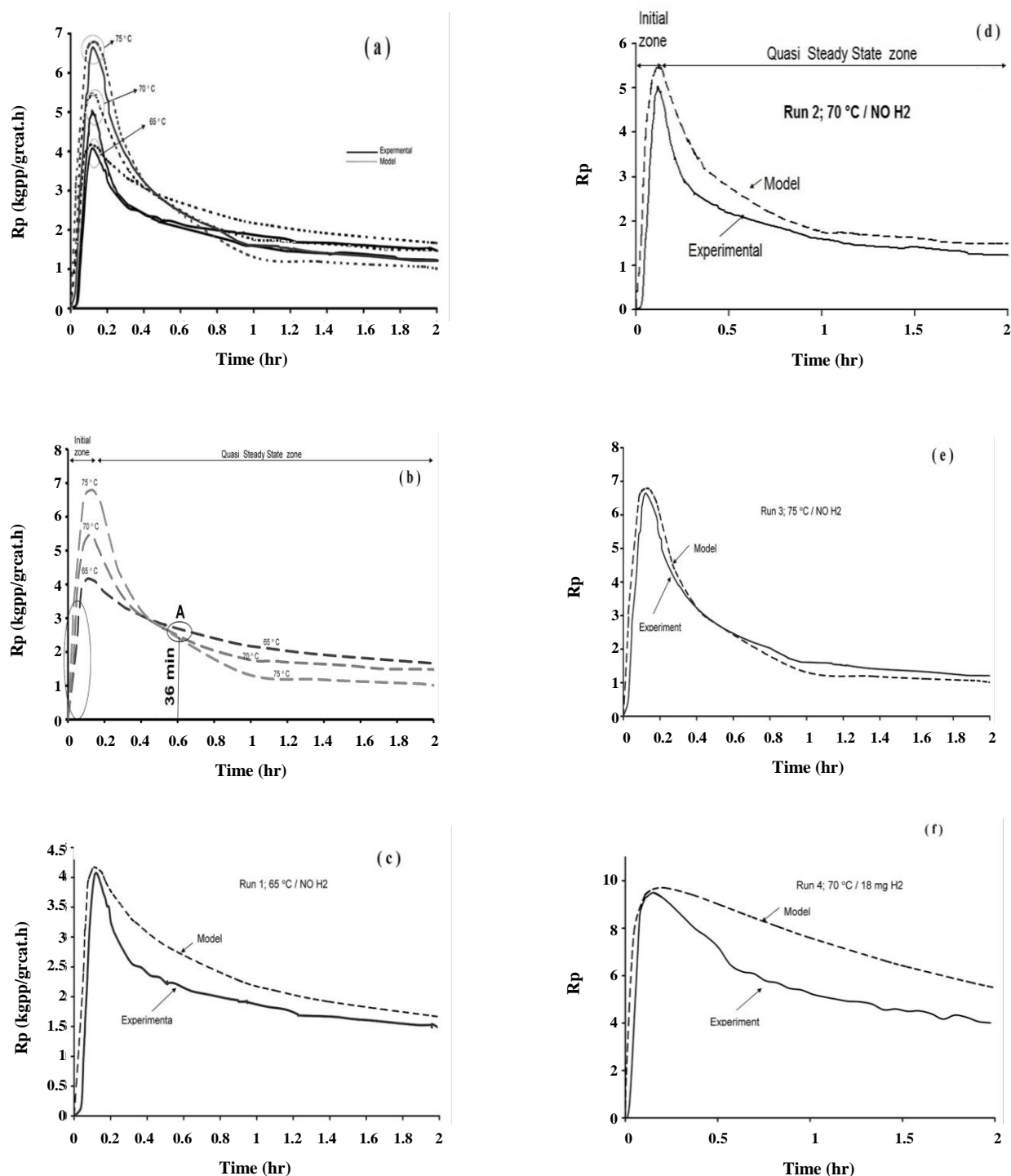


Fig. 4: The comparison of experimental and model profile rate in the absence of hydrogen at a different temperature, i.e. Runs (1, 2 and 3); (a) the total comparison of the model and experimental (b) the effect of increasing temperature on the profile rates come from model; (c) The comparison of experimental and model profile rate in the absence of hydrogen at 65°C, i.e. Run 1; (d) The comparison of experimental and model profile rate in the absence of hydrogen at 70°C, i.e. Run 2; (e) the comparison of the model The comparison of experimental and model profile rate in the absence of hydrogen at 75°C, i.e. Run 3; (f) The comparison of experimental and model profile rate at 18 mg hydrogen and 70°C the best condition in this study, i.e. Run 4.

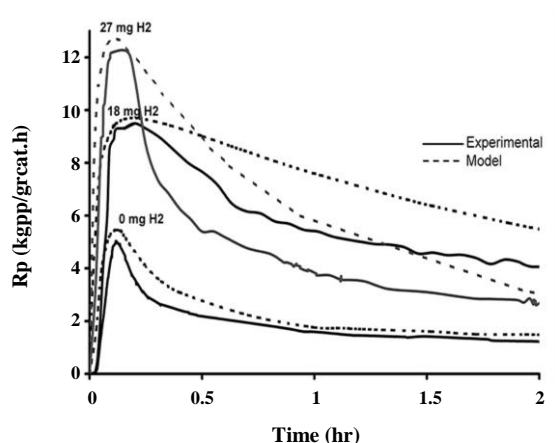


Fig. 5: The comparison of the experimental and model profile rate in the presence of different hydrogen concentration at a constant temperature of 70°C, i.e. (Runs 2, 4 and 5).

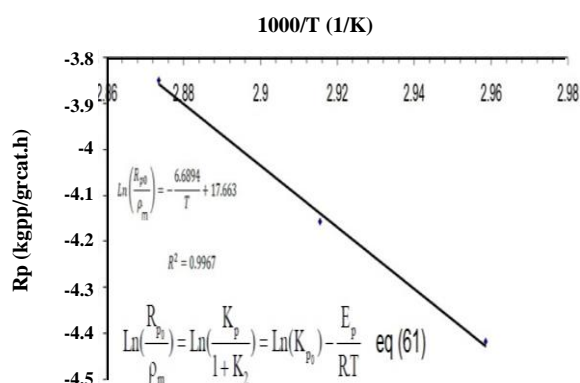


Fig. 6: Calculation of propagation constant K_p and E_p by using Eq (14).

absence of hydrogen as well. It means that the polymer chains length come close to uniformity that is desired event. Consequently, it could be concluded that 70°C of reaction temperature could be considered as the best temperature condition in this study.

The comparison of experimental and model profile rate in the absence of hydrogen at a constant temperatures, i.e. 65°C (Run 1), 70°C (Runs 2) and 75°C (Runs 2) are shown in Fig. 4 c, d and e respectively. Fig. 4 (f) belongs to the comparison of experimental and model profile rate at 18mg hydrogen and 70°C the best condition in this study, i.e. Run 4.

Fig. 5 compared the comparison of experimental and model profile rate in the presence of different hydrogen

amounts at a constant temperature, i.e. 70°C (Runs 2, 4 and 5). The figure illustrates that increasing hydrogen amounts leads to raising the rate of the polymerization. The reason of this matter can be justified by dormant site theory as mentioned earlier; but the most interesting results to emerge from the data, i.e. Table 3 are as follows:

1- The yield of the catalyst (Y), average molecular weight (M_n and M_w) attain own maximum amount at 18mg hydrogen amount. Either model outputs or experimental results confirm this matter (i.e. Run 4 in comparing with Run 2, 5).

2- Poly dispersity Index (PDI) as an indicator of the Molecular Weight Distribution (MWD) obtains its minimum amount at 18mg hydrogen amount as well. It means that the polymer chains length come close to uniformity that is desired event.

Accordingly, it could be concluded that 70°C of reaction temperature and 18 mg hydrogen amounts could be considered as the best process condition in this study.

According to dormant site theory, hydrogen gives rise to increasing activated site from dormant sites that have not activated already. In this study, quantity and quality of this event have modeled and shown with a term as f_{H_2} .

Because 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, one of the criteria of the accuracy and validity of the model is at least the difference between the activation energy of propagation reactions E_p and E_a and the overall activation energy of polymerization.

By using equation (14) for calculating E_p from the dormant site generation theory and plotting the natural logarithm of (R_{p0} / ρ_m) versus $1000/T(1^\circ K)$, a linear fit can be made. From the slope of the fitted line, the activation energy of propagation (E_p) has been easily obtained as shown in Fig. 6. The figure shows an excellent fit with a linear correlation coefficient (R^2) of 0.9967. It is interesting to note that with comparing E_a and E_p , the difference is only 4% error (Table 5). This finding could be another reason that the model was well enough validated and acceptable. Moreover, the Dormant Site Theory has accurately justified the profile curve rate of propylene polymerization in presence of hydrogen in the polymerization system.

Table 5: The compaction of reported activation energies (Ea) in propylene polymerization system [15].

	condition	Overall Ea [kJ/mol]	Ep [kJ/mol]	Err. %	K_{p_0} [m ³ /gr _{cat} .hr]	K_2 [-1]
Al-haj Ali et al[11] Slurry-bulk	Liquid Pool	58.6	67.22	12.82	6.41×10^8	8.02
	$K_1 = -32.2 \cdot T^2 + 2.26 \cdot T - 3.86 \times 10^6$ Catalyst System: MgCl ₂ /TiCl ₄ /phthalate/silane/TEA					
This work	Slurry In Heptane	53.0599	55.61	4.5	4.69×10^6	8.97
	$K_1 = -1.529 \cdot T^2 + 555.24 \cdot T - 4.226 \times 10^6$ Catalyst System: MgCl ₂ /TiCl ₄ /phthalate/silane/TEA					

Using the Dormant theory, equation (10) is obtained. On the other hand, K1 and K2 can be estimated using the output of the model and Fig. 6. The equation predicts the fraction of the activated sites of the catalyst 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 sites are active, that is to say, about 90% of the catalyst sites remain idle and unused (Fig. 7 a). The impact of this issue on Y and Rp0 is exactly clear and the model is able to predict them (Ref. Figs.7 b,c,d,e,f and Table 3).

As the end consequence, by increasing very slightly hydrogen content to X=0.00466, the fraction activated sites of the catalyst speedily increase until 85.5% of the total sites on the catalyst (Fig. 7a). But the increasing hydrogen content caused to be increasing deactivation catalyst K_d that this event is unpleasant (Fig.7c). In other words, increasing hydrogen leads to dropping the life of the catalyst in the polymerization reactor. On the other side, the increased hydrogen content has an inverse effect on the Rp0 and Y, in the other words; it may lead to changing final product properties and even producing off-grade or wax product (Fig. 7 b and d). Considering all aspects mentioned, Fig. 6 specifies the optimum hydrogen content is 0.00466 molar ratios or 18 mg.

CONCLUSIONS

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 end used product, Number average molecular weight (Mn), Weight average molecular weight (Mw) and Poly Dispersity Index (PDI), and hydrogen response of propylene polymerization system.

The model output was in good agreement with experimental results and revealed that there was an optimum temperature (70°C) and hydrogen concentration (18mg) to achieve the maximum amount of polymer yield. At the optimum temperature, the PDI was a minimum amount, indicating optimum dispersity of polymer chains.

In this study, observed that increasing temperature above 70°C lead to a reduction of molecular weight in absence of hydrogen. 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. To find why 70°C of the reaction temperature is the best temperature condition in the polymerization system might be the problem of future research.

Notation

C	Total active site concentration, kgmol/m ³
C _d	Dead-site concentration, kgmol/m ³
C _j	Component j bulk concentration, kgmol/m ³
C _{j,R}	Concentration into the reactor, kgmol/ m ³
C _k	Type k active specie concentration, kgmol/m ³
C _p	Potential site concentration, kgmol/m ³
D _{k n}	Dead polymer chain concentration with n monomers originated from site k, kgmol/m ₃
DPI	Polydispersity index
K	Two-site equilibrium constant, kg/mol
M _w	Mass average molecular weight, kg/kgmol
NC	Number of liquid-phase components
n _{j, R}	Moles of component j into reactor, kgmol
n _{j, a}	Moles of j sorbed in the amorphous polymer phase, kgmol
n _{j, l}	Moles of j in the liquid phase, kgmol

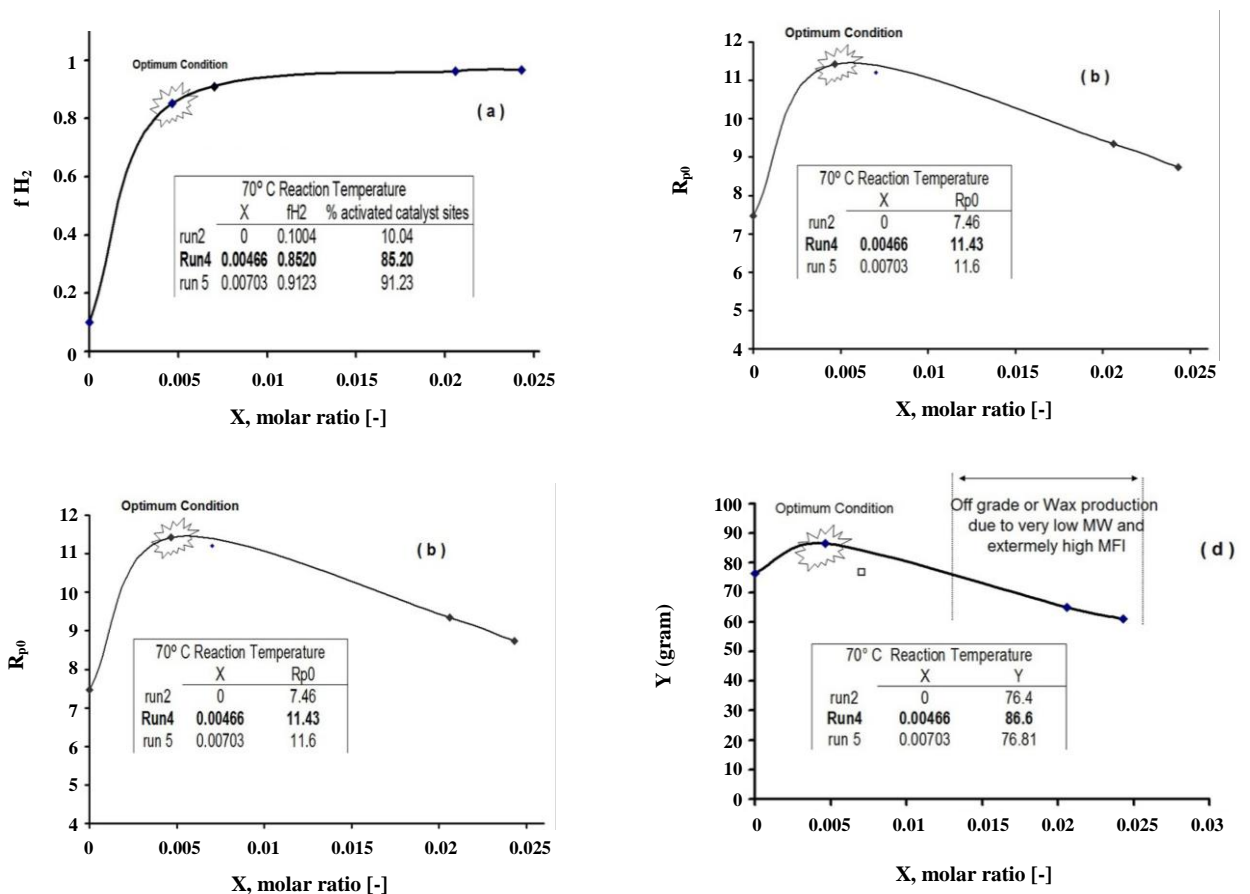


Fig. 7: The effect of variation hydrogen concentration on the kinetic parameters; (a) f_{H_2} ; (b) R_{p0} ; (c) K_d ; (d) Yield.

Nm	Number of monomers
Ns	Number of sites
Ork	Order of reaction r for site k
Pn,ik	Growing polymer chain with n monomers with end-group i from site k, kgmol/m ³
P0k	Vacant site k concentration, kgmol/m ³
Rp	Polymerization rate, kg/gcat hr
Rp0	Initial polymerization rate, kg/gcat hr
t	Time, s
Tr	Reactor temperature, K
T	Feed stream temperature, K
VR	Reactor volume, m ³
Y	Yield, gr PP
Rrk,n	r reaction from site k for a growing chain with n monomers, kgmol/(s . m ³)
Rj	j component reaction rate, kgmol/(s . m ³)

Greek letters

Γ_j	Equilibrium constant for j component between liquid phase and amorphous polymer phase
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Ξ	Ratio between solid-phase components concentration at reactor output flow and into reactor
H	Ratio between liquid-phase components concentration at reactor output flow and into reactor
X	Volume fraction of monomer in the amorphous polymer phase
Pl	Liquid-phase density, kgm ³
pp	Polymer density, kg/m ³
ρ_R	Reactor slurry density, kgm ³
$\mu_{\delta_1,i}^k$	Live moment rate Equations
$\lambda_{\delta_1,i}^k$	Bulk moment rate Equations

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