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ORIGINAL PAPER

Determination of kinetic parameters of ethylene polymerization with and without hydrogen by Ziegler-Natta catalyst

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ABSTRACT

Slurry polymerization kinetics of ethylene with $TiCl_4/Mg(OEt)_2/AlR_3$ Ziegler-Natta catalysts in various conditions using the model of sum square error (SSE) (method I) and model of least square error (LSE) (method II) was investigated. For this purpose, the molecular weight distributions of the samples were deconvoluted to the minimum number of Flory type distributions, which each represented a different active center type of Ziegler-Natta catalyst. The first method used to determine the leading apparent polymerization kinetic constants for each site in absence of hydrogen by simultaneously fitting the instantaneous polymerization rate, cumulative polymer yield, and molecular weight distribution measured for various samples with various conditions. Second method was used to determine all kinetics parameters such as initiation, propagation, termination and transfer to monomer reaction in absence and also in the presence of hydrogen. For the later, transfer to hydrogen also determined. The results showed that this simulation package is a powerful tool for design and scale up this kind of processes. **Polyolefins J (2020) 7: 121-130**

Keywords: ethylene polymerization; slurry phase; kinetic parameters; model of sum square error; model of least square error; method of moments.

INTRODUCTION

Polyethylene is extensively used in wide range of applications such as pipes, containers, films and electrical conduits. Its continuous consumption rise leads to continuous development of various grades by a vast number of polymerization techniques and conditions [1-3]. Ziegler-Natta catalysts particularly those based on titanium, are employed to produce a majority of commercial polyethylenes [3, 4]. Thereupon, understanding how these multisite catalysts make polyethylene is interesting from an industrial and academia point of view.

The polymerization kinetics of Ziegler-Natta catalysts with simplified mathematical models which quantify overall polymerization rates and average molecular weights have been extensively described in literature [5-8]. Also, the mechanism of polymerization with

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these catalysts has been great deal of research interest.

Kalajahi et al. [9] investigated ethylene polymerization kinetics by moment equation modeling to study the effect of different active centers of a catalyst on homopolymerization kinetics. Kim and his coworkers [10] derived reaction rate profile for ethylene slurry polymerization and studied the effect of deactiviation reactions on the reaction rate. The polymerization kinetics in the presence of diffusion phenomena was investigated by Ray et al. [11]. Gemoets and his coworkers [12] used polymerization kinetics model based on lumping two catalyst sites to predict ethylene polymerization rates and polymer average molecular weights. Study of the effects of hydrogen and external donors on propylene polymerization kinetics was carried out by Alshaiban and Soares [13]. They estimated apparent kinetic rate constants and activation energies for a lumped on site-type model.

These models could not explain the incontestable multisite nature of Ziegler-Natta catalysts. Most studies that use the implication of multiple active site types, focus on elucidating the broad molecular weight distribution (MWD) and often bimodal chemical composition distributions of Ziegler-Natta polyolefins [14, 15].

To the best of our knowledge, few publications delineate methods to estimate polymerization kinetics parameters for each site type on multisite catalysts. However, they did not estimate the minimum number of active site types required to simultaneously clarify instantaneous polymerization kinetics, cumulative polymer yields as well as MWD using a fundamental mechanism for coordination polymerization [15-16]. Comprehensive kinetics has been considered in some studies to predict experimental results with models [17-19].

Chen and coworkers [19] introduced a method which identifies the minimum number of active site types required to simultaneously clarify instantaneous polymerization kinetics and MWDs evolution for ethylene and α-olefin polymerizations with multisite catalysts. They quantified apparent site activation, monomer/comonomer propagation and site deactivation rate constants for each site type and estimated the MWDs of polymer populations made on each site type. It is well known that transfer reactions play key role in the mechanism and kinetic of coordination polymerization, especially with Ziegler-Natta catalysts. However, Chen et al. did not consider these reactions which are essential in polymerization reaction engineering. Therefore, in this study we have estimated transfer reactions by using the model of least square error in addition of apparent site activation monomer propagation and site deactivation rate constants.

In the present study, the Ziegler-Natta catalyst, $TiCl_4/Mg(OEt)_2/AlR_3$, developed for industrial scale ethylene polymerization was used. In this research method, new comprehensive calculations have been proposed for estimating the kinetic parameters and also for an ethylene polymerization system in slurry conditions. All kinetic constants with or without the presence of hydrogen were obtained, which could predict well the conditions of the process and the main properties of the polymer. It should be noted that by calculating the kinetic constants, the process of ethylene polymerization in the slurry phase can be predicted and even process engineering documents can be prepared on different scales, which is very important in the petrochemical industries.

EXPERIMENTAL

Materials

Polymerization grade ethylene (99.9995%) was passed through a 4Å molecular sieve before use.

N-Hexane, a highly pure industrial grade (98%) supplied by Daejung Petrochemical Company, was dried over a 4Å molecular sieve and Na wires. Triethylaluminum was purchased from Merck and used without further purification. Supported titanium catalyst ($TiCl_4/Mg(OEt)_2/AlR_3$), synthesized by National Petrochemical Research and Technology Company, was used as received. To degas the reactor, ultra-pure (99.999%) nitrogen was passed through molecular sieve (4Å) and then was flowed into the reactor. All solution and catalyst components were kept and transformed under a dry N2 blanket.

Polymer synthesis

Polymerizations were conducted in a 1.5 L semi-batch stirred autoclave reactor. A jacketed reactor with cir-

Table 1. Samples designation and polymerization conditions in absence of hydrogen (80°C).

Sample Code	Catalyst (mg)	Cocatalyst (mg)	Polymerization time (min)	Solvent (L)	Total pressure(bar)	Yield ([$g_{pol.}$ /$g_{cat.}$])
211	20	400	60	0.5	6.45	4727
212	20	800	60	0.625	7.2	3799
226	20	200	18	0.625	7.6	913
227	20	200	29	0.625	7.5	1523
228	20	200	60	0.625	7	4376

culating bath for cooling and heating was used and a thermocouple controlled the reactor temperature during the polymerization within ±0.1°C of the set point. Each experiment was repeated three times and rate profiles showed good adaptation and repeatability.
The reaction was performed in semi-batch condition. The catalyst and cocatalyst (triethylealuminum) were initially injected then ethylene was continuously injected at constant pressure and temperature. The polymerization conditions are detailed in Tables 1 and 2.

MWD determination

The MWD of samples was measured by a GPC instrument (Agilent Technology, PL 220 and RID and bridge viscometer detectors, 3×300 mm PLgel MIXED B, 10 µm particle size, 7.5 mm ID with 10 µm Guard 7.5×50 mm or 3×PLgel 10µm MIXED-B 300×7.5 mm with 10 µm Guard 7.5×50 mm) at 145°C with 1.0 mL min^{-1} 1,2,4-trichlorobenzene (TCB) as eluent. The polymer solutions of 1 mg/mL were prepared by TCB at 145°C under stirring (the sample solutions were prepared by dissolving of the polymer samples in TCB at 145°C under continuous shaking in concentration of 1 mg/mL). The narrow polystyrene standards were used for 12-point universal calibration.

MODEL DEVELOPEMENT

The mathematical method used in this study was based on three categories of experimental data:

- Polymerization rate data obtained directly from polymerization tests
- Data on the efficiency of polymerization reactions
- Molecular weight and its distribution data of the product

The main steps for estimating kinetic constants are as follows:

- Achieving an algebraic equation or a system of ordinary differential equations involving a direct or differential relationship between the rate of polymerization and time.
- Deconvolution of molecular weight distribution curves into its constituent parts in order to determine the number of catalyst sites, the average molecular weight and the weight fraction of the polymer obtained from each site.
- Investigating the thermodynamics of the polymerization medium using a state equation for accurate estimation of the monomer concentration in the solvent medium. (In addition to the concentration of the monomer, the concentration of all the components of the reaction medium is not less important than the kinetics of the reaction).
- Using an appropriate method such as the least squares error method for alignment fit for the rate of polymerization based on experimental data or combining the least squares error method with conventional algorithms for solving ordinary differential equations such as Runge-Kutta to adapt the differential relationship of polymerization rate to the results of polymerization rates.

Table 2. Samples designation and polymerization conditions in presence of hydrogen (80°C).

Sample Code	Catalyst (mg)	Cocatalyst (mg)	Polymerization time (min)	Solvent (L)	Total pressure(bar)	Hydrogen pressure(bar)	Yield([$g_{pol.}$ / $g_{cat.}$])
224	20	200	60	0.625	9.5	2	4686
219	20	200	61	0.625	11.35	4	3389
220	20	200	60	0.625	15.5	8	3877

Modeling of MWD and polymerization kinetics

GPC Deconvolution

It is well known that polyolefins made on the multi-site catalysts have broad MWD due to superposition of narrower MWDs of polyolefin population made on each site type. According to this perception, every site type makes the polymer with most probable Flory distribution, envisaging distribution for the linear polymer made by coordination polymerization [20]. It should be noticed that Flory's most probable distribution is ruled by relation PDI=2.0:

$$w(r,j)=\tau_j^{\,2} r\ \exp(-\tau_j r) \qquad ; \qquad \tau_j=\frac{k_{tM}^j[M]+k_{tA}^j[A\,l]}{k_p^j[M]} \tag{1}$$

Where w(r,j) is the polymer weight fraction with length r on the active site j.
Weight chain length distribution (WCLD) is given by:

$$\hat{W}(r)=\sum_{j=1}^{Nsite} m(j)w(r,j) \qquad ; \qquad \sum_{j=1}^{Nsite} m(j)=1 \tag{2}$$

m(j) is the polymer weight fraction obtained by active site j. In order to minimize the difference between theoretical and experimental the following equation is used:

$$\chi^2=\sum_{i=1}^{m}(W(r)_i-\hat{W}(r)_i)^2 \tag{3}$$

It is generally agreed that broad molecular weight distribution of products synthesized by Ziegler-Natta catalysts is less influenced by diffusion barriers [21, 22].

Adaptation of ethylene polymerization rate curve using sum square error (method I)

In the present work, we describe the kinetics of homopolymerization by Ziegler-Natta catalyst for each site type and consider spontaneous activation as well as activation by cocatalyst.

$$C_p \xrightarrow{k_{aSp}^j} P_{0,j} \tag{4}$$

$$C_p + Al \xrightarrow{k_{aA}^j} P_{0,j} \tag{5}$$

$$P_{r,j} + M \xrightarrow{k_p^j} P_{r+1,j} \tag{6}$$

$$P_{r,j} \xrightarrow{k_d^j} inactive\ species + D_{r,j} \tag{7}$$

Where the subscript j indicates site type and,
C_p is the catalyst precursor;
$P_{0,j}$ is the active site;
M is the monomer;
$P_{r,j}$ is the living chain of length r, and
$D_{r,j}$ is the dead chain of length r.
This multisite polymerization mechanism represents the real behavior of supported Ziegler-Natta catalysts, and ignores intra-particle mass and heat transfer limitation due to any significant effect in slurry polymerization [18].

The ethylene polymerization rate, Rp (mol L^{-1} min^{-1}) is given by:

$$R_p^j = k_p^j[M]P_*^j \tag{8}$$

[M] is the monomer (ethylene) molar concentration in the liquid phase in the reactor (mol L^{-1}), P^*_j is the total number of moles of chain growing on site type j.

In order to calculate ethylene molar concentration in the liquid phase under our experimental conditions, the equation of state by Sanchez Lacome et al. [23] was used.

The concentration of active site is given by:

$$\frac{dP_*^j}{dt}=k_{aA}^{\,j}C_P[A\,l]+k_{aSp}^{\,j}C_P-k_d^{\,j}P_*^j \tag{9}$$

$$C_p=C_P^0\exp(-k_a^{\,j}t) \tag{10}$$

$$k_a^{\,j}=(k_{aA}^{\,j}[A\,l]+k_{aSp}^{\,j}) \tag{11}$$

Where, [Al] is the cocatalyst concentration (mol L^{-1}) and CP is the catalyst active sites concentration.
P^*_j is found by integrating Eq. (9) with the initial condition t=0; P^*_j=0

$$P_*^j=\frac{k_a^jC_p^0}{k_d^j-k_a^j}\{\exp(-k_a^jt)-\exp(-k_d^jt)\ \} \tag{12}$$

Substituting Eq. (12) in Eq. (8) results in a convenient expression for ethylene polymerization rate:

$$R_p^j=\frac{Mw_{mon}C_p^0V_0}{m_{cat}}[M]\frac{k_p^jk_a^j}{k_d^j-k_a^j}\{\exp(-k_a^jt)-\exp(-k_d^jt)\ \}\frac{V}{V_0} \tag{13}$$

Where Mwmon is the molar weight of ethylene monomer, mcat is the catalyst weight (g), V0 is the initial volume of liquid phase and V is the volume of liquid phase. We assumed that the volume of the system in the liquid phase does not change . By definition of we found that:

$$R_p^j = Mw_{mon}[M]\frac{k_p^j k_a^j}{k_d^j - k_a^j}C_{peff}\left\{\exp(-k_a^j t) - \exp(-k_d^j t)\ \right\} \quad (14)$$

The cumulative polymer yield of each site type during polymerization in a semi-batch reactor, Qj, is found by integrating Eq. (14) during reaction time, treaction:

$$Q^j = Mw_{mon}[M]\frac{k_p^j k_a^j}{k_d^j - k_a^j}C_{peff}\left\{\frac{1-\exp(-k_a^j t_{reaction})}{k_a^j} - \frac{1-\exp(-k_d^j t_{reaction})}{k_d^j}\ \right\} \quad (15)$$

Incorporating Eqs. (14) and (15), the Rpj is obtained. Finally, the summation of Rpj led to the final expression for ethylene polymerization rate:

$$R_p \quad Q_{total}\sum \frac{\exp(-k_a^j t) - \exp(-k_d^j t)}{\frac{\exp(-k_a^j t_{reaction})}{k_a^j} \quad \frac{\exp(-k_d^j t_{reaction})}{k_d^j}} \quad (16)$$

Estimating the MWDs from Eq. (2), the parameters were measured for various samples by minimizing the following objective function.

$$\sum_{j=1}^{n}[\min] = \sum\left\{(R_p^{\exp} - R_p^{\mathrm{mod}el})^2 + (Q_p^{\exp} - Q_p^{\mathrm{mod}el})^2 + [W_{\log Mw}^{\exp} - W_{\log Mw}^{\mathrm{mod}el}]^2\ \right\} \quad (17)$$

Adaptation of ethylene polymerization rate curve using least square error with differential equations of polymerization rate (Method II)

Population balance along with the method of moments was extensively used in the simulation of olefins polymerization process. Incorporation of these methods leads to a set of differential equations. The polymerization behavior and average of molecular weight can be obtained by solving these equations.

The sum square error method about Algebraic equations is useful for polymerization rate in the absence of hydrogen. However, in case of hydrogen existence based on the reactions presented in the Appendix I (supporting information), according to Kissin theory [24], population balance and moments equations can be achieved (please see Appendix I in supporting information).

Intended equation for applying in least square error is as follows:

$$R_p = \sum_{j=1}^{N_{sites}} Q_j \frac{Y_j^{(0)}}{\int_0^{t_{reaction}} Y_j^{(0)} dt} \quad (18)$$

$$r_n^j = \frac{X_j^{(1)} + Y_j^{(1)}}{X_j^{(0)} + Y_j^{(0)}} \quad (19)$$

Where X(0) and X(1) are the zero moment and the first moment of terminated polymer molecules produced on site type j, respectively. Also, Y(0) and Y(1) are the zero and first moment of propagating polymer molecules produced on site type j, respectively.

$$E = \sum_i f_i^2 \quad (20)$$

For example: $f_i = R_{p_{rate\_equation}} - R_{p_{\exp}}$ or $f_i = r_n - r_{n,deconvolution}$

All the parameters were estimated using MATLAB software which we wrote for this purpose.

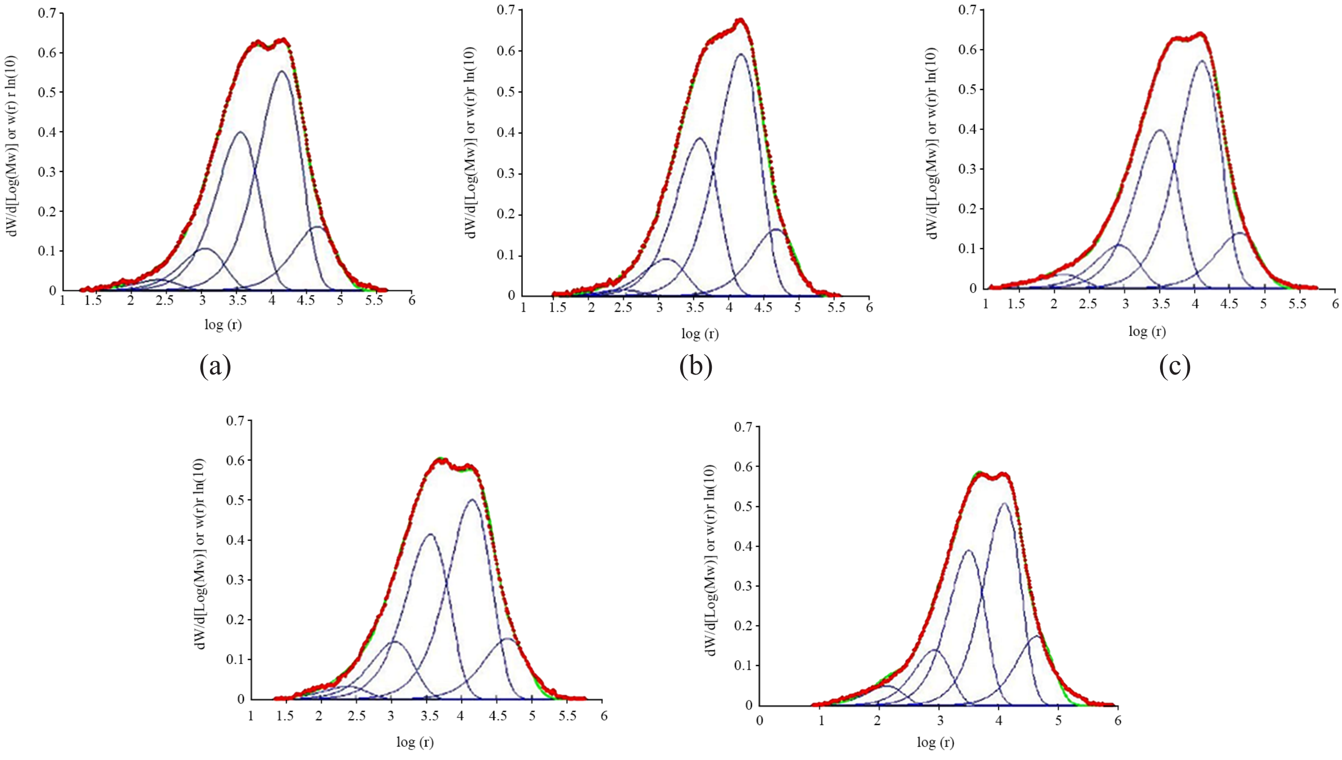
RESULTS AND DISCUSSION

GPC Deconvolution results

Figures. 1 and 2 show the results of GPC deconvolution in the absence and presence of hydrogen, respectively. The model parameters of MWD, Mn and mj for all samples in the absence and presence of hydrogen are summarized in Tables 3 and 4, respectively.

Estimation of ethylene kinetic parameters using sum square error

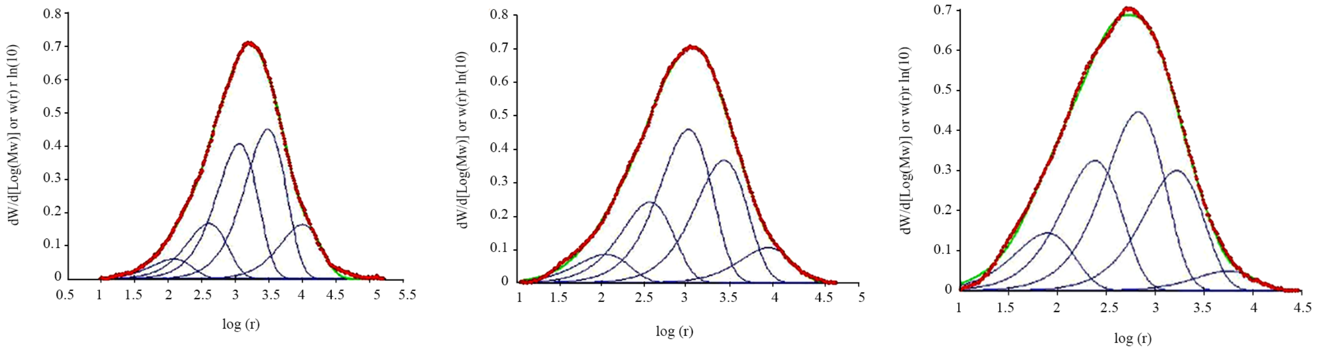
The results of adaptation of Eq. (16) on the experimental data are shown in Figure 3. Also Figure 4 depicts the rate curve for various sites of sample 228. As it can be seen from Figure 3, Eq. (16) has great ability to modeling of polymerization rate behavior, which was carried out in the absence of hydrogen. It should be noted that in this equation, the monomer concentration was assumed to be constant and the rate of activation/deactivation reactions is the only effective kinetic parameter (Table 5).



(a) (b) (c)

(d) (e)

Figure 1. Results of GPC deconvolution in absence of hydrogen A) 228, B) 227, C) 226, D) 211 E) 212 samples.



(a) (b) (c)

Figure 2. Results of GPC deconvolution in presence of hydrogen A) 224, B) 219, C) 220 samples.

Table 3. Average molecular weight (Mn) of ethylene samples for each site type.

Sample Code	M_n^j (g/mol)				
	Site I	Site II	Site III	Site IV	Site V
228	3965	17049	51505	202081	647404
227	3965	17049	51505	202081	647404
226	3965	17049	51505	202081	647404
211	1936	12123	45717	181000	627390
212	1936	12123	45717	181000	627390
224	1635	5269	15297	41498	137390
219	1437	4540	13131	34977	115960
220	864	2570	7396	18798	62531

Table 4. Mass fractions of ethylene samples for each site type in absence and presence of hydrogen.

Sample Code	m_j				
	Site I	Site II	Site III	Site IV	Site V
228	0.0119	0.0733	0.3092	0.4744	0.1312
227	0.0243	0.0882	0.3173	0.4429	0.1275
226	0.0300	0.1186	0.3283	0.4019	0.1211
211	0.0273	0.0862	0.3188	0.4572	0.1106
212	0.0390	0.1106	0.3093	0.4029	0.1381
224	0.0440	0.1224	0.3221	0.3743	0.1372
219	0.0579	0.1700	0.3604	0.3174	0.0944
220	0.0694	0.2238	0.3350	0.3073	0.0645

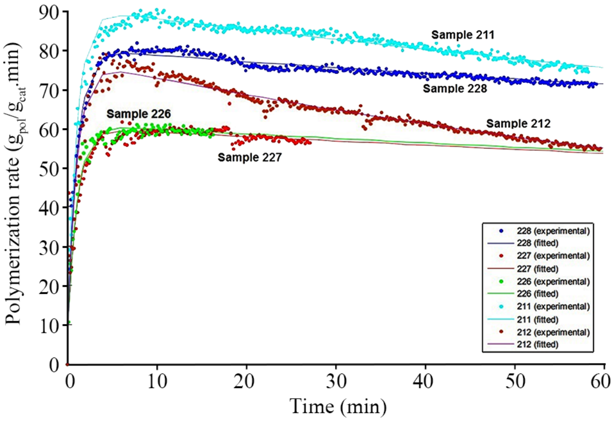


Figure 3. Results of polymerization rate data adaptation in absence of hydrogen using SSE.

Estimation of kinetic rate constants of ethylene polymerization using comprehensive modeling

Table 5. Activation and deactivation reaction rate constants for ethylene homopolymerizaion in absence of hydrogen.

	Samples 228,227,226,210	Sample 211	Sample 212
K_a (total) s^{-1}	0.9510	0.9510	0.9510
Site1: K_d[Al] s^{-1}	0.0019	0.0031	0.0055
Site2: K_d[Al] s^{-1}	0.0019	0.0031	0.0056
Site3: K_d[Al] s^{-1}	0.0019	0.0032	0.0057
Site4: K_d[Al] s^{-1}	0.0019	0.0032	0.0057
Site5: K_d[Al] s^{-1}	0.0020	0.0033	0.0059

This method is able to estimate all kinetic parameters in ethylene polymerization. At the stage I, we estimated activation, deactivation, transfer to monomer, transfer to cocatalyst reaction constants and also propagation rate constant in the absence of hydrogen. After that, at stage II, in order to estimate kinetic parameters of transfer to hydrogen and chain initiation after transfer to hydrogen reactions, experiments were carried out in the presence of hydrogen. Figure 5 demonstrates the results of polymerization rate data adaptation and the kinetic parameters obtained from stage-I, which are detailed in Table 6.

According to these results, this modeling was able to predict slurry polymerization rate curves in the absence of hydrogen with great accuracy.

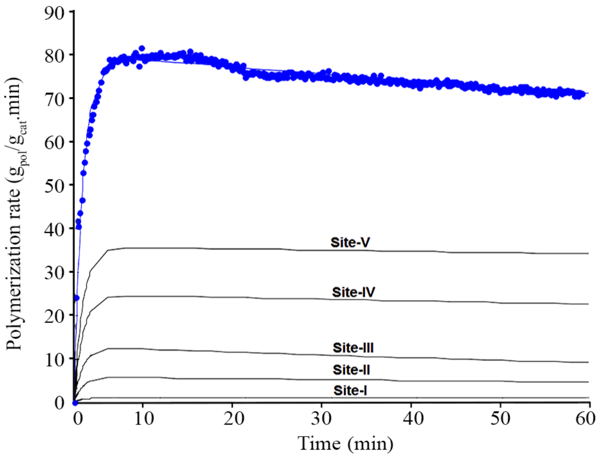


Figure 4. Rate curves for various active sites of sample 228.

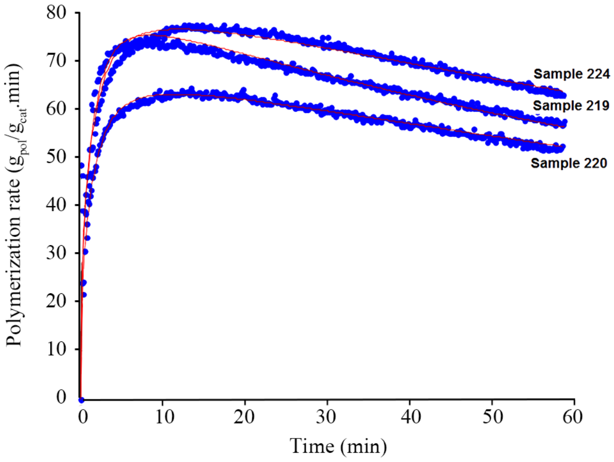


Figure 5. Results of polymerization rate data adaptation in absence of hydrogen using LSE.

Table 6. Kinetic parameters for ethylene homopolymerizaion in absence of hydrogen.

	Site I	Site II	Site III	Site IV	Site V
k_a s^{-1}	0.0230	0.0805	0.3560	0.4711	0.1224
$k_d[Al]$ s^{-1}	0.0008	0.0014	0.0020	0.0021	0.0021
k_i $Lmol^{-1}s^{-1}$	224.8	2.1047e3	1.0376e4	4.2348e4	1.6306e5
k_p $Lmol^{-1}s^{-1}$	224.8	2.1047e3	1.0376e4	4.2348e4	1.6306e5
$k_{trA}[A]$ s^{-1}	0.4426	0.3938	0.1999	0.1776	0.0710
k_{tM} $Lmol^{-1}s^{-1}$	0.4842	2.4026	4.8580	5.1773	6.5150

Using these kinetic parameters, we could extract kinetic parameters which appear in the presence of hydrogen. Figure 6 shows the results of polymerization rate data and the kinetic parameters obtained from Figure 6, which are listed in Table 7.

The comprehensive modeling of ethylene polymerization kinetic in the slurry phase was able to estimate all kinetic parameters in this polymerization process.

To investigate validity of the model, we selected a new sample with conditions listed in Table 8.

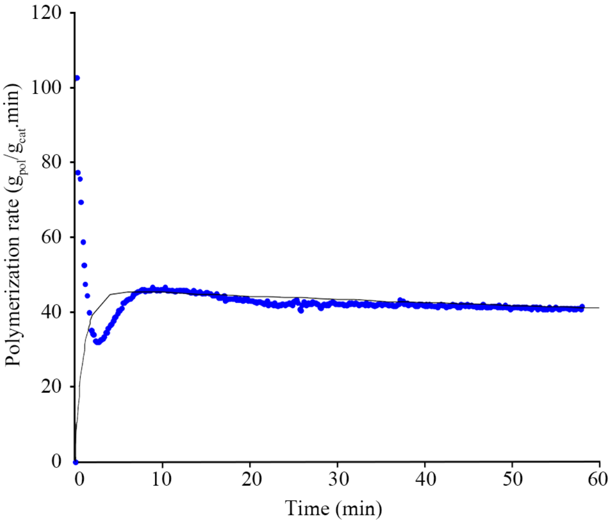


Figure 7. Results of polymerization rate data adaptation for sample 210.

The results of polymerization rate data adaptation for this sample using Eq. (20) are shown in Figure 7. As it is seen, the kinetic parameters can predict polymerization behavior of the sample with great accuracy. As a result, since the model predicted polymerization behavior of external random sample, the validity of the model was approved. The model parameters of MWD, Mn and mj for sample 210 are summarized in Tables 9 and 10.

The molecular weight values obtained from the model and GPC deconvolution for sample 210 are listed in Table 10. As it is seen, all sites except site I showed difference of less than 5%, indicating that kinetic parameters predicted the experimental result of Rp and MWD with good accuracy.

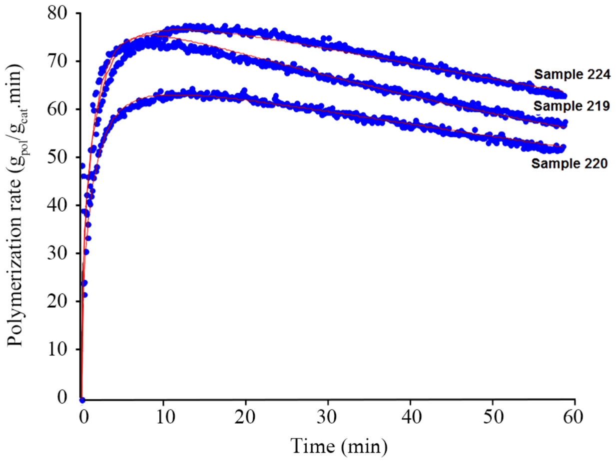


Figure 6. Results of polymerization rate data adaptation in presence of hydrogen using LSE.

Table 7. Kinetic parameters related to transfer to hydrogen and initiation after transfer to hydrogen reactions.

	Site I	Site II	Site III	Site IV	Site V
k_{tH} $Lmol^{-1}s^{-1}$	0.2229	0.1695	1.3276	2.2310	0.0854
k_{iH} $Lmol^{-1}s^{-1}$	2.2858	1.2958	3.8631	3.7998	5.9426

Table 9. Mn and mj for Sample 210 from deconvolusion.

	Site I	Site II	Site III	Site IV	Site V
M_{nj} (g/mol)	2384	12830	46746	181622	631640
m_j	0.0116	0.0704	0.3107	0.4743	0.1330

Table 10. Mn obtained from GPC deconvolution and theoretical estimation from the model for sample 210.

(g/mol)	Site I	Site II	Site III	Site IV	Site V
$M_{nj\ GPC}$	2384	12830	46746	181622	631640
$M_{nj\ estimated}$	1963	12223	47793	189402	657963
Error (%)	17.7	4.7	-2.2	-4.3	-4.2

Table 8. Sample designation and polymerization conditions.

Sample code	Catalyst (mg)	Cocatalyst (mg)	Polymerization time(min)	Solvent(L)	Total pressure(bar)	Yield([gpol. / gcat.])
210	40	400	66	0.625	6.4	2466

CONCLUSIONS

Determination of the reaction kinetic constants is the main challenge in ethylene polymerization reactions with Ziegler-Natta catalysts. These constants depend on nature of active sites and the related reaction parameters are not limited to components concentration and temperature. Calculation of kinetic constants and finding out their relationship with process parameters are beneficial in academic and industrial point of views to provide the controlling tools for polymer microstructure like molecular weight and its distribution (MWD).

In this study, kinetic of ethylene slurry polymerization by $TiCl_4/Mg(OEt)_2/AlR_3$ Ziegler-Natta catalysts was investigated in various conditions and using two methods (I and II). For each site type, the method I estimated activation/deactivation rate constants by simultaneously fitting three parameters including instantaneous polymerization rates, cumulative polymer yields, and MWDs of polymers. The polymerizations were conducted under different conditions.

In order to better understanding of the polymerization nature, estimation of all parameters is essential for polymerization reaction engineering. Therefore, we used method II in the absence and presence of hydrogen and apparent site activation/deactivation rate constants to estimate monomer propagation rate constant, transfer reaction as well as initiation after transfer to hydrogen constants. The results of polymerization rate data adaptation showed a good adjustment with the experimental data.

To evaluate the validity, we applied the methods to a commercial Ziegler-Natta catalyst. The results demonstrated that the method II would work well and predict the molecular weight distribution of the samples.

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Symbols and Abbreviations

A or Al	cocatalyst [mol L^{-1}]
C_P^0	initial concentration of catalyst active sites [mol L^{-1}]
$D_{r,j}$	terminated polymer chain with length r on type j active site
H_2	hydrogen concentration [mol L^{-1}]
k_a^j	activation constant of type j active site [s^{-1}]
k_{dSp}^j	auto deactivation constant of type j active site [s^{-1}]
k_{tA}^j	cocatalyst transfer constant of type j active site [$Lmol^{-1}s^{-1}$]
k_d^j	deactivation constant of type j catalyst [s^{-1}]
k_{tH}^j	hydrogen transfer constant of j type active site [$Lmol^{-1}s^{-1}$]
k_{tM}^j	monomer transfer constant of type j active site [$Lmol^{-1}s^{-1}$]
k_{iH}^j	monomer initiation constant of type j active site [$Lmol^{-1}s^{-1}$]
k_i^j	initiation with monomer constant of type j active site [$Lmol^{-1}s^{-1}$]
k_p^j	propagation constant of type j active site [$Lmol^{-1}s^{-1}$]
[M]	monomer concentration [mol L^{-1}]
m_j	polymer weight fraction by active site of j
M_w	molecular weight of monomer [g mol^{-1}]
$P_{0,j}$	active site of j [mol L^{-1}]
$P_{r,j}$	propagating polymer chain with length r, on active site of j [mol L^{-1}]
$P_{H,,j}$	type j hydrogen terminated site
P_j^*	total number of moles of chain growing on site type j (mol)
Q_P	cumulative total polymer yield [g s^{-1}]
r_n^j	polymer produced on site j with the length of n monomer
R_p	total rate of polymerization reaction of type j active site [g PE / g cat.min]
t	time
τ_j	ratio of monomer transfer rate to propagation rate
$w_{\log Mw}$	molecular weight of polymer (log (M_w))
$X^{(i)}_j$ or $\mu_i^{(j)}$	i^{th} moment of terminated polymer chain on j type active site including zero, first and second moments
$Y^{(i)}_j$ or $\lambda_i^{(j)}$	i^{th} moment of propagating polymer chain on j type active site including zero, first and second moments

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