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Research Article

System Identification for Experimental Study for Polymerization Catalyst Reaction in Fluidized Bed

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Abstract

In this work, system identification method is used to capture the reactor characteristics of production rate of polyethylene (PE) based on published experimental data. The identification method is used to measure the percentage effect on the production rate of PE by measuring the effect of input factors of temperature of reaction, hydrogen concentration, and [Al]/[Ti] molar catalyst ratio. Temperature of reaction has big effects equal 52.4 % on the output of the system and 47.6 % on interaction of the system's parameters compare to other two factors. Also, hydrogen concentration has big effect equal 45.66 % on the output of the system and 14.7 % on interaction of the system's parameters. [Al]/[Ti] molar catalyst ratio has big effect on interaction of the system equal 28.6 and 1.94 % on the output of the system but less than the reaction temperature and hydrogen concentration. All these results depend on experiment results and these results are very important in industrial plants. ©2011 BCREC UNDIP. All rights reserved

Keywords: Catalysts, Co-catalyst, System identification, reaction temperature, hydrogen concentration

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1. Introduction

Fluidized catalytic bed continuous reactors (FCR) entail very complex flow behavior (Ibrehem *et al.*, 2008). Moreover, the presence of four phases in the reaction media complicates the transport phenomena involved which dictates the need for a thorough understanding of parameters effect on production rate and crystallization characteristics.

System identification method (Ibrahem & Hikamt, 2009) should have sufficient accuracy of prediction, wide applicability, the minimum assumption about the most parameters effects like temperature of reaction, hydrogen concentration, and [Al]:[Ti] molar ratio. In the area of production rate for polyethylene system and identify which is most input variable effects on the production rate by using experiment work was very little. In 2009, Zohuri group made a very good experiment work design techniques for polymerization process based on experimental data only. We depend on this important work to specify which is the most active input parameters whose effect on the system depends on experimental results and new identification method to specify the percentage effect of production of high molecular weight of

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polyethylene.

High molecular weight polymers and their morphological development are the most important achievements of heterogeneous catalyst polymerization of the Ziegler-Natta type (Peacock, 2000; Jamjah *et al.*, 2008; Dasilva & Defigueiredo, 2002; Shiraishi *et al.*,1990). $MgCl_2$ and SiO_2 are the most common bisupports used to heterogenize olefin polymerization catalysts (Pater *et al.*, 2003; Jamjah *et al.*, 2006; Zohuri *et al.*, 2006; Moore, 2005), and SiO_2 is also used to support metallocene and late transition metal catalysts (Galli & Vecellio, 2004; Barbe *et al.*, 1986). The morphological development of the catalyst originally obtained from its support could replicate the polymer in controlled conditions. Heterogeneous catalyst particles break up during the early stages of the polymerization, possibly due to the chemical reaction of the catalyst component, mechanical stress and also polymer growth, respectively [Silva *et al.*, 2005; Shaotian *et al.*, 2001). In Ziegler-Natta polymerization, the rate/time profiles are mainly a decay type with very high polymerization activity at the early stage of the reaction. Therefore, the fast growth of the polymer into the pore and channel of the catalyst could fragmentize the catalyst particles. To achieve a reasonable morphology, the fragmentation must be controlled, since uncontrolled fragmentation may produce fine particles. Using SiO_2 and $MgCl_2$ components of a solid, support not only raised the activity of the catalyst but also improved its morphology. SiO_2 also improved the mechanical and thermal stability of the catalyst (Kono *et al.*, 2001; Yamahiro *et al.*, 1999). Interaction between co catalyst (TEA) and catalyst are very important and explained very well in Ibrahem *et al.* (2009) and Hatzantonis *et al.* (2000).

Morphological development of support, catalyst and polymer is the major area of study nowadays. Ultra high molecular weight polyethylene has many desirable physical and mechanical characteristics comparable to some engineering plastics (Fukuda *et al.*, 2003; Zohuri *et al.*, 2003; Zohuri *et al.*, 2001). The present work studies the effect of co catalyst Al/Ti flow rate, temperature input and hydrogen concentration on production rate of polyethylene.

2. Dynamic analysis and identification for mathematical model

System identification involves building a dynamical model from an input/output data and without use of any laws concerning the fundamental nature and properties of the nonlinear system. The batch reactor process involves many variables, which contribute to its operation, and this makes it a Single-Input Single-Output (SISO) process. These variables are classified as follows: Input or manipulated variables (MVs) are chosen from those variables that have direct effect on the process performance, and practically easy to actuate. In our case, these are: percent ratio of Al/Ti as a co catalyst (Qc), temperature input and concentration of hydrogen. The controlled variables (CVs) are selected from the process outlet streams that are usually of foremost importance such as the production polyethylene (PE). A schematic diagram representing the previously mentioned variables is shown in Figure (1).New knowledge in this work shows effects of three important inputs variables of polymerization system on the rate of production compared to other works.

So, the identification steps can be defined for PASA as follows (Ibrahem & Hikamt, 2009):

1. To make actual calculations for the system from nominal conditions xn,i to calculate yn,i.
2. To repeat step one with +H% perturbed parameter input vector (H× xn,i) to produce the + H % perturbed output yi matrix.
3. To subtract each element from matrix in first step from the corresponding element in matrix in second step and divide the difference by yn,i. (yi- yn,i) / yn,i.
4. Similarly calculate the change in parameters (xi- xn,i) / xn,i.
5. Divide each element in third step by fourth step to produce the sensitivity matrix k that depends completely on scale matrix without using any a proper factor.
6. Calculate k matrix for negative direction which mean calculate k+ H % and k- H % so as, we can check the effect of each parameters on output as seen in Table (2) .
7. Then find kaverage slope to find average angle (θ) that is represented overall effect of each parameters on the measured output (θ1 represents the effects of Al/Ti, θ2 represents the effects of reaction temperature and θ3 represents the effects of hydrogen concentration on the system as shown in Figure 9 . From parameters average slope analysis, we can see a preliminary partitioning of estimating into different groups that depend on slope angle (θ) of kaverage and these groups can be specified as follows:

$(\theta) \geq 20^o$: Large effects on the system.
$20^o > (\theta) > 15^o$: Middle effects on the system.

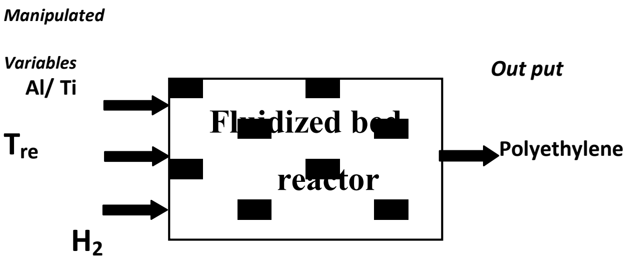

Figure 1. Representation of variables in polymerization system as a MISO system

15° ≥ (θ) ≥ 10°: Weak effects on the system.
10° < (θ): Cannot be established.

$$\theta\text{total} = \theta\text{in the system} + \theta\text{interaction} \quad (1)$$

$$\theta\text{total} = \theta 1 + \theta 2 + \theta 3$$

3 Reaction Kinetics

In the present study, a comprehensive mechanism is considered to describe the copolymerization kinetics of ethylene and 1-butane over a Ziegler-Natta catalyst with two different catalyst porosity and rigid catalyst sites based on the kinetic model proposed by Mc-Auley *et al.* (1990). Rates of formation, initiation, propagation and chain transfer are different for each site type. This mechanism comprises of series and parallel elementary reactions as listed in Table 1. The rate constants used in this study are those given by Kinetic and Pseudokinetic (Mc-Auley *et al.*, 1990) and the activation energies are taken from for porous catalysts the effects of adsorption, desorption and surface reaction are included in the rate of chemical reaction. The reactions are listed in Table 1. From the kinetic mechanism, the rate expression for the active sites (r_a) for each species can be written as follows:

r_a = Active site formation – Active site consumption

$$k^n[P^0] - \sum_{j=1}^{2} k_j^i [P_0][M_j] \quad (2)$$

The derivation of the rate expressions based on the kinetic mechanism for rigid catalyst is given in Table 2. The over all rate expression for live and dead moment is represented in equation (3) and (4) respectively, as seen below. Rate expressions for live moments is given as:

$$R^k_{\mu_{n,i}} = -r_{P_0} \times P_{n,i} - (r_{H_2} \times P^k_{n,i}) - (r_{P_{n,i}} \times P_{n,i}) + \delta(n)(\sum_{j=1}^{n} k^h \mu_0 M_i + k^i M_i)$$
$$(1-\delta(n))\sum_{j=1}^{n} k_j^P M_i P_{n-1,j} - \sum_{j=1}^{n} k_j^P M_j P_{n,j} \quad (3)$$

where *δ(n)* is the Kronecker's delta function (e.g., *δ (n)*=1 for n=1 and *δ(n)*=0 for n ≠1). Rate expressions for dead moments is given as:

$$R^k_{\nu_{n,i}} = (k^f[M] + k^h[H_2])\mu_n \quad (4)$$

The dynamic mass balance for the catalyst is given as:

$$\frac{dC_{cat}}{dt} = \frac{F_{cat}}{W_s} - \frac{Q_0 C_{cat} \rho_{cat}}{W_s} \quad (5)$$

Similarly, the mass balance for the potential active sites and active sites are:

$$\frac{d[P^0]}{dt} = \frac{F_{cat} P^0_{in}}{W_S} - \frac{Q_0 P^0 \rho_{cat}}{W_S} - r_{P^0} \quad (6)$$

and

$$\frac{d[P_0]}{dt} = \frac{F_{cat} P_0}{W_S} - \frac{Q_0 P_0 \rho_{cat}}{W_S} - r_{P_0} \quad (7)$$

The rate expression for each species of porous catalyst can be written and the rate expression for the active sites r_a can be written as follows:

$$M_j = \left[\frac{m_T - P_{n,i}/K_D}{1 + P_A K_A}\right] P_A K_A \quad (8)$$

From the kinetic mechanism, the rate expression for the active sites r_a can be written as follows:

r_a = Active site formation – Active site consumption

$$= k^n P^0 - \sum_{j=1}^{2} k_j^i P_0 \left[\frac{M_T - P_{n,i}/k_D}{1 + P_A k_A}\right] P_A k_A$$

$$= k^n P^0 - \sum_{j=1}^{2} k_j^i P_0 M_j \quad (9)$$

4. Experimental study

SiO_2 (PQ3050) was acquired from PQ Corporation (USA). The compound was calcinated at about 400 °C for nearly 5 h before use [19]. Spherical adducted $MgCl_2.nC_2H_5OH$ was prepared according to literature (Shiraishi *et al.*, 1990). Slurry polymerization of ethylene was carried out in a 1-L stainless-steel reactor of Buchi (BDS300), a semibatch type, equipped with a stirrer speed control, temperature and pressure control. The reactor was purged with nitrogen. A volume of 400 mL heptane was charged into the reactor and degassed at least three times. When the polymerization temperature reached the required temperature, the catalyst components were added in the following order; TEA, the solid catalyst, and hydrogen (if any). All the reagents were added as slurry in n-heptane or a gas. The pressure inside the reactor was maintained constant with the monomer gas. Therefore, the required amount of the monomer to feed into the reactor is equal to the consumption of the monomer. At the end of the reaction time, mainly one hour, the monomer feed was stopped. The polymerization waste ruminated by draining the slurry polymer into a small volume of acidified methanol. The polymer obtained was filtered and dried at 70°C for overnight (Zohuri *et al.*, 2001).

5. Catalyst preparation

The $SiO_2/MgCl_2/TiCl_4$ catalyst was prepared using the adducted spherical $MgCl_2.nC_2H_5OH$. The ethanol was chemically removed during the catalyst preparation procedure. The calcinated SiO_2 (2.5 g) and $MgCl_2.nC_2H_5OH$ (2.5 g) were added to a catalyst preparation reactor containing a sinter glass heated with a jacket. The chemicals were suspended in toluene (100 mL), and then $TiCl_4$ (40 mL) was added dropwise, while, the contents of the reactor were stirred at 5 °C. The temperature was raised to 115 °C in increments of 20 °C, while stirring at each step for at least one hour. The product was filtered, and washed with n-heptane (100 mL). Toluene (100 mL) and $TiCl_4$ (40 mL) were added at 40 °C. The temperature was raised to 115 °C incrementally, as before. The final catalyst was filtered, washed with n-heptane to completely remove unreacted $TiCl_4$, and dried. All the steps were carried out under an atmosphere of dried N_2 (Zohuri *et al.*, 2001). Co catalyst is very important to be added with catalyst as particular ratio 2 g of catalyst per 0.8-1 gm of co catalyst as can be shown in the Figure 2.

Figure 2. Side view for experimental study

6. Results and discussion

Figure 3 shows the relation between Al/Ti and production rate of PE. The optimum value for Al/Ti =770/1 molar ratio gives production rate of PE = 1845 at constant reaction temperature = 60 ^oC. Depend on paragraph 2, can see all calculations in Table 3. The average slope = 0.52 and θaverage = 27.49^o, that is, mean Al/Ti ratio has large effects on the system = 30.54%. Figure 4 shows the relation between hydrogen concentration and production rate of PE which is an inverse relation; when the concentration of hydrogen increase, the production rate will be decreased because addition of H2 closes the rate of live reaction and make dead polymer to stop polymerization by competing with monomer in adsorption on active center that reduce polymerization. Also, in Table 4 average slope = 1.3929 and θaverage = 54.32^o, that is, mean H_2 concentration has large effects on the system = 60.36%. Figure 5 shows the relation between reaction temperature and production rate of PE. The optimum value for reaction temperature = 60 ^oC. gives production rate of PE = 1845 at Al/Ti =770/1 molar ratio. In Table 5 the average slope = 1.4885 and θaverage = 89.99^o, that is, mean reaction temperature has largest effects on the system = 99.9%. Figure 6 represents all three effects inside the system that are represented by average angle slope. From equation (1):

θ total=89.99^o + 54.32^o + 27.49^o = 171.8^o
θin the system = 90^o
θinteraction = θ total - θin the system
θinteraction = 171.8^o – 90^o = 81.8^o
θinteraction / θ total ≈ θ2 / θ1

Table 6 shows the percentage effects of a temperature, hydrogen concentration and catalyst ratio in the system and interaction between these inputs variables. Al/Ti has a big interaction effect 28.6 % on the temperature and hydrogen concentration because co catalyst enters as a protect catalyst from poison that leads to increase temperature of reaction that effects on rate of site activation reactions as can be explained in paragraph 2.

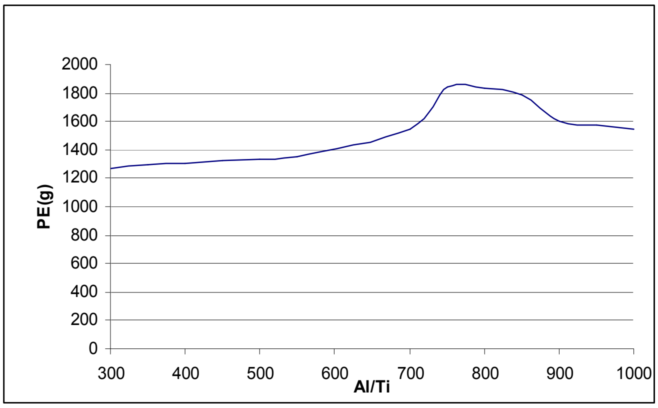

Figure 3. Effect of Al/Ti molar ratio on production rate of polyethylene, temperature 60 °C

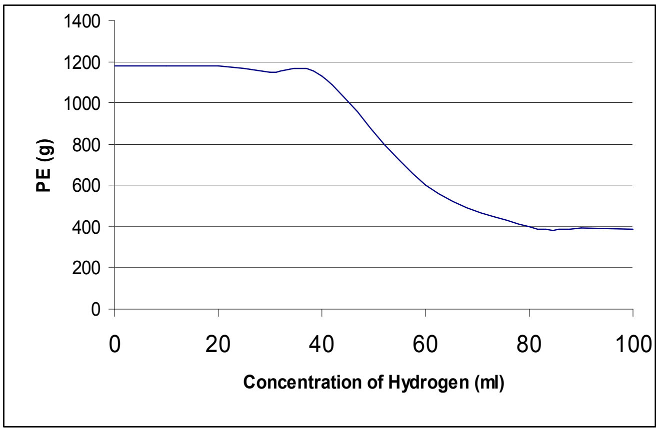

Figure 4. Effect of H_2 concentration on production rate of polyethylene, temperature 60°C, Al/Ti = 770:1

Table 1. Numerical values of the kinetic rate constants for adsorption, surface and desorption reactions inside the catalyst layers

Rate constant (s^{-1}) Activation energy (E) (kcal/mol)	Site type 1	Site type 2
Reactant-adsorption (K_A)	0.001	0.001
E	9	9
Surface reaction (K_s)	0.001	0.001
E	9	9
Product desorption (K_D)	0.00047	0.00047
E	9	9
$M_j + s \rightleftarrows M_{j,s}$	Reactant adsorption	
$M_{j,s} \longrightarrow P_{n,i,s}$	surface reaction	
$P_{n,i,s} \longrightarrow P_{n,i} + s$	product desorption	

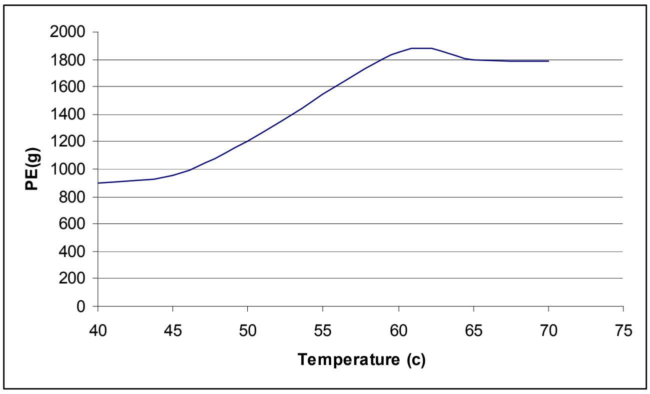

Figure 5. Effect of temperature on production rate of polyethylene, Al/Ti = 770:1

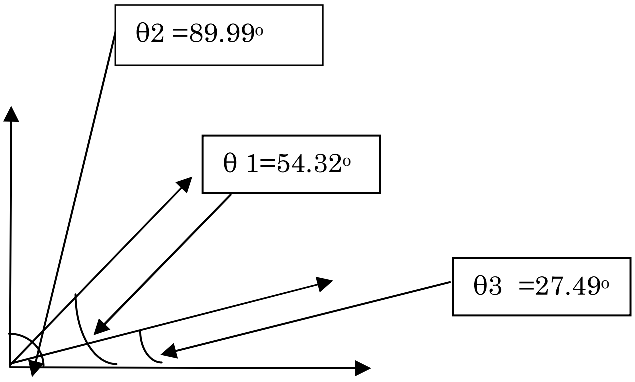

Figure 6. Representation of the average angle slope

Table 2. Kinetic mechanism of olefin copolymerization for rigid Ziegler-Natta catalyst

Spontaneous activation: $P^0 \xrightarrow{k^n} P_0$

Initiation: $P_0 + M_j \xrightarrow{k_j^i} P_{1,j},$ j=1,2

(Formation of $P_{1,i} : P_0 + M_i \xrightarrow{k_i^i} P_{1,i},$ i=1,2)

Propagation: $P_{n,i} + M_j \xrightarrow{k_{i,j}^P} P_{n+1,j}, \quad i, j = 1,2, n = 1,2,...,\infty$

(Consumption of $P_{1,i} : P_{1,i} + M_i \xrightarrow{k_{i,j}^P} P_{2,j}, \quad i, j = 1,2, n = 1,2,...,\infty$)

(Formation of $P_{n,i} : P_{n-1,i'} + M_i \xrightarrow{k_{i',i}^P} P_{n,i}, \quad i', i = 1,2, n = 1,2,...,\infty$)

Chain transfer: $P_{n,i} + M_j \xrightarrow{k_{i,j}^f} P_{1,j} + Q_n, \quad i, j = 1,2, n = 1,2,...,\infty$

$P_{n,i} + H_2 \xrightarrow{k_i^h} P_0^* + Q_n, \quad i, j = 1,2, n = 1,2,...,\infty$

(Formation of $P_{1,i} : P_{n,i'} + M_i \xrightarrow{k_{i',i}^f} P_{1,i} + Q_n, \quad i', j = 1,2, n = 1,2,...,\infty$)

(Consumption of $P_{1,i} : P_{1,i} + M_j \xrightarrow{k_{i,i}^f} P_{1,j} + Q_1, \quad i, j = 1,2$)

(Consumption of $P_{1,i} : P_{1,i} + H_2 \xrightarrow{k_i^h} P_0^* + Q_1, \quad i, j = 1,2$)

Table 3. Calculation of the percent difference for catalyst ratio against output profile

Ratio AlTi (xi)	(xi - xn,i) / xn,i	PE-mmol(yi- yn,i) / yn,i	Slope (k)
300	0.538	0.117	0.217
350	0.461	0.096	0.208
400	0.384	0.088	0.229
450	0.307	0.074	0.241
500	0.23	0.071	0.308
550	0.153	0.065	0.424
700	0.076	0.053	0.697
750	0.153	0.292	1.908
800	0.23	0.289	1.256
850	0.307	0.205	0.667
900	0.384	0.107	0.278
950	0.461	0.086	0.186
1000	0.538	0.079	0.146
Kaverage			0.52
θ Average			27.49o
% effect(θ Average×100)/90°			30.54

Table 4. Calculation the percent difference for hydrogen concentration against output profile

Hydrogen concentration (ml)	(xi - xn,i) / xn,i	PE-mmol(yi- yn,i) / yn,i	Slope (k)
0	1	1.275	1.275
10	0.8	1.225	1.531
20	0.6	1.125	1.875
30	0.4	0.9	2.25
40	0.2	0.5	2.5
60	0.2	0.3	1.5
70	0.4	0.4	1
80	0.6	0.5	0.833
90	0.8	0.512	0.64
100	1	0.525	0.525
Kaverage			1.3929
θ Average			54.32o
% effect(θ Average×100)/90o			60.36%

Table 5. Calculation of the percent difference for reaction temperature against output profile

Temperature (co)	(xi - xn,i) / xn,i	PE-mmol(yi- yn,i) / yn,i	Slope (k)
40	0.272	0.512	1.882
45	0.181	0.489	2.701
50	0.09	0.368	4.088
60	0.09	0.022	0.244
65	0.181	0.001	0.005
70	0.272	0.003	0.011
Kaverage			1.4885
θ Average			89.99o
% effect(θ Average×100)/90o			99.9%

Table 6. Calculation of the percent effects for in the system and interaction between the inputs variables

Action	Temperature	Hydrogen concentration	Ratio AL/Ti
Percentage effects inside the system	52.4	45.66	1.94
Percentage interaction effects	47.6	14.7	28.6

very flexible analysis of polymerization system to reach to important results that can be used and which depend in industry. The most active input parameter is reaction temperature compare to other factors because it is effected 52.4% in the system for production PE and 47.6% for interaction effects between the two factors. Also, hydrogen input factor has big effect on the system because it is effected 45.66% directly in the rate of live and dead polymer for production PE and 14.7% for interaction effects between the two factors. Al/Ti ratio has small effect 1.94% in the system but it is big effect 28.6% in interaction sides between the two factors (reaction temperature and hydrogen concentration). Reaction temperature and hydrogen concentration mainly effect for all active sites of catalyst surface reaction. All these results are very important in industrials of polymerization system. The initial stage of the polymerization, including the reaction of the catalyst with the co-catalyst and the high polymerization activity, broke up the catalyst particles into smaller particles of irregular shape and size. The morphology of the polymer particles was almost the same as that of the catalyst, which reacted with the cocatalyst at the early stage of the polymerization. In addition, the morphology of the particles may be affected by polymerization conditions, such as temperature and monomer pressure. However, the parameters of the initial stages may also be critical.

Nomenclatures

k_i	Rate constant of reaction,1/s
k_A	Thermal conductivity between layers of catalyst particles, J/m^2/s/k
k^n	Rate constant of spontaneous reaction 1/s
k^f	Rate constant of chain transfer 1/s
K^h	Rate constant of chain transfer to hydrogen 1/s
$[M_e]$	Active metal concentration, mol Me/m^3
$[M_i]$	"I"monomer concentration, mol Me/m^3
P_A	Partial pressure of A in gas phase
P^O	Potential active sites kmol/m^3
P_o	Active sites concentration kmol/m^3
S_P^K	Concentration of potential "k" catalyst active sites, mol/m^3
r_a	Rate expression for the active sites kmol/kg.catalyst
$R^k_{\mu n,i}$	Rate expression for live moments
$R^k_{\nu n,i}$	Rate expression for dead moments
R_X^K	Reaction rate of species X at "k" catalyst activesites,mol/m^3/s

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