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Investigation of Ethylene Polymerization Using Soluble Cp_2ZrCl_2/MAO Catalytic System via Response Surface Methodology

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ABSTRACT

Response surface methodology was used to investigate the kinetics of slurry homopolymerization of ethylene which was catalyzed by soluble metallocene catalytic system of Cp_2ZrCl_2/MAO. Polymerization temperature, monomer pressure, and molar ratio of cocatalyst to catalyst were considered as the main parameters which affect catalyst activity and viscosity average molecular weight of the final product. A Box-Behnken design was used to produce models for objective responses based on parameters that have significance probabilities (P-value<0.1). It was developed by using the three parameters at three levels including 50, 60, and 70°C for temperature; 2, 4, and 6 bar for pressure; and 3219, 4828.5, and 6438 for molar ratios of cocatalyst to catalyst. Analysis of variance showed that monomer pressure is the most affecting parameter on catalyst activity (P-value<0.0001). It was found that at high levels of cocatalyst concentration, the further increase of its concentration to higher levels decreases the catalyst activity which can be attributed to excessive complexation of MAO with active centres. Polymerization temperature was found to show the significant effect on viscosity average molecular weights of polymers (P-value = 0.0002). It is believed that higher activation energies of chain transfer and deactivation reactions relative to propagation reaction decrease the molecular weight at elevated temperatures. At higher molar ratio of cocatalyst to catalyst, molecular weight also decreases because of more chain transfer to cocatalyst.

Key Words:

ethylene polymerization;
experimental design;
metallocene catalysts;
polymerization kinetics;
response surface methodology.

INTRODUCTION

Development of metallocene/aluminoxane catalytic systems has had a revolutionary effect on production of polyolefins. Remarkable finding of Kaminsky et al. was the starting point of industrial application of metallocene catalysts that has been showed the reaction of small amounts of water in system with aluminum alkyl cocatalysts yields highly active polymerization catalyst [1]. However, the exact structure of methylaluminoxane (MAO) still uncovered is under research [2]. Its structure has been reported to have a marked effect on catalyst activity. Increasing the degree of oligomerization of MAO leads to increase of catalyst activity [1].

The main advantages of metal-

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locene catalysts such as extremely high activity and ability of producing polyolefins with controlled microstructure are responsible for growing interest of academic and industrial researches toward them.

Their structure can be modified by variation of (1) transition metal, (2) ligand, (3) bridge, and (4) substitutes on ligands and bridges to give several number of catalyst types [3]. This controllable catalyst structure allows formation of unique active centres compared to traditional Ziegler-Natta catalysts, which have several types of active centres of very low level of control on their specifications. Because each active centre has its own kinetic rate constants, and makes polymer chains with specific structure, the bulk polymer made with heterogeneous Ziegler-Natta catalysts is in fact a mixture at molecular level. This variety of active centre types in Ziegler-Natta catalysts, leads to complexity of the reaction kinetics and difficulty in controlling the properties of final product.

On the contrary, every aspect of polymer microstructure like molecular weight and its distribution, tacticity, comonomer content and its distribution, and short and long chain branchings and their distribution are adjustable by design of a catalyst structure or controlled combination of different metallocene catalysts [4-10].

Many researchers have attempted to investigate the kinetics of polymerization of olefins with metallocene catalysts. Most of investigations are limited to special polymerization conditions and can not be used for other conditions [11-18]. Thus, investigation of polymerization kinetics in an operational window is very useful which makes one to be able to compare the effects of each parameter at different operational conditions.

Response surface methodology (RMS) is an effective method for developing regression equations that describe interrelations between input parameters and output responses [19]. The goal of this work is to investigate the slurry polymerization of ethylene with soluble Cp_2ZrCl_2/MAO catalyst by using RMS system in a well defined operational window.

EXPERIMENTAL

Materials

The metallocene catalyst Cp_2ZrCl_2 and MAO (10 %wt in toluene) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Polymerization grade ethylene of 99.99% purity was supplied by Iran Petrochemical Co. (Tehran, Iran) and was purified by passing through columns of activated 13X and 4Å molecular sieves. Nitrogen gas of 99.99% purity was purchased from Roham Co. (Tehran, Iran) and was purified by passing through columns of P_2O_5, KOH, activated silica gel, and 4Å molecular sieve. Industrial toluene, supplied by Iran Petrochemical Co. (Tehran, Iran) was further purified through several distillations on sodium wire and benzophenone. Decaline of 97% purity was purchased from Merck Schuchardt OHG (Hohenburn, Germany) and was used with 0.1% antioxidant (2,6-ditert-butyl-*p*-cresol).

Polymerization

All polymerization runs were carried out in a 1L stainless steel Buchi reactor model bmd 300. To ensure the absence of moisture and oxygen in the reactor, it was purged with nitrogen gas at 90°C for about 30 min. The reactor was filled with 500 mL toluene and purged five times by dried nitrogen stream, followed by purging with ethylene gas for further five times, at least. Agitation was started with a paddle mixer at 800 rpm and reactor was filled with ethylene to saturate the toluene. MAO was added to the reactor by means of a syringe. After a few minutes of agitation, catalyst was added in the same manner. After filling of reactor with ethylene and reaching to desired monomer pressure, the reaction was begun by starting the mixing. The reactor temperature was controlled by circulation of water around its jacket. A Huber circulator model Polysat CC3 was used to control the temperature. At the end of the polymerization time, the reaction was terminated by degassing the reactor.

Catalyst concentration was selected in a way to avoid temperature control difficulties and to obtain the measurable amounts of polymerization yield. The online measurement of monomer consumption was carried out by using Pressflow gas controller. Cumulative amount of consumed monomer was reported at time intervals of 1 s. The viscosity average molecular weights of polyethylenes were determined by using Ubbelohde viscometer with decaline at 135°C and Mark-Houwink equation with $k = 6.77 \times 10^{-2}$ ($molg^{-1}$) and $a = 0.67$ [20].

Experimental Design

Response surface methodology was used to design experiments and analyze the effects of considered parameters [19]. Monomer partial pressure, temperature, and cocatalyst concentration were considered as the important parameters that affect on catalyst activity and polyethylene molecular weight. A Box-Behnken design of experiments by each of these parameters at three levels, i.e., polymerization temperatures (50, 60, and 70°C), monomer pressures (2, 4, and 6 bar), and cocatalyst concentrations (3.621×10^{-3}, 5.432×10^{-3}, and 7.243×10^{-3} mol/L) was used to investigate polymerization kinetic in a closed operational window (Table 1).

Standard order of experiments in column 2 of Table 1 is a conventional textbook ordering of the array of low and high factor levels [19].

The standard order of experiments was interrupted randomly to minimize the effects of tolerances of environmental conditions. Column 1 in Table 1 shows the order which was used for performing experiments. Once a model was selected, an analysis of variance was calculated to assess how closely the model represents the data. The analysis of variance was carried out to compare the relative significance of each parameter and develop a polynomial model for each objective response.

RESULTS AND DISCUSSION

Table 1 lists the Box-Behnken experimental design employed in this work. An additional run was carried out for testing reproducibility of experimental results. Results of polymerization yield and viscosity average molecular weights ($\overline{M_v}$) are listed in Table 1. Catalyst activities can be calculated by dividing yields to catalyst concentration and polymerization time. Equilibrium concentrations of ethylene in toluene, estimated from Peng-Robinson equation of state based on algorithm presented by Atiqullah et al. are also listed in Table 1 [21].

Results of Table 1 were analyzed and the best polynomial models were developed. Regression analysis was conducted using backward elimination procedure. In this method a general quadratic equation was considered for objective response. Then significance probabilities (P-value) were calculated and parameters with P-

Table 1. Design of experiments and polymerization results.

Run	Standard order	T (°C)	P (bar)	MAO (mol/L×10³)	M* (mol/L×10)	Yield (g)	$\overline{M_v}\times10^{-5}$
1	14	60	4	5.432	3.51	37.00	2.99
2	3	50	6	5.432	6.13	46.78	3.65
3	2	70	2	5.432	1.42	23.38	1.47
4	6	70	4	3.621	3.08	37.39	2.51
5	9	60	2	3.621	1.66	33.00	2.84
6	7	50	4	7.243	4.02	39.21	3.38
7	4	70	6	5.432	4.74	36.86	2.13
8	1	50	2	5.432	1.94	26.88	3.97
9	12	60	6	7.243	5.38	39.36	3.47
10	10	60	6	3.621	5.38	44.89	3.27
11	5	50	4	3.621	4.02	41.02	4.46
12	8	70	4	7.243	3.08	32.93	2.55
13	13	60	4	5.432	3.51	37.90	2.80
14	11	60	2	7.243	1.66	26.27	2.13

(*)M = monomer concentration. Polymerization conditions: [Zr]: 1.125 × 10-6 mol/L, toluene: 500 mL, stirrer speed: 800 RPM, reaction time: 1 h.

Table 2. Results of analysis of variance.

	Catalyst activity		$\overline{M_v}$	
	F-value	P-value	F-value	P-value
Model	32.39	< 0.0001	11.17	0.0013
T (°C)	15.59	0.0034	38.95	0.0002
P (bar)	97.53	< 0.0001	4.81	0.0648
[Al]/[Zr]	9.83	0.0120	3.69	0.0886
T × [Al]/[Zr]	-	-	3.75	0.0800
P^2	6.59	0.0303	-	-
Lack of fit	12	0.2198	9.12	0.2509
R- squared	0.9350		0.8388	

values higher than 0.1 were eliminated. A parameter has a significant effect on the objective response whenever the corresponding P-value be lower than 0.1. Regression analysis was carried out again with new polynomial equation and elimination procedure was repeated until an equation was produced by parameters with P-values less than 0.1. Table 2 lists P-values for parameters of final derived polynomial equations. Response equations are expressed only in terms of significant parameters.

Equation 1 describes the surface response of catalyst activity in (kg/mol Zr.h) as a function of polymerization temperature (T) in Celsius, monomer pressure (P) in bar, and molar ratio of cocatalyst to catalyst ([Al]/[Zr]). For comparing the effects of each parameter, they should be coded in a way to equalize their values. All parameters were coded to vary between -1 and 1 while their central values were zero. Eqn (2) describes the developed model in terms of coded factors:

$$\text{Activity} = 31858.89 - 259.22 \times T + 8393.33 \times P - 1.28 \times [Al]/[Zr] - 643.89 \times P^2 \quad (1)$$

$$\text{Activity} = 33400 - 2592.22 \times T + 6484.44 \times P - 2058.89 \times [Al]/[Zr] - 2575.56 \times P^2 \quad (2)$$

Figure 1 shows the differences between actual and predicted catalyst activities. Deviation from line of 45º indicates the amount of difference between measured and predicted values. It shows that these predictions are very close to measured values.

Figure 2 shows the surface plot of catalyst activity as a function of temperature and pressure at the middle level of [Al]/[Zr]. As it may be concluded from eqn (2) and Figure 2, temperature and [Al]/[Zr] ratio have negative effects on catalyst activity while pressure has positive one.

According to Table 2 pressure is the most affecting parameter on catalyst activity. F-value is a test for comparing model variance with residual (error) variance. The model F-value of 32.39 implies the model is valid. There is only a 0.01% probability that this large model F-value could be due to noise. The lack of fit F-value of 12.00 implies that the lack of fit is not high relative to the pure error. There is a 21.98% probability that this lack of fit F-value could occur due to noise.

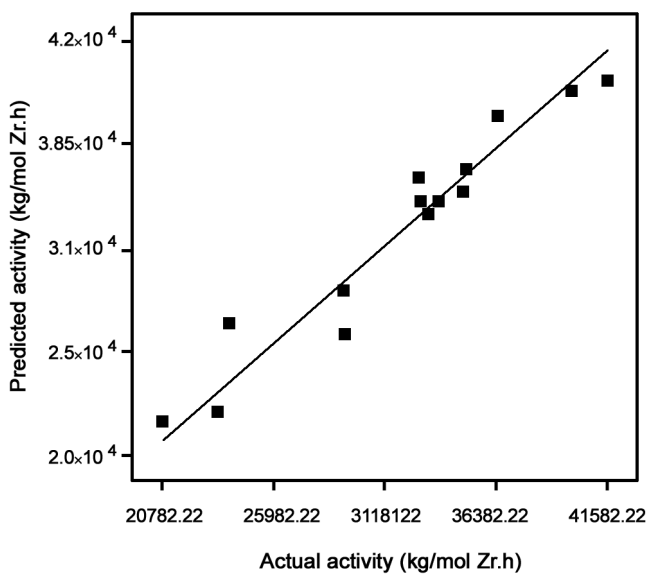

Figure 1. Plot of differences between actual and predicted catalyst activities.

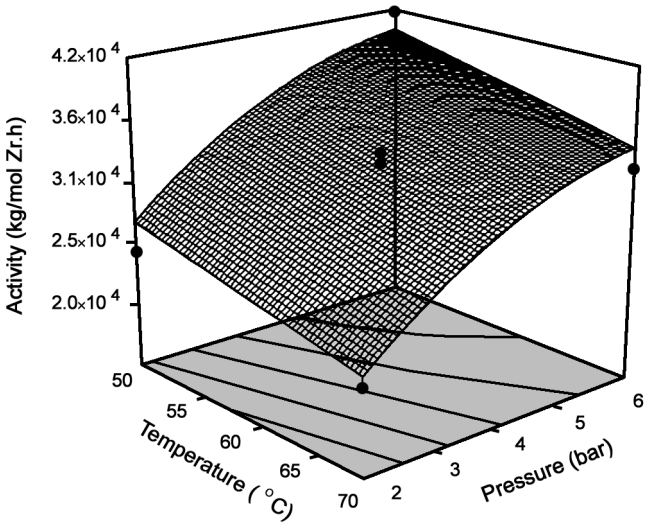

Figure 2. Surface plot of catalyst activity as a function of temperature and pressure at the middle level of [Al]/[Zr] molar ratio.

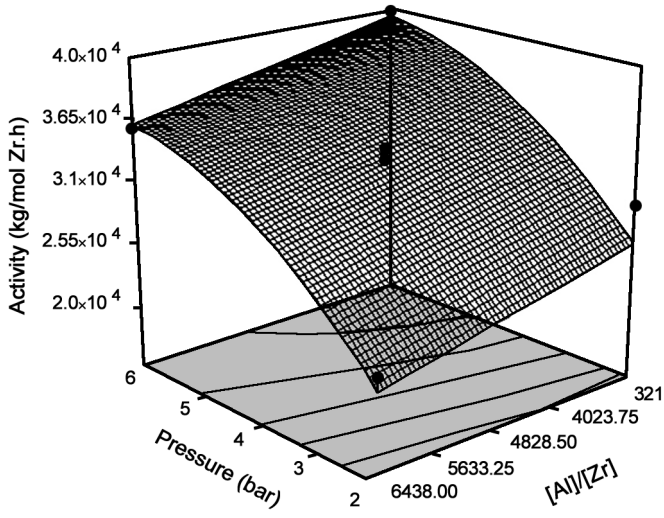

Figure 3. Surface plot of catalyst activity as a function of [Al]/[Zr] molar ratio and pressure at the middle level of temperature.

Polymerization rate (R_p) is a direct function of monomer concentration as shown in eqn (3) where k_p is kinetic coefficient of chain propagation reaction and C* is the concentration of active centres:

$$R_p = k_p C^* [M] \quad (3)$$

Thus, catalyst activity would increase at higher monomer pressures. In addition, polymerization rate is a function of temperature since the concentration of active centres, ethylene solubility, and the kinetic rate constants are dependent on temperature and the kinetic rate constants were assumed to have Arrhenius relation with temperature. On the other hand, decline of catalyst activity is mainly due to decrease of monomer solubility in toluene according to Table 1.

It has been found for some zirconocene/MAO catalytic systems, that at high levels a further increase in [Al]/[Zr] ratio to higher values would cause a decrease in catalyst activity [15,22] which is observed in Figure 3. Chien et al. have reported that the activity of $Et(IndH4)_2ZrCl_2$/MAO catalyst system in propylene polymerization increases by increasing of MAO concentration to [Al]/[Zr] molar ratio of about 3000 and then, decreases at higher ratios. Besides they have reported a linear increase of catalyst activity by increasing of MAO concentration in $Et(Ind)_2ZrCl_2$/MAO catalyst system to [Al]/[Zr] ration of about 1×10^5 [22]. Charpentier has reported that for average activity of Cp_2ZrCl_2/MAO catalyst system in polymerization of ethylene, the maximum is reached at the [Al]/[Zr] molar ratio of 1600 which remains constant up to the highest studied [Al]/[Zr] molar ratio of 3200 [13]. In this work, we have found that catalyst activity of Cp_2ZrCl_2/MAO catalyst system in ethylene polymerization decreases at higher [Al]/[Zr] molar ratios above 3200. Chien et al. have explained that the linear increase in activity of MAO at low [Al]/[Zr] molar ratios is a reflection of the formation of active centres, and the decrease at high amounts of MAO might be attributed to excessive complexation of MAO with active centres. Therefore, the vacant coordination positions at these active centres become unavailable for monomer complexation [22].

Eqns (4) and (5) describe the surface response for $\overline{M}_v$ as a function of polymerization temperature in Celsius, monomer pressure in bar and [Al]/[Zr] in terms of actual and coded factors, respectively:

$$\overline{M}_v = 1316661 - 16900 \times T + 13187 \times P - 116 \times [Al]/[Zr] + 1.74 \times T \times [Al]/[Zr] \quad (4)$$

$$\overline{M}_v = 297285 - 85000 \times T + 26375 \times P - 19375 \times [Al]/[Zr] + 28000 \times T \times [Al]/[Zr] \quad (5)$$

Figure 4 shows the differences between actual and predicted values of $\overline{M}_v$. It demonstrates that predicted val-

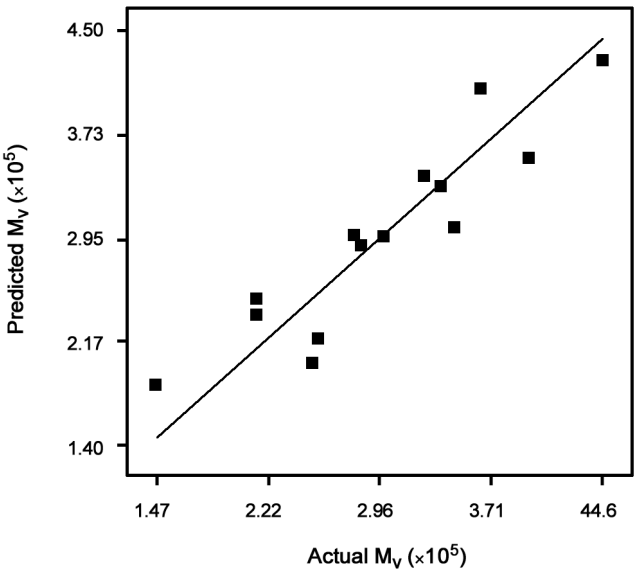

Figure 4. Plot of differences between actual and predicted $\overline{M_v}$ values.

ues are close to measured molecular weights. Surface plot of $\overline{M_v}$ as a function of temperature and pressure at the middle level of [Al]/[Zr] molar ratio is shown in Figure 5. It is obvious that temperature and [Al]/[Zr] molar ratios have negative effect on $\overline{M_v}$ while pressure has positive one. According to Table 2 temperature is the most affecting parameter on $\overline{M_v}$. The model F-value of 11.71 implies that the model is valid. There is only a 0.13% probability that this large model F-value could be due to noise. The lack of fit F-value of 9.12 implies that the lack of fit is not significant relative to the pure error. There is a 25.09% probability that this lack of fit F-value could occur due to noise.

Instantaneous chain length is a function of polymerization kinetics according to eqn (6) where k_{tm} and k_{tc} are kinetic rate constants of chain transfer to monomer and cocatalyst, respectively and [Al] is MAO concentration:

$$X_n = \frac{R_p}{R_{tr} + R_d} = \frac{k_p[M]}{k_{tm}[M] + k_{tc}[Al] + k_d} \quad (6)$$

According to this equation, the molecular weight is a direct function of monomer pressure in the absence of chain transfer to monomer, but it would reach a constant value of k_p/k_{tm} at high monomer concentrations if chain transfer to monomer exists. According to this fact it can be concluded that, in current polymerization, chain transfer to ethylene is a significant termination mechanism and cannot be ignored in kinetic analysis, particularly at high ethylene concentrations. In addition $\overline{M_v}$ decreases by temperature, because activation energies of chain transfer and deactivation reactions are higher than activation energy of propagation reaction [23,24].

Figure 6 shows surface plot of $\overline{M_v}$ as a function of temperature and [Al]/[Zr] molar ratio at the middle level of pressure. Molecular weight decreases as the [Al]/[Zr] molar ratio increases, because of more chain transfer to cocatalyst. The interaction between temperature and [Al]/[Zr] molar ratio is also an important factor as is

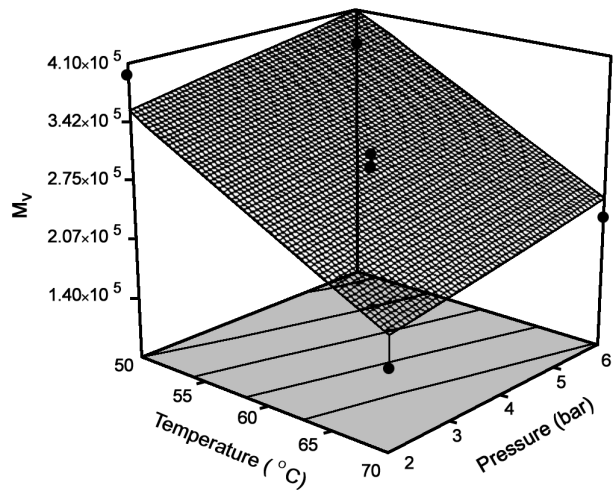

Figure 5. Surface plot of $\overline{M_v}$ as a function of temperature and pressure at the middle level of [Al]/[Zr] molar ratio.

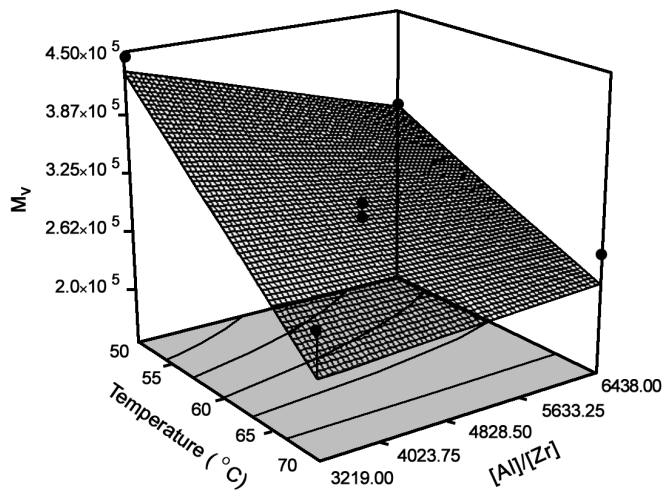

Figure 6. Surface plot of $\overline{M_v}$ as a function of temperature and [Al]/[Zr] molar ratio at the middle level of pressure.

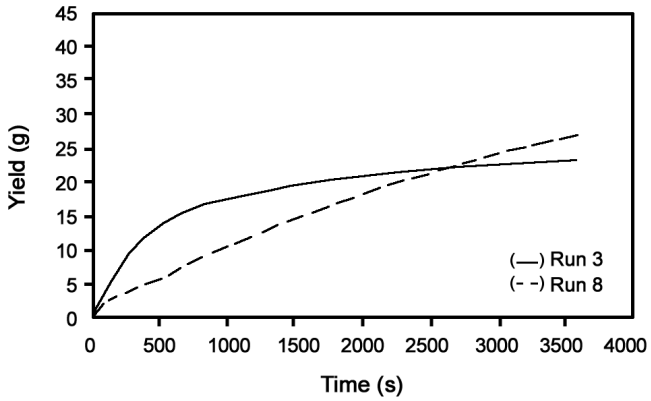

Figure 7. Plots of polymerization yield vs. time, for three temperatures as experimental conditions were described in Table 1.

shown in Table 2. The positive sign for the interaction term in eqns (4) and (5) indicates that they have synergistic effect as shown in Figure 6. $\overline{M}_v$ value would increase more rapidly when temperature and [Al]/[Zr] molar ratio are at their lowest levels.

Figure 7 shows instantaneous yield calculated from online measurement of monomer consumption for two runs. These runs differ only in polymerization temperature. By increasing temperature, peak of reaction rate or initial slop of yield increases as a result of high activation energy of initiation reaction. On the other hand, final slop of yield reduces because of more increase in deactivation rate relative to propagation. Monomer pressure and [Al]/[Zr] molar ratio do not make changes in shape of yield curve because they have not effects on kinetic constants. They may only affect the size of curves. As shown in Figure 8, there are no significant differences in shapes of curves when [Al]/[Zr] molar ratio varies.

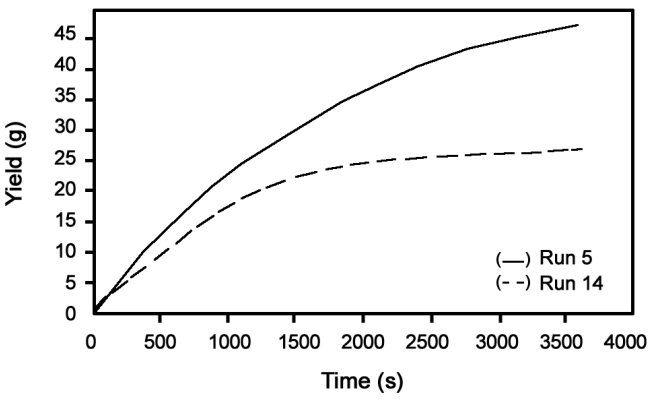

Figure 8. Plots of polymerization yield vs. time, for three [Al]/[Zr] molar ratios as experimental conditions were described in Table 1.

CONCLUSION

Response surface methodology was used to investigate kinetics of ethylene polymerization catalyzed by soluble metallocene catalytic system of Cp_2ZrCl_2/MAO. Polymerization temperature, monomer pressure, and [Al]/[Zr] molar ratio were considered as the most affecting parameters. A Box-Behnken design was developed by these three parameters while three levels were considered for each of them. Catalyst activity and viscosity average molecular weight were selected as the objective responses. Analysis of variance was used to find relative significance of parameters and the best model.

Pressure was found to be the most affecting parameter on catalyst activity while temperature was the most affecting parameter on viscosity average molecular weight. Activity increased by monomer pressure as expected. Influence of polymerization temperature was less noticeable, which decreased catalyst activity.

Catalyst activity was also decreased by [Al]/[Zr] molar ratio. It was probably due to excessive complexation of MAO to active centres at high MAO concentrations, which brings vacant sites unachievable for monomers. $\overline{M}_v$ decreased by polymerization temperature because of more relative growth of chain transfer and deactivation rates. Pressure increased $\overline{M}_v$ by less impact as a result of chain transfer to monomer. Interaction between temperature and [Al]/[Zr] molar ratio parameters was also an effective factor which increases $\overline{M}_v$ more when they were at their lowest levels.

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