

## A MATHEMATICAL MODEL FOR DETERMINING THE BEST PROCESS CONDITIONS FOR AVERAGE MOLECULAR WEIGHT AND MELT FLOW INDEX OF POLYPROPYLENE

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**ABSTRACT.** The present work describes a mathematical model based on a population balance approach for determining the effect of the reaction temperature and hydrogen amount on the vital final product properties including average molecular weight and polydispersity index and flow index of polypropylene and also the profile rate of the polymerization. The aim of this study was to find the best operating condition through a model which is validated by the experimental data. The software program was coded in MATLAB/SIMULINK. The model profile rates compared with the experimental results to show the accuracy of the model. In this study, it was concluded that increasing the reaction temperature until a certain limit is useful and improve some indices of the final product and after that rising the reaction temperature has a harmful effect on the indices. Exactly the same issue is true in the case of increasing the amount of hydrogen.

**KEY WORDS:** Mathematical modeling, Propylene polymerization, Melt flow index, Population balance, Average molecular weight, hydrogen

### INTRODUCTION

Polypropylene is one of the most valuable polyolefin products which having excellent physical-mechanical properties and relatively low prices. The final product properties categorize its applications and highly depend on the kinetics of the reaction. Owing to the complexity of the catalyst kinetics and despite a long history of consuming Ziegler-Natta catalyst more than sixty years, the polymerization performance still remains unknown and unclear [1, 2].

The crucial indices of the final product properties are comprising of flow index (MFI); number and weight average molecular weight (Mw and Mn) which are classified the polymer applications. Among them, the average molecular weight is the most significant index, which must be precisely controlled. Weight average molecular weight depends strongly on the polymerization kinetics and the polymerization rate profiles (R<sub>pt</sub>). For controlling the average molecular weight, it is necessary to find a clear image of the behavior of the polymerization system as a function of operating conditions such the reaction temperature and hydrogen amount in the polymerization system. Due to the complexity of the kinetics and a large number of polymerization reactions, only a validated mathematical model might approach us to the aim.

Varshouee *et al.* focused on providing a validated model that able to predict polymerization profile graphically and proposed a model to show the percentage of the total existing catalyst sites which be activated by the used hydrogen amount [3]. In the following, they investigated the effect of the reaction temperature and the hydrogen amount on the deactivation constant (K<sub>d</sub>) and the yield of the catalyst used and also evaluated the variation of the melt flow index of the final product by imperial equation in absence of hydrogen [4]. Afterward, they decided to expand their model to cover the above mentioned existing gap and also proposing a new model

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to predict the variations of melt flow index with hydrogen amounts. This article is the result of the decision. This study presents a validated model based on a kinetic model which is able to make a profound sense of the polymerization performance. The main advantages of this model are that it can easily estimate the final product properties such as number and weight average molecular weight (Mw and Mn), flow index (MFI) and determining the best process conditions of the polymerization recipe namely the reaction temperature and hydrogen amount in the polymerization system.

The most previous studies in this regard have focused on an experimental approach, whereas this method is not reliable, because of their results heavily dependent on test and laboratory conditions. The other constraint of the method is the different type of the catalyst used that their results cannot be used for each other [5-7]. Reginato *et al.* modeled an industrial-scale loop reactor by assuming that a non-ideal continuous stirred tank model can be used instead of loop reactor model, they claimed that their model was validated by commercial plant data [2]. Al-haj Ali *et al.* proposed a generalized model for hydrogen response based on the dormant site theory in bulk propylene polymerization but they used an experimental profile rate of the polymerization in their study. There was no validated model which might be able to predict the profile rate of the polymerization and the vital indices of final product properties such as average molecular weight mathematically at the same time [5].

Although some other researchers have endeavoured on the propylene polymerization modeling, the existing gap still remains. Most of their models were proposed based on mathematical calculations without validation with experimental data. Their studies have only focused on a loop or fluidized-bed reactors (FBRs) in bulk or gas phase polymerization [2, 8-10]. Yang *et al.* have modeled a commercial loop propylene polymerization reactor in bulk media without paying attention to kinetic study and final product properties [11]. Thereafter, another researcher has been attempted to model a multi-scale polypropylene reactor in the fluidized bed reactor (FBR) using moment equations [12]. In 2016, Kim *et al.* have also simulated Sheripol technology in bulk polymerization without paying attention to some final product properties such as average molecular weight and polydispersity as well [13].

This study proposes a validated model to determine some crucial indices such as melt flow index (MFI); number and weight average molecular weight (Mw and Mn) as the best way. The model is able to show the profile rate of the polymerization graphically and also able to determine the best condition of the polymerization, namely the best reaction temperature and hydrogen amount in the polymerization system.

By using the model, the chemists, who are working on the catalyst preparation could improve their new catalyst. In addition, the model might be beneficial for the process engineers to replace new catalyst in the commercial reactor without risk and hazard; and also he can design a new recipe for new economical grades or a tailor-made polymer in order to a certain application by using the available catalyst.

Population balance approach (moment balance method) was selected as the modeling approach for slurry polymerization. The advantages of the approach can be listed as follows: (1) The profile rate of the polymerization can be calculated and plotted with acceptable accuracy and (2) The vital final property such as average molecular weight is obtained directly from kinetic equations.

The software program was coded in MATLAB/SIMULINK. The model was validated by experimental data from a lab scale semi-batch reactor with an acceptable margin of error. For this study, it is concluded that 70 °C and 18 mg of hydrogen amount are the best conditions for the catalyst used in the polymerization system.

## EXPERIMENTAL

The 4th generation of spherical MgCl<sub>2</sub> 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. A typical polymerization procedure exists for reactor preparation, polymerization, and discharge. The detailed procedure of the polymerization was according to the reference [3, 4].

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 230 °C and load of 2.16 kg.

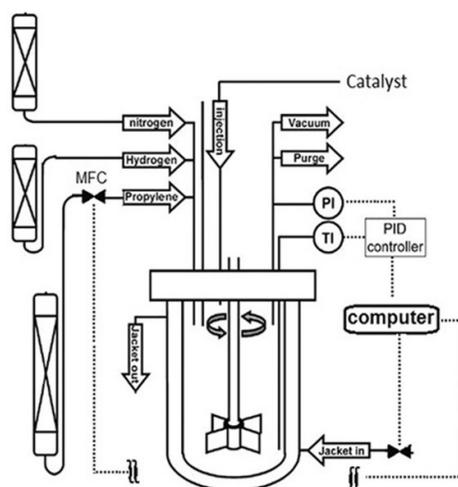


Figure 1. Simplified schematic of the reactor system [4].

#### Modeling description

##### 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) [14] for calculating the amount of  $X = CH/C_m$ , the hydrogen molar ratio. (2) It was assumed that  $\gamma_1 = \gamma_2 = \dots = \gamma_{NC}$ , where  $\gamma$  is equilibrium constant and  $NC$  is a number of solvent in slurry phase components [2]. (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 [5, 10].

**Formulation**

The used reaction equations in this model are listed in Table 2. The ODE mass balance equations in the model are as follows:

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

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

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

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

$Q_f$ ,  $Q_0$ , 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  $R_j$  are defined as reactor volume and  $j$  component reaction rate in equation 1.

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  $\eta$  and  $\zeta$  are meaningless in 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:

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

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  $P_0$  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 ( $M_n$ ), 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:

$$\overline{M}_n = \frac{\sum_{K=1}^{Ns} \sum_{i=1}^{Nm} \lambda_{\delta_i}^k \overline{M}_i}{\sum_{K=1}^{Ns} \sum_{i=1}^{Nm} \lambda_{\delta_i}^k} \quad (2)$$

$$\overline{M}_w = \lambda_2 \cdot \frac{\sum_{k=1}^{Ns} \lambda_0^k \overline{M}_n}{\left( \sum_{K=1}^{Ns} \sum_{i=1}^{Nm} \lambda_{\delta_i}^k \right)^2} \quad (3)$$

$$\text{Then : } DPI = \frac{\overline{M}_w}{\overline{M}_n} \quad (4)$$

Table 1. The probable reactions and their rate equations in propylene polymerization used in the model [2].

Reaction step	Component	Reaction	Rate equation
Site activation	Hydrogen	$C_p + H_2 \rightarrow P_0^K$	$R_{aH}^K = k_{aH}^k C_p C_{H,a}^{O,K}$
	Al-alkyl	$C_p + A \rightarrow P_0^K + B$	$R_{aA}^K = k_{aA}^k C_p C_{A,a}^{O,K}$
	Monomer <i>i</i>	$C_p + M_i \rightarrow P_0^K + M_i$	$R_{aMi}^K = k_{aMi}^k C_p C_{Mi}^{O,K}$
Chain initiation	Monomer <i>i</i>	$P_0^K + M_i \rightarrow P_{\delta_i,i}^K$	$R_{P0i}^K = k_{P0i}^k P_0^K C_{Mi,a}$
Chain propagation	Monomer <i>j</i>	$P_{n,i}^K + M_j \xrightarrow{Kp} P_{n+\delta_j,j}^K$	$R_{Pji}^K = k_{Pji}^k P_{n,i}^K C_{Mj,a}$
Chain transfer	Hydrogen	$P_{n,i}^K + H_2 \xrightarrow{Kh} P_0^K + D_n^k$	$R_{cHi}^{K,n} = k_{cHi}^k P_{n,i}^K C_{H,a}^{O,K}$
	Monomer <i>j</i>	$P_{n,i}^K + M_j \xrightarrow{Km} P_{\delta_j,j}^K + D_n^k$	$R_{cMji}^{K,n} = k_{cMji}^k P_{n,i}^K C_{Mj,a}^{O,K}$
Site deactivation	Hydrogen	$P_{n,i}^K + H_2 \rightarrow C_d + D_n^k$	$R_{dHi}^{K,n} = k_{dHi}^k P_{n,i}^K C_{H,a}^{O,K}$
		$P_0^K + H_2 \rightarrow C_d$	$R_{dH0}^K = k_{dH0}^k P_0^K C_{H,a}^{O,K}$
	Al-alkyl	$P_{n,i}^K + A \rightarrow C_d + D_n^k$	$R_{dAi}^{K,n} = k_{dAi}^k P_{n,i}^K C_{A,a}^{O,K}$
	Spontaneous	$P_{n,i}^K \rightarrow C_d + D_n^k$	$R_{dSpi}^{K,n} = k_{dSpi}^k P_{n,i}^K$
		$P_0^K \rightarrow C_d$	$R_{dSp0}^K = k_{dSp0}^k P_0^K$

### Melt flow index

The melt flow index (MFI) is one of the most important of polymer rheology index, Which is an indicator to determine the application polymer. It has inversely proportional to Weight average molecular weight. A power-law-Equation based on Mark-Houwink model was suggested as a model that is able to calculate MFI as follows [2]:

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

If  $X = 0$  (i.e. no hydrogen in system; as defined by Eq (6)), a and b parameters which should be obtained according to experimental data. The equation is fairly fitted only in the absence of hydrogen in the polymerization system. In the presence of hydrogen, some other researchers such as McAuley and MacGregor for polyethylene and Wang *et al.* for polypropylene suggested another model for predicting MFI [16-17]:

$$X = CH_2/C_m \quad X \text{ is the hydrogen-monomer molar ratio:} \quad (6)$$

$$\log(MFI) = \alpha + \beta \cdot \log(X) + \gamma \cdot \log(T) \quad \text{If } X = 0 \text{ (i.e. hydrogen exists in system)} \quad (7)$$

Where T is the reaction temperature (°C);  $\alpha$ ,  $\beta$  and  $\gamma$  are equation constants such as before should be determined by experimental data. The amount of the  $\alpha$ ,  $\beta$ , and  $\gamma$  for this study will be inserted in results and discussion as well.

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

Hydrogen	$R_H = -\sum_{K=1}^{Ns} [R_{dH}^k + R_{dH}^k + R_{dH0}^k + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} (R_{cH}^{k,n} + R_{dH}^{k,n})]$
Cocatalyst	$R_A = -\sum_{K=1}^{Ns} [R_{dA}^k + R_{dA0}^k + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} R_{dAi}^{k,n}] - R_{eA}$
Electron donor	$R_E = -\sum_{K=1}^{Ns} [R_{dE0}^k + \sum_{\substack{l=1 \\ l \neq K}}^{Ns} R_{dEl}^k] + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} (\sum_{l=1}^{Ns} (R_{dEi}^{k,l} + R_{dEi}^{k,n})) - R_{eE}$
Poison	$R_Y = -\sum_{K=1}^{Ns} [R_{dY0}^k + \sum_{i=1}^{Nm} \sum_{n=\delta_i}^{\infty} R_{dYi}^{k,n}] - R_{eE} - R_{eA}$
Potential sites	$R_{Cp} = -\sum_{K=1}^{Ns} (R_{dH}^k + R_{dA}^k + R_{dSp}^k + \sum_{i=1}^{Nm} R_{dMi}^k)$
Dead sites	$\alpha_i^k = k_{cH}^k C_{H,a}^{O_{2n}^k} + k_{cSp}^k + \sum_{j=1}^{Nm} k_{cMj,i}^k C_{Mj,a} + \sum_{\substack{l=1 \\ l \neq K}}^{Ns} (k_{dEl}^{kl} C_{E,a}^{O_{2n}^k} + k_{dSpi}^{kl}) + k_{dH}^k C_{H,a}^{O_{2n}^k} + k_{dA}^k C_{A,a}^{O_{2n}^k}$
Monomer	$R_{Mi} = -\sum_{K=1}^{Ns} R_{P0i}^k + \sum_{j=1}^{Nm} \sum_{n=\delta_j}^{\infty} (R_{Pij}^{k,n} + R_{cMi,j}^k)$
Moments equations	
Live polymer	$R_{P_{n,i}^k} = \delta(n - \delta_i) [R_{P0i}^k + \sum_{j=1}^{Nm} \sum_{m=\delta_j}^{\infty} R_{cMi,j}^{k,m}] + \sum_{j=1}^{Nm} k_{pij}^k C_{Mi,a} P_{n-\delta_i,j}^k - \sum_{j=1}^{Nm} k_{pij}^k C_{Mj,a} P_{n,i}^k$
Dead polymer	$R_{D_n^k} = \sum_{i=1}^{Nm} \alpha_i^k P_{n,i}^k \quad \text{where}$ $\alpha_i^k = k_{cH}^k C_{H,a}^{O_{2n}^k} + k_{cSp}^k + \sum_{j=1}^{Nm} k_{cMj,i}^k C_{Mj,a} + \sum_{\substack{l=1 \\ l \neq K}}^{Ns} (k_{dEl}^{kl} C_{E,a}^{O_{2n}^k} + k_{dSpi}^{kl}) + k_{dH}^k C_{H,a}^{O_{2n}^k} + k_{dA}^k C_{A,a}^{O_{2n}^k}$
Live moment	$\mu_{\delta_i,j}^k = \sum_{n=1}^{\infty} n^{\delta_i} P_{n,i}^k$
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	$R_{\mu_{0,i}^k} = R_{P0i}^k + \sum_{j=1}^{Nm} k_{cMi,j}^k C_{Mi,a} \mu_{0,j}^k - \alpha_i^k \mu_{0,i}^k$ $+ \sum_{j=1}^{Nm} [k_{pij}^k C_{Mi,a} \mu_{0,j}^k - k_{pij}^k C_{Mj,a} \mu_{0,i}^k]$
First-order; live polymer moments	$R_{\mu_{\delta_i}^k} = \sum_{i=1}^{Nm} \delta(i-1) [R_{P0i}^k + \sum_{j=1}^{Nm} k_{cMi,j}^k C_{Mi,a} \mu_{0,j}^k] - \sum_{i=1}^{Nm} \alpha_i^k \mu_{\delta_i}^k + \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} k_{pij}^k C_{Mi,a} \mu_{0,j}^k$
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	$R_{\lambda_2} = \sum_{K=1}^{Ns} \sum_{j=1}^{Nm} [R_{P0i}^k + \sum_{i=1}^{Nm} k_{cMj,i}^k C_{Mj,a} \mu_{0,i}^k] + \sum_{k=1}^{Ns} \sum_{i=1}^{Nm} \sum_{j=1}^{Nm} k_{pij}^k C_{Mj,a} (\mu_{0,i}^k + 2\mu_{0,j}^k)$

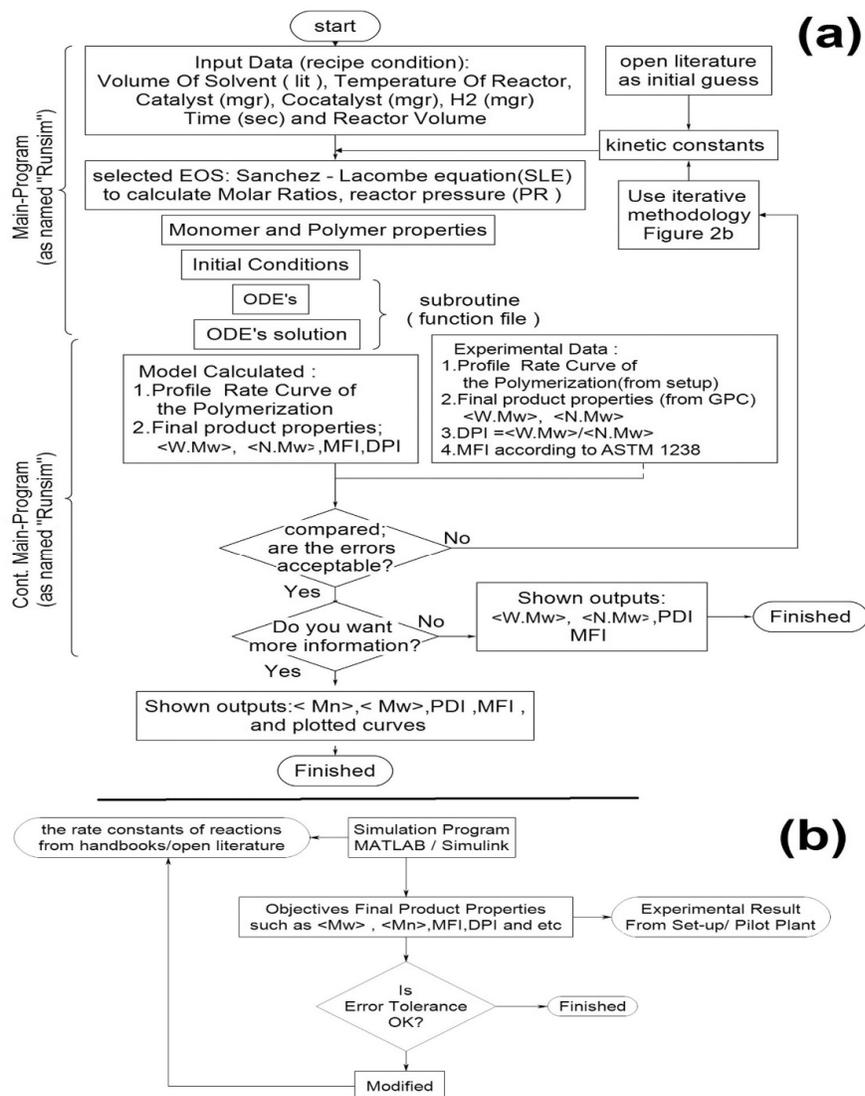


Figure 2. (a) The general algorithm modeling in this work; (b) The iterative methodology used for adjusting kinetic parameter in this work [3, 4].

#### Modeling algorithm

This study has outlined the algorithm for programming the mathematical model in a MATLAB/SIMULINK environment, as shown in Figure 2a. It is composed of two part; main-program (as named "Runsimsim") 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 Figure 2b.

In this study, from literature [2, 8], 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 Figure 2b. Comparing the polymerization profile rate of the model outputs and the experimental data in Figure 3a and 3b implies that the fairly accurate kinetic constants have been adjusted and applied in the model.

## RESULTS AND DISCUSSION

The aim of this study was to be established a validated model that it is able to predict the vital indices of final product properties such as number and weight average molecular weight (Mw and Mn) and flow index (MFI); and also be able to determine the best process conditions of the polymerization recipe namely the reaction temperature and hydrogen amount in the polymerization system. For this purpose, a new model for the polymerization has been done by using population balance method to obtain directly the final product properties from kinetic equations. The model was coded in MATLAB/SIMULINK software program, according to the algorithm that shown in Figure 2a. The reaction equation used in the model is listed in Table 1 and the components rate and moment equation used in the model is summarized in Table 2.

One of the most important advantages of this model is that it is able to show the profile rate of the polymerization graphically, then it is possible to compare the model profile and the experimental profile rates come from the lab Set-up. By having the profile rate of the polymerization, it is easily possible to study the kinetics of the polymerization and also to determine the crucial indices belong to the kinetic study [3, 4]. The experimental condition runs are listed under the title "recipe conditions" and also the results which come from the model and experimental are summarized in detail in Table 3.

The comparison between the model and experimental profile rates graphically at a different reaction temperature in the absence of hydrogen is shown in Figure 3a. The conclusions in this regard can be listed as follows: (1) The model profile rates are in line with the experimental profiles rates with a relatively acceptable error, it means that the model has been validated and adjusted kinetic parameter (constants) in a proper way manner by using the proposed algorithm in Figure 2b. In this regard, the other conclusion in this regard is that selected population balance approach is a suitable technique for the polymerization. (2) However, the error in modeling is inevitable; it can be explained by the source of error including the global numerical error that is the summation of truncation, method, and rounds off error; personal and systematic errors; the equation of state error; and the assumption errors.

Increasing reaction temperature gives rise to increase rate of reaction (obviously, according to Arrhenius equation). But rising the reaction temperature to 70 °C increases the catalyst yield and the average molecular weight (Figure 5a) and decreases polydispersity index (as favorite aspects); and from 70 °C to up, increasing temperature has exactly the opposite effect of these items (unfavorite aspects); refer to Table 3. It is concluded that the reaction temperature at 70 °C is the best condition in the absence of hydrogen in this study (run 3). Figure 3b illustrates the comparison between the model profile rates and the experimental profiles rate at 70 °C in the absence of hydrogen in the polymerization system.

Hydrogen as chain transfer agent not only effects on final product properties but also has an influence on increasing activated site on the catalyst used and the kinetics of the polymerization as well. So far, three theories have been proposed to explain the influence of the hydrogen on polypropylene polymerization as follows: Theory 1: Increase in the number of active sites theory. Theory 2: The change in oxidation states theory. Theory 3: Dormant sites theory.

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

Run No.	Recipe				Results ( Experimental/model)					
	T (°C)	H <sub>2</sub> (mg)	Molar ratio X=CH <sub>2</sub> /Cm	Catal yst (mg)	Y (gr)	< Mn >	< Mw >	PD I	MFI	
1	65	0	0	20	Experimental result	63.29	210259	863057	4.1	0.75
					Model result	65.13	205570	834523	4.06	0.81
2	70	0	0	20	Experimental result	72.66	304642	1134374	3.71	0.42
					Model result	76.4	323780	1214440	3.75	0.33
3	75	0	0.	20	Experimental result	63.07	236154	1124367	4.76	0.4
					Model result	67.25	270243	1178300	4.36	0.36
4	70	18	0.00466	10	Experimental result	81.33	29962	144192	4.81	37
					Model result	88.4	32812.7	148874	4.54	36.99562
5	70	27	0.00703	10	Experimental result	74.61	24016	116939	4.87	62
					Model result	76.81	24981.1	123303	4.94	61.98627
6 <sup>1</sup>	70	2000	0.0206	10	Experimental result					650
					Model result	64.92	9952.25	70163.4	7.06	670.59
7 <sup>1</sup>	70	2500	0.0243	10	Experimental result					900
					Model result	61.26	8353.86	61651.5	7.38	925.20

X: Hydrogen molar ratio, it is calculated by Aspen Software polymer software based on SLE (SOE). <sup>1</sup>as the product was off or wax grade only MFI of product was measured 3.

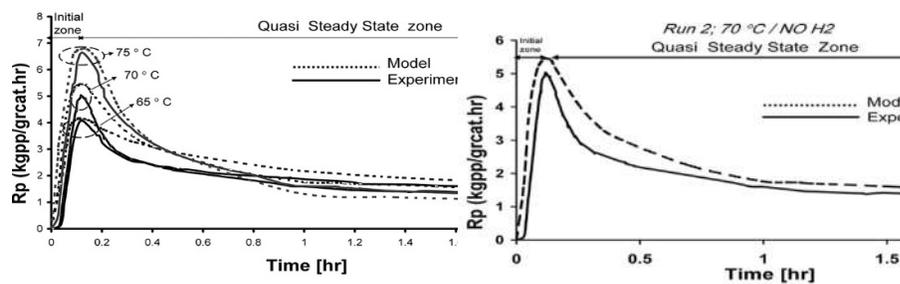


Figure 3. (a) The comparison of the experimental and model out of the profile rate in the absence of hydrogen at a different temperature. (b) The comparison of the experimental and model out of the profile rate in the absence of hydrogen at the constant temperature of 70 °C.

So far, the first and second theories studies have been rejected and the reasons for the rejection of theories exist in the open literature [14]. For the sake of brevity, the detailed discussion in this regard is avoided in this paper. But it should be mentioned that the dormant sites theory is still the strongest theory in this field. The comparison between the model and experimental profile rates graphically at a different hydrogen amount in the polymerization system at the constant reaction temperature of 70 °C is shown in Figure 4a.

Before proceeding to discuss the effect of hydrogen on the polymerization, it is necessary to remark that as mass flow controller (MFC) of lab setup shows the amounts of hydrogen which are entered to the reactor as per milligram, firstly the amounts were listed as per [mg] in Table 3. Then their equivalents in molar ratio were inserted in a separated column in front of them. Molar Ratio was calculated by ASPEN Software based on Sanchez and Lacombe Equation (SLE).

As can be seen from Figure 4a, it is concluded that increasing hydrogen amount leads to increase the rate of reaction and the reason for this event can be explained by dormant sites theory. The theory says hydrogen causes to raise the activated site on the catalyst used. The quality and quantity of this event on the catalyst used have been modeled in previous work [3]. The results belong to runs 2, 4 and 5 from Table 3 show that rising hydrogen amount to 18 mg gives rise to increase rate of the polymerization, the catalyst yield and reduces the average molecular weight to allowance limit (and also Figure 5b) and decreases polydispersity index (as favorite aspects); and from 18 mg to up, increasing hydrogen amount not only decreases rate of polymerization but also has exactly the opposite effect of these items except average molecular weight to reduce more to make product as off grade (as unfavorable aspects). It is concluded that the hydrogen amount at 18 mg at the constant temperature (70 °C) is the best condition in this study (run 4). Figure 4b illustrates the comparison between the model profile rates and the experimental profiles rate at 70 °C and hydrogen amount at 18 mg in the polymerization system.

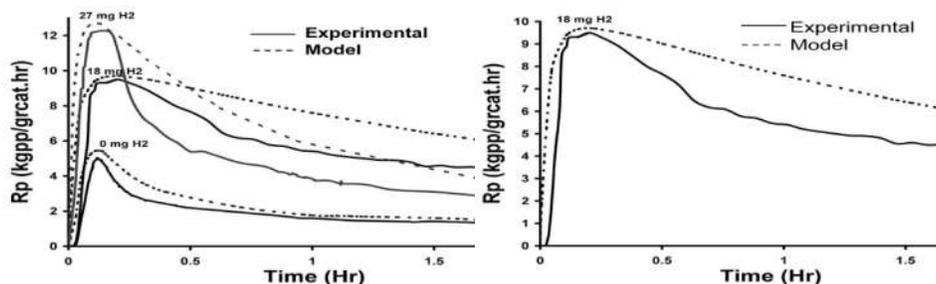


Figure 4. (a) The comparison of the experimental and model out of the profile rate at a different hydrogen amount and the constant temperature of 70 °C (b) The comparison of the experimental and model out of the profile rate at 18 mg hydrogen amount and the constant temperature of 70 °C.

Figure 5b shows changing the average molecular weight by increasing hydrogen amount in the polymerization system, from point A to B, the functionality of hydrogen is as chain transfer agent reacts with the active site on the chain, therefore, hydrogen causes to terminate the growth of the polymer chain then the average molecular weight is decreased; afterward from B to C excess hydrogen amount reacts with the activated site on the catalyst surface and for that reason the rate of the polymerization and the yield of the catalyst also decrease slightly.

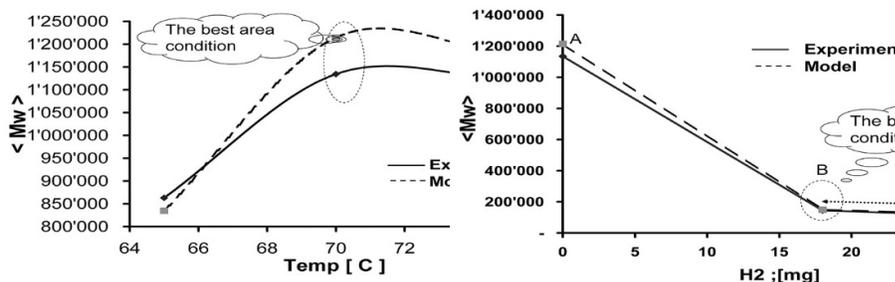


Figure 5. (a) The comparison of the experimental and model outputs of the average molecular weight of the polymer in the absence of hydrogen at different temperatures. (b) The comparison of the experimental and model outputs of the average molecular weight of the polymer in the presence of different hydrogen concentration at the constant temperature of 70 °C.

As melt flow index (MFI) is one of the vital rheology indexes, in this study, it is concluded that in absence of hydrogen, the melt flow index (MFI) might be a function of average molecular weight (Mw) and obeys from the power-law-equation based on Mark-Houwink model, i.e. equation (5). The constants of a and b were obtained as  $a = 9.4841 \times 10^{13}$  and  $b = -2.3747$  with a linear correlation coefficient ( $R^2$ ) of 0.99 [3]. It is concluded that increasing reaction temperature to 70 °C leads to decreasing MFI according to the same aforementioned reasons for Mw; but after 70 °C, MFI increase by increasing the reaction temperature. Therefore MFI has a minimum point at 70 °C in the absence of hydrogen, as shown in Figure 6.

In contrast, in presence of hydrogen, the Mark-Houwink model does not predict MFI correctly; according to McAuley and MacGregor's comments for polyethylene and Wang's opinion for polypropylene, the melt flow index (MFI) is a function of reaction temperature and hydrogen concentration in the system. Given this orientation, equation (7) was considered as a suitable model to calculate and predict of MFI in presence of hydrogen. For this study as shown in Figure 7a, the  $\alpha$ ,  $\beta$ , and  $\gamma$  of equation (4) were fitted and obtained with a correlation coefficient ( $R^2$ ) of 0.98 as follows:  $\alpha = 13.42$ ,  $\beta = 1.948$  and  $\gamma = -3.756$ .

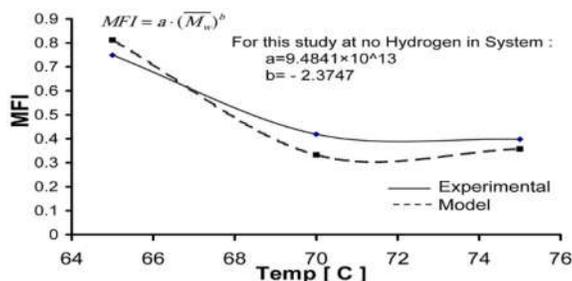


Figure 6. The variation of MFI with the reaction temperature changes and the constant temperature of 70 °C.

Figure 7a, shows the variation of MFI with hydrogen changes and the constant temperature of 70 °C. Within the scope of this research, the model curve with the experimental curve is completely consistent as shown in Figure 7b.

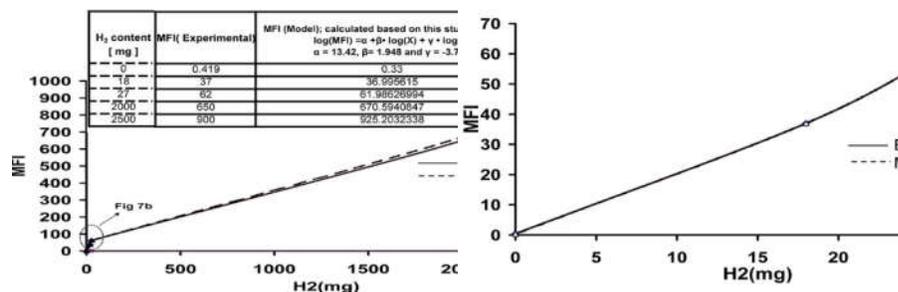


Figure 7. (a) The variation of MFI with hydrogen changes and the constant temperature of 70 °C. (b) The variation of MFI with hydrogen changes and the constant temperature of 70°C within the scope of this research.

## CONCLUSION

In this work, a validated model is presented which is able to calculate and show graphically the profile rate of propylene polymerization. In this paper, the comparisons between the profile rates come from the experimental and model output have been down. It is concluded that the model profile rates are in line with the experimental profiles rates with a relatively acceptable error and also concluded that the selected approach is a suitable technique for this study; the model was tuned in a proper way by the proposed algorithm. The software program was coded in MATLAB/SIMULINK and validated by the experimental data come from a lab setup reactor.

In addition, the variation of the melt flow index in the absence and the presence of hydrogen were investigated and concluded that MFI only obeys from the power-law-Equation based on Mark-Houwink model in absence of hydrogen. A new model for MFI as a function of the reaction temperature and the hydrogen amount was proposed and the constants of the model were determined and shown that the proposed model has an acceptable performance in this study. Finally, it is concluded that the reaction temperature at 70 °C and hydrogen amount at 18mg could be considered as the best process condition in this study. It is suggested that to be investigated in this field of the catalyst deactivation model and also the average molecular weight distribution for future studies.

### Notation

$C$	total active site concentration, $\text{kgmol}/\text{m}^3$	$R_p$	polymerization rate, $\text{kg}/\text{gcat hr}$
$C_d$	dead-site concentration, $\text{kgmol}/\text{m}^3$	$R_{p0}$	initial polymerization rate, $\text{kg}/\text{gcat hr}$
$C_j$	component $j$ bulk concentration, $\text{kgmol}/\text{m}^3$	$t$	time, s
$C_{j,R}$	concentration into the reactor, $\text{kgmol}/\text{m}^3$	$T_r$	Reactor temperature, K
$C_k$	type $k$ active specie concentration, $\text{kgmol}/\text{m}^3$	$T$	feed stream temperature, K, $f$
$C_p$	potential site concentration, $\text{kgmol}/\text{m}^3$	$V_R$	reactor volume, $\text{m}^3$
$Dk_n$	dead polymer chain concentration with $n$ monomers originated from site $k$ , $\text{kgmol}/\text{m}^3$	$Y$	yield, gr PP

$DPI$	polydispersity index	$Rr_{k,n}$	$r$ reaction from site $k$ for a growing chain with $n$ monomers, $\text{kgmol}/(\text{s} \cdot \text{m}^3)$
$K$	two-site equilibrium constant, $\text{kgmol}^{-1}$	$R_j$	$j$ component reaction rate, $\text{kgmol}/(\text{s} \cdot \text{m}^3)$ .
$M_w$	mass average molecular weight, $\text{kg}/\text{kgmol}$	<i>Greek letters</i>	
$NC$	number of liquid-phase components	$\Gamma_j$	equilibrium constant for $j$ component between liquid phase and amorphous polymer phase
$n_j, R$	moles of component $j$ into reactor, $\text{kgmol}$	$\Xi$	ratio between solid-phase components concentration at reactor output flow and into reactor
$n_j, a$	moles of $j$ sorbed in the amorphous polymer phase, $\text{kgmol}$	$H$	ratio between liquid-phase components concentration at reactor output flow and into reactor
$n_j, l$	moles of $j$ in the liquid phase, $\text{kgmol}$	$X$	volume fraction of monomer in the amorphous polymer phase
$N_m$	number of monomers	$Pl$	liquid-phase density, $\text{kg}/\text{m}^3$
$N_s$	number of sites	$\rho_p$	polymer density, $\text{kg}/\text{m}^3$
$Or_{k,n}$	order of reaction $r$ for site $k$ growing polymer chain with $n$ monomers with end-group $i$ from site $k$ , $\text{kgmol}/\text{m}^3$	$\rho_R$	reactor slurry density, $\text{kg}/\text{m}^3$
$P_{n,ik}$			<sup>#</sup> Live moment rate Equations

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