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Full Length Research Paper

System identification for experimental study for ultra high molecular weight for polyethylene process by using Bi-supported SiO_2 / $MgCl_2$ / $TiCl_4$ catalyst

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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 effect which is equal to 52.4% on the output of the system as compared to the other two factors. Also, hydrogen concentration has big effect which is equal to 45.66% on the output of the system. [Al]/[Ti] molar catalyst ratio has big effect which is equal to 1.94%, 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.

Key words: Catalysts, Ziegler-Natta polymerization, ultracentrifugation, identification.

INTRODUCTION

Fluidized catalytic bed continuous reactors (FCR) entail very complex flow behavior (Ibrehem et al., 2008). More-over, 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 and 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, identification of most input variable effects on the production rate by using experiment work was very little. In 2009, Gholamhossein Zohuri group made a very good experi-ment work design technique 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 polyethylene.

High molecular weight polymers and their morpholo-gical development are the most important achievements of heterogeneous catalyst polymerization of the Ziegler-Natta type (Peacock et al., 2000; Zohuri et al., 2008; Dasilva et al., 2002; Shiraishi et al., 1990). $MgCl_2$ and SiO_2 are the most common bi-supports used to heteroge-nize 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 et al., 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 poly-merization, 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 pro-files are mainly a decay type with very high polymeriza-tion activity at the early stage of the reaction. Therefore, the fast growth of the polymer into the pore and channel of the catalyst

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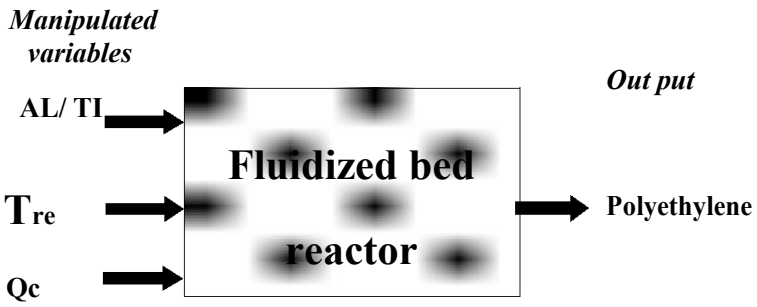

Figure 1. Representation of variables in polymerization system as a MISO system.

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 $MgCl_2$ com-ponents 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).

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 catalyst spherical Ziegler-Natta flow rate, temperature input and hydrogen concentration on production rate of polyethylene.

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 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.

So, the identification steps can be defined for PASA as follows (Ibrahem and 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 use the kaverage slope to find the average angle (θ) that represents the overall effect of each parameter 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 2 . 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.
$15^{o} \geq (\theta) \geq 10^{o}$: Weak effects on the system.
$10^{o} < (\theta)$: Cannot be established.

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

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

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 (Zohuri et al., 2001). 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 polymerrization temperature reached the required temperature, the catalyst

Table 1. Calculation of the percent difference for catalyst ratio against output profile.

Ratio Al/Ti (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			27.49°
%effect (θ average×100)/90°			30.54

Table 2. 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			54.32°
% effect(θ Average×100)/90°			60.36

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 overnight (Zohuri et al., 2001).

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 drop wise, 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 GH et al., 2001).

RESULTS AND DISCUSSION

Figure 2 shows the relation between Al/Ti and production

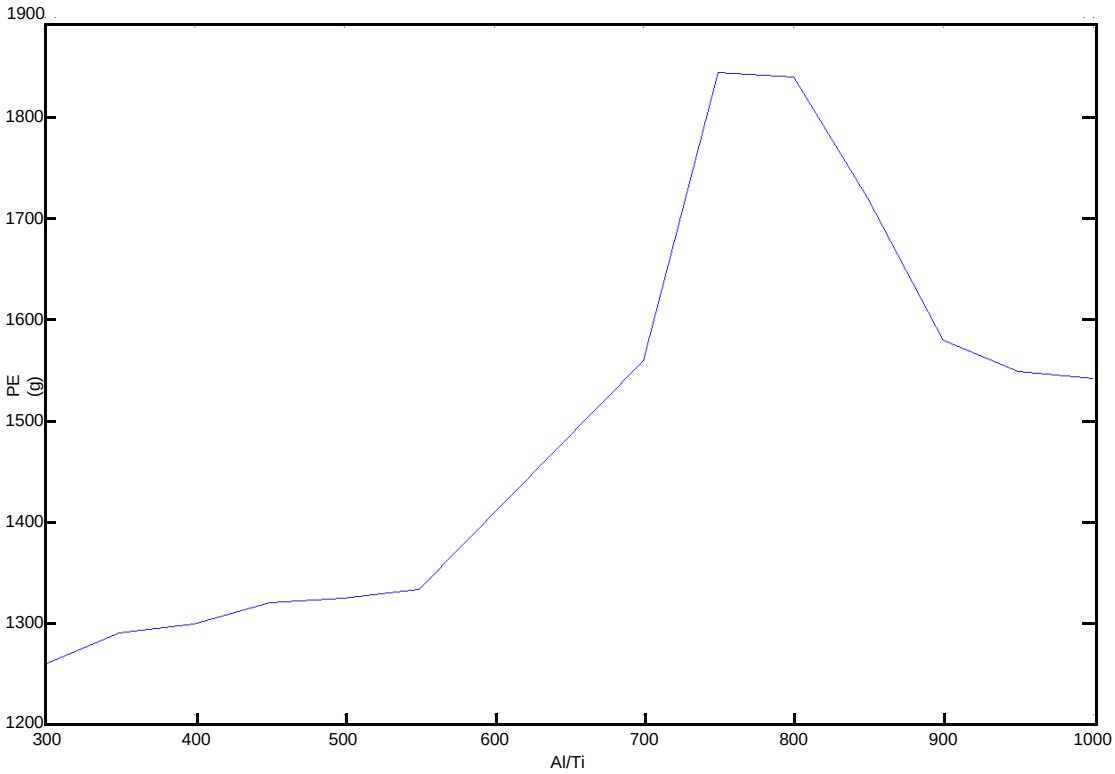

Figure 2. Effect of Al/Ti molar ratio on production rate of polyethylene, temperature 60°C

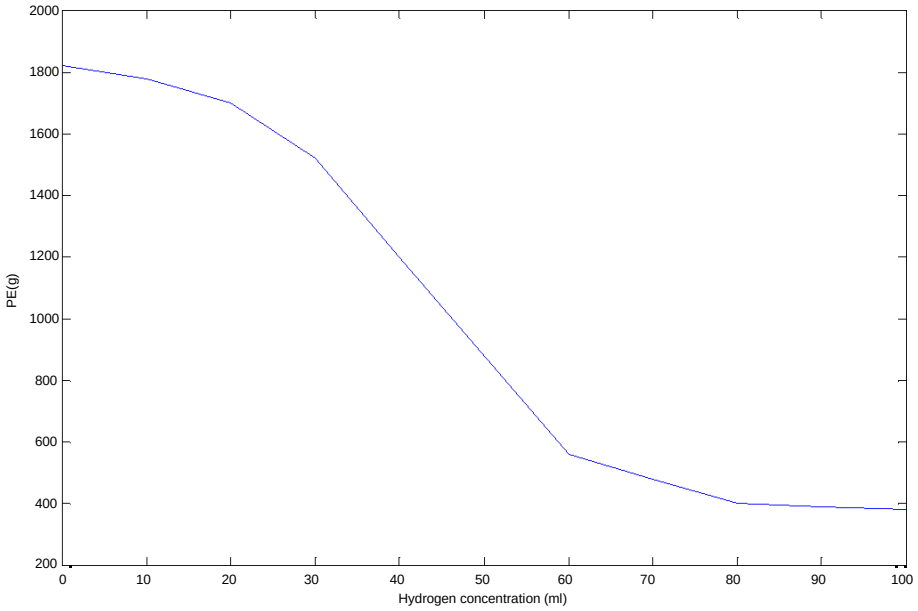

Figure 3. Effect of H_2 concentration on production rate of polyethylene, temperature 60°C, Al/Ti=770:1.

rate of PE. The optimum value for Al/Ti = 770/1 molar ratio gives production rate of PE = 1845 at constant reaction temperature of 60°C. As regard to Figure 2, all calculations are in Table 1. The average slope = 0.52 and θ average = 27.49°, that is, mean Al/Ti ratio has large effects on the system = 30.54%. Figure 3 shows the

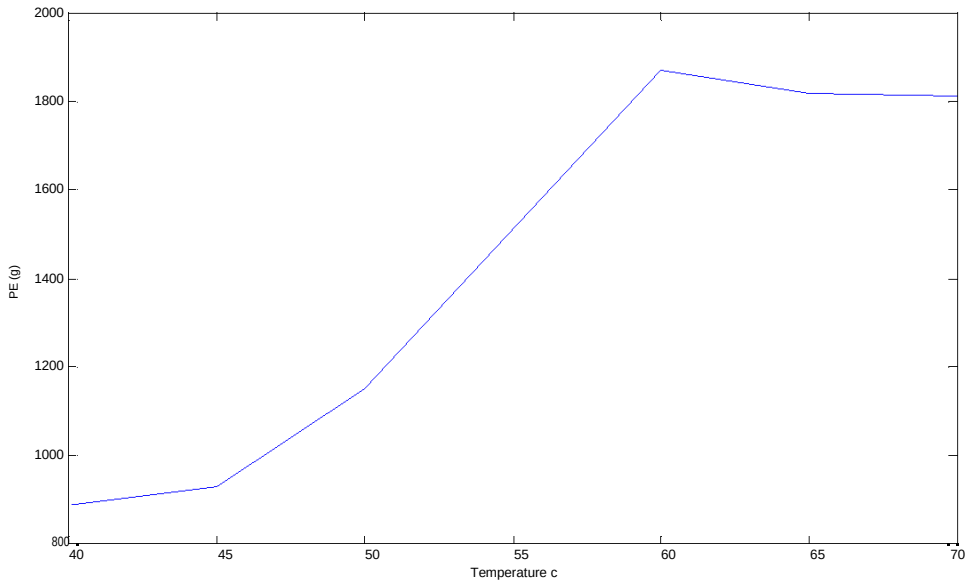

Figure 4. Effect of temperature on production rate of polyethylene, Al/Ti=770:1.

Table 3. Calculation of the percent difference for reaction temperature against output profile.

Temperature (°C)	(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(θaverage×100)/90o			99.9%

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 H_2 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 2, average slope = 1.3929 and θ average = 54.32°, that is, mean H_2 concentration has large effects on the system at 60.36%. Figure 4 shows the relation between reaction temperature and production rate of PE. The optimum value for reaction temperature (60°C) gives production rate of PE = 1845 at Al/Ti =770/1 molar ratio. In Table 3, the average slope = 1.4885 and θ average = 89.99°, that is, mean reaction temperature has largest effects on the system at 99.9%. Figure 5 represents all three effects inside the system that are represented by average angle slope. From equation (1), θ total = 89.99° + 54.32° + 27.49° = 171.8°; θ in the system = 90°; θ interaction = θ total – θ in the system; θ interaction = 171.8° – 90° = 81.8°; θ interaction / θ total ≈ θ2 / θ1

Table 4 shows the percentage effects of a temperature, hydrogen concentration and catalyst ratio in the system and interaction between these inputs variables.

Conclusion

Using this active identification method gives us very flexible analysis of polymerization system to reach important results that can be used and which depend on industry. The most active input parameter is reaction temperature, compared to other factors because it is affected by 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 by 45.66% directly in the rate of live and dead polymer for production PE and 1 4.7% for

Table 4. 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

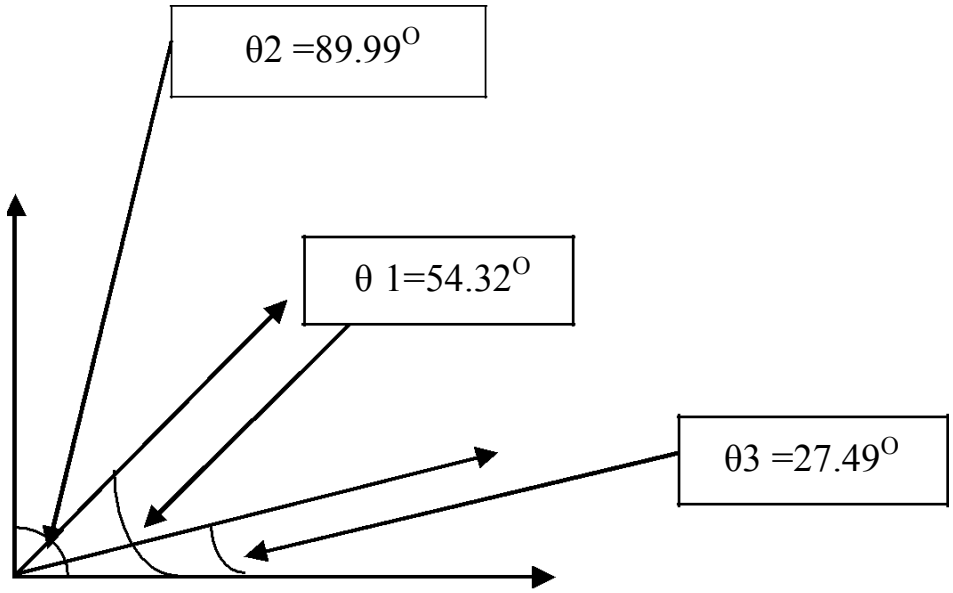

Figure 5. Representation of the average angle slope.

interaction effects between the two factors. Al/Ti ratio has small effect (1.94%) in the system but has big effect (28.6%) in interaction sides between the two factors (reaction temperature and hydrogen concentration). Reaction temperature and hydrogen concentration mainly affect 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 co-catalyst 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.

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