

Polymerization of propylene with Ziegler–Natta catalyst: optimization of operating conditions by response surface methodology (RSM)

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Abstract Optimization of operational conditions for the polymerization of propylene with Ziegler–Natta catalyst was carried out via RSM. Response surface methodology (RSM) based on a three-level, four-variable Box–Behnken design was used to evaluate the interactive effects of reaction conditions such as reaction temperature (60–80 °C), monomer pressure (5–8 bar), hydrogen volume (130–170 mL), and cocatalyst to catalyst ratio (Al/Ti, 340–500) on the catalyst activity and melt flow rate (MFR). The optimum reaction conditions derived via RSM were: temperature 70 °C, pressure 8 bar, hydrogen volume 151 mL, and cocatalyst to catalyst ratio 390. The experimental catalyst activity and MFR were 8 g polypropylene/mg catalyst and 10.9 g/10 min, respectively, under optimum conditions. Optimum values were determined from process cost point of view and offered better operational conditions.

Keywords Response surface methodology (RSM) · Box–Behnken design · Propylene polymerization · Ziegler–Natta · Catalyst activity · MFR

Introduction

A polymer product is composed of macromolecules with different molecular weights, and the processability and subsequent utility of a polymer product, depends greatly on the molecular weight distribution (MWD) of the macromolecules. Since MWD is influenced strongly by the polymerization reactor operating conditions, the production of a high quality polymer requires optimal operation of the reactor. In the polymer industry, batch and semi-batch reactors are widely used for the

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production of low volume high-value polymers. In these reactors, it is essential to operate the reactors tightly according to an optimal recipe. The recipe includes the loading conditions, reactor temperature profile, and feed rate profiles. The recipe is usually determined by trial and error method, dynamic optimization, experience, experimentation, or combination of these [1]. Traditionally, trial and error method has been practiced to optimize operating conditions. These studies were conducted by monitoring the influence of one factor at a time on an experimental response. While only one parameter is changed, others are kept at a constant level. This

Table 1 Experimental Box–Behnken design runs and corresponding results (the responses)

Run	Factor 1 temperature (°C)	Factor 2 pressure (bar)	Factor 3 hydrogen std. volume (mL)	Factor 3 cocatalyst to catalyst ratio (Al/Ti)	Response 1 catalyst activity (g polypropylene/ mg catalyst)	Response 2 MFR (g/10 min)	Isotacticity index (%)
1	70	7	140	410	7.4	15.9	99.7
2	70	7	170	340	4.9	13.7	99.4
3	60	5	140	410	3.9	11.6	–
4	70	5	130	410	3.6	37.3	–
5	70	7	140	410	7.4	15.9	99.7
6	60	7	140	340	4.8	5.7	98.1
7	70	7	140	410	7.4	15.9	99.7
8	70	8	140	410	5.5	17.9	–
9	80	7	140	500	5.4	38.4	99.1
10	80	8	140	410	6	23.8	–
11	80	7	170	410	2.5	38.0	98.7
12	80	7	130	410	4.2	37.0	99.3
13	70	8	140	340	6	10.7	–
14	70	5	140	340	4.9	39.1	–
15	80	7	140	340	3.9	32.9	98.5
16	80	5	140	410	3.8	49.0	–
17	70	5	170	410	2.4	31.4	–
18	60	8	140	410	5.9	4.1	–
19	60	7	140	500	3.9	6.1	98.8
20	70	8	130	410	5.4	15.5	–
21	70	7	130	500	5	17.3	99.5
22	70	7	170	500	2.9	20.2	98.7
23	70	8	140	500	6.7	18.5	–
24	70	7	140	410	7.4	15.9	99.7
25	70	7	130	340	4.3	18.1	99.3
26	60	7	170	410	3.8	8.3	96.7
27	70	5	140	500	2.9	30.2	–
28	70	7	140	410	7.4	15.9	99.7
29	60	7	130	410	3	10.2	97.7

optimization technique is called one-variable-at-a-time. Its major disadvantage is that it does not include the interactive effects among the variables studied. As a consequence, this technique does not depict the complete effects of the parameter on the response [2–4]. Another disadvantage of the one-factor optimization is the increase in the number of experiments necessary to conduct the research, which leads to an increase in time and expenses as well as an increase in the consumption of reagents and materials. As a solution, the statistical method of response surface methodology (RSM) has been proposed to include the influences of individual factors as well as their interactive influences by fitting of a polynomial equation to the experimental data. RSM which is a technique for designing experiment helps researchers to build models, evaluate the effects of several factors and achieve the optimum conditions for desirable responses in addition to reducing the number of experiments [5, 6]. Analysis of variance (ANOVA) provides the statistical results and diagnostic checking tests which enables researchers to evaluate adequacy of the models. Therefore before applying the RSM methodology, it is necessary to choose an experimental design that will define which experiments should be carried out in the experimental region being studied. Experimental design is defined by a matrix composed by the different level combinations of the variables studied. There are some experimental matrices for this purpose. Experimental designs for first-order models (e.g., factorial designs) can be used when the data set does not present

Table 2 ANOVA results for parameters of the catalyst activity response

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	69.58	14	4.97	88.58	<0.0001 ^a
Temperature (A)	0.10	1	0.10	1.84	0.1961 ^b
Pressure (B)	16.44	1	16.44	293.00	<0.0001 ^a
Hydrogen volume (C)	1.82	1	1.82	32.53	<0.0001 ^a
Cocatalyst to catalyst (D)	2.55	1	2.55	45.49	<0.0001 ^a
AB	0.028	1	0.028	0.50	0.4926 ^b
AC	1.45	1	1.45	25.78	0.0002 ^a
AD	1.43	1	1.43	25.46	0.0002 ^a
BC	0.47	1	0.47	8.29	0.0121 ^a
BD	2.27	1	2.27	40.48	<0.0001 ^a
CD	2.16	1	2.16	38.45	<0.0001 ^a
A ²	19.46	1	19.46	346.83	<0.0001 ^a
B ²	2.15	1	2.15	38.37	<0.0001 ^a
C ²	23.35	1	23.35	416.28	<0.0001 ^a
D ²	8.32	1	8.32	148.24	<0.0001 ^a
Residual	0.79	14	0.056		
Lack of fit	0.79	10	0.079		
Pure error	0.000	4	0.000		
Cor total	70.36	28			

^a Significant at “Prob > F” less than 0.05

^b Insignificant at “Prob > F” more than 0.05

curvature [4, 7]. However, to approximate a response function to experimental data that cannot be described by linear functions, experimental designs for quadratic response surfaces should be used, such as three level factorial, Box–Behnken, central composite, and Doehlert designs. In the experimental design there are “Factors” or independent variables which are experimental variables that can be changed independently of each other. Each variable has “Levels” which are different values of a variable at which the experiments must be carried out. In each experimental design, the measured values of the results from experiments are “Responses” or dependent variables. Using RSM requires special precautions to be taken to determine all critical variables sufficiently as well as not to work with too many variables over wide ranges [8].

Motivation for this work comes from the need for more efficient operation of existing industrial semi-batch polymerization reactors. To realize this objective, the approach of calculating an optimal recipe is used.

In the present study, catalyst activity and melt flow rate (MFR) from the slurry polymerization of propylene using a highly active Ziegler–Natta catalyst, and operating conditions to get a reasonable catalyst activity and MFR, are discussed and optimized via RSM for batch runs designed with Box–Behnken. Four factors; the polymerization temperature and pressure, hydrogen volume as a chain transfer

Table 3 ANOVA results for parameters of the MFR response

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> value	Prob > <i>F</i>
Model	3923.48	14	280.25	35.97	<0.0001 ^a
Temperature (A)	2011.31	1	2011.31	258.18	<0.0001 ^a
Pressure (B)	608.70	1	608.70	78.14	<0.0001 ^a
Hydrogen volume (C)	6.18	1	6.18	0.79	0.3883 ^b
Cocatalyst to catalyst (D)	1.86	1	1.86	0.24	0.6326 ^b
AB	73.02	1	73.02	9.37	0.0085 ^a
AC	2.37	1	2.37	0.30	0.5896 ^b
AD	7.79	1	7.79	1.00	0.3342 ^b
BC	15.71	1	15.71	2.02	0.1775 ^b
BD	68.54	1	68.54	8.80	0.0102 ^a
CD	9.83	1	9.83	1.26	0.2803 ^b
A ²	52.03	1	52.03	6.68	0.0216 ^a
B ²	51.74	1	51.74	6.64	0.0219 ^a
C ²	54.52	1	54.52	7.00	0.0192 ^a
D ²	5.95	1	5.95	0.76	0.3969 ^b
Residual	109.07	14	7.79		
Lack of fit	109.07	10	10.91		
Pure error	0.000	4	0.000		
Cor total	4032.55	28			

^a Significant at “Prob > *F*” less than 0.05

^b Insignificant at “Prob > *F*” more than 0.05

agent and cocatalyst to catalyst ratio, were selected as independent parameters while catalyst activity and MFR were selected as responses or dependent parameters. The batch data were analyzed through Design-Expert 8.0 software and optimum operational parameter values were determined for maximum catalyst activity.

Experimental

Materials

Polymerization-grade propylene with high purity was obtained from Arak Petrochemical Co., Iran. High purity *n*-heptane provided by Bandar Imam Petrochemical Co., Iran. Hydrogen 99.99% purity and argon were provided by Roham Gas Co., Tehran, Iran. Triethyl aluminum (TEA) with purity of 93% and Donor were obtained from Merck, Germany. The Ziegler–Natta catalyst was purchased from Maroon Petrochemical Co., Iran.

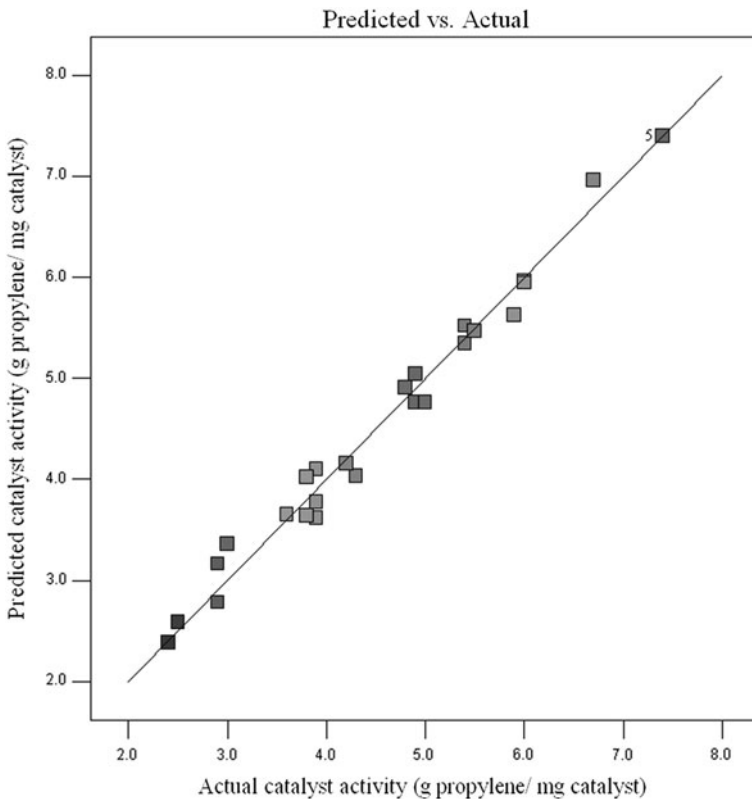


Fig. 1 Experimental catalyst activity versus predicted catalyst activity

Catalyst preparation

The catalyst system used was a commercially available Ziegler–Natta catalyst and composed of TiCl_4 crystals over a magnesium dichloride (MgCl_2) support. It contained triethyl aluminum (TEA) as a cocatalyst, di-methoxy ethyl cyclohexyl silane (DiMECHS) as the external electron donor for regulation of stereo-specificity and di-butyl phthalate (DiBPH) as the internal electron donor. The final catalyst

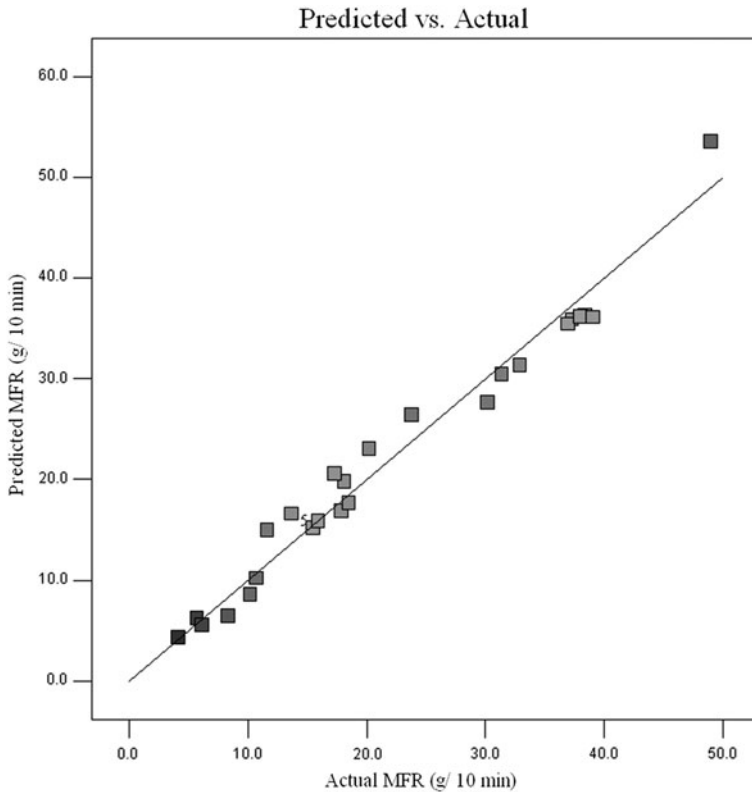


Fig. 2 Experimental MFR versus predicted MFR

Table 4 Model summary statistics

Response	P^a	R^2	Adjusted R^2	AP ^b	SD ^c	CV% ^d	PRESS ^e
Catalyst activity	<0.0001	0.9888	0.9777	29.451	0.24	4.82	5.38
MFR	<0.0001	0.9730	0.9459	24.545	2.79	13.17	1024.57

^a Probability of error

^b Adequate precision

^c Standard deviation

^d Coefficient of variance

^e Predicted residual error sum of squares

titanium content was 2.7 wt%. The catalyst was prepared in a glove box under argon atmosphere where the moisture and oxygen was measured and kept below 10 ppm.

In all of the polymerization tests, the Al/Si ratio was kept constant at value of 20 and typically 10 mg of catalyst was used.

Polymerization procedure

Polymerization reactions were carried out in a 1 L stainless steel Büchi reactor. Utility oil in the reactor jacket was used for cooling/heating and temperature control. The reaction mixture was stirred continuously with a speed controlled stirrer of Büchi Magnetic Drives (bmd 300) equipped with an anchor blade impeller. The propylene feed line was equipped with a mass flow meter (Brooks Instruments, Netherlands), measuring propylene feed rate continuously. All reaction variables were stored in a standard PC process computer, which was connected with the reactor instruments through a data acquisition board. Data acquisition and control algorithms were implemented with software Propylene Soft v1.0.4, developed by current research team, manipulating the data acquisition board.

Before starting reaction, the reactor was warmed up to 110 °C and then purged with argon to remove oxygen and humidity. For start-up, the reactor was cooled down to 45 °C while kept purging with argon. The reactor was then charged with 500 mL *n*-heptane under argon atmosphere, at ambient temperature. The solvent kept over

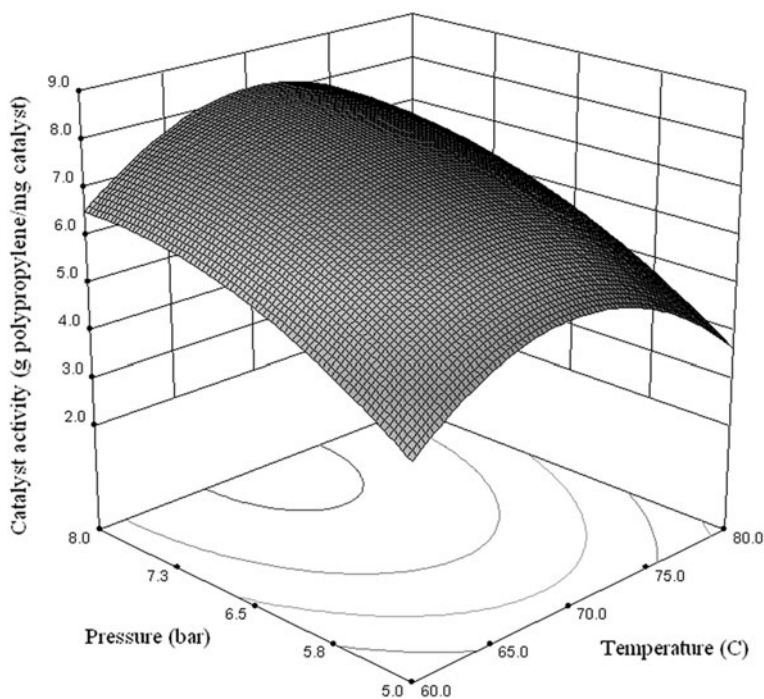


Fig. 3 Catalyst activity as a function of temperature and pressure

4 Å/13X type molecular sieves to keep its water content below 2 ppm. Afterwards, TEA/donor mixture, diluted in *n*-heptane was transferred to the reactor using special container under argon atmosphere. After 5 min hydrogen was fed into the reactor vessel by Büchi press flow gas controller (bpc 6010). After hydrogen addition, the desired amount of catalyst in heptane diluent and calculated amount of extra TEA/donor mixture due to the weight of added catalyst were transferred to the reactor using special containers under argon atmosphere. As soon as the last injection was carried out, the propylene valve was opened and the software was started to regulate the flow of propylene monomer or to control the reactor pressure. In order to reach the desired operating conditions, heating of the reactor and continuous feeding of propylene were started simultaneously. Therefore in this case, a so-called non-isothermal pre-polymerization was used. According to the desired reaction temperature, it was taken 10–15 min to heat the reactor from 45 °C up to the reaction temperature. After the prescribed polymerization time, typically 2 h, the polymerization reaction was halted by opening the vent valve, allowing the unreacted monomer to evaporate quickly. Then the reactor was opened and the product was dried overnight in an oven at 40 °C.

Experimental design and data analysis

The Design-Expert 8.0 software was used for the statistical design of experiments and data analysis. In order to ascribe the effect of factors on response surface in the region of investigation, a Box–Behnken design with four factors at three levels was

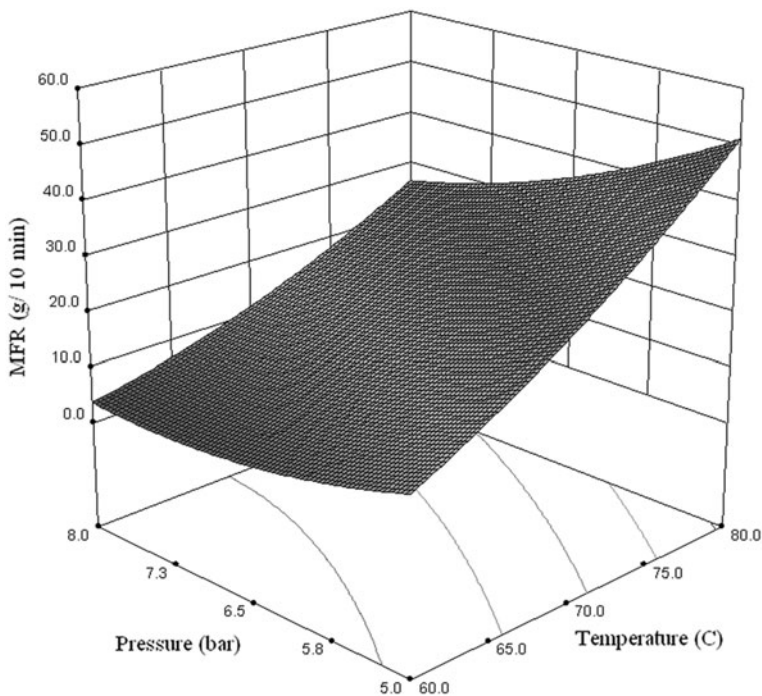


Fig. 4 MFR as a function of temperature and pressure

performed. Investigated factors as the reaction conditions, which were considered to have the greatest influence on catalyst activity and MFR were: the polymerization temperature and pressure, hydrogen volume as a chain transfer agent and ratio of cocatalyst to catalyst.

Box and Behnken suggested how to select points from the three-level factorial arrangement, which allows the efficient estimation of the first- and second-order coefficients of the mathematical model. This design is, in this way, more efficient and economical than its corresponding 3^k designs, mainly for a large number of variables. In Box–Behnken design [4, 9, 10], the experimental points are located on a hypersphere and its principal characteristics are:

1. Experiment number according to $N = 2k(k - 1) + cp$, where k is the number of factors and cp is the number of the central points;
2. All factor levels have to be adjusted only at three levels.

Twenty-nine experiments were augmented with five replications at the central point to evaluate the pure error. The first five columns of Table 1 show run number and experimental conditions of the runs arranged by Box–Behnken design and the last column shows isotacticity index of some of the runs as one of the experimental results. Performance of the process was evaluated by analyzing the responses, which were catalyst activity and MFR. In the optimization process the responses can be related to chosen factors by linear or quadratic models. A quadratic model, which also includes a linear model, is given as

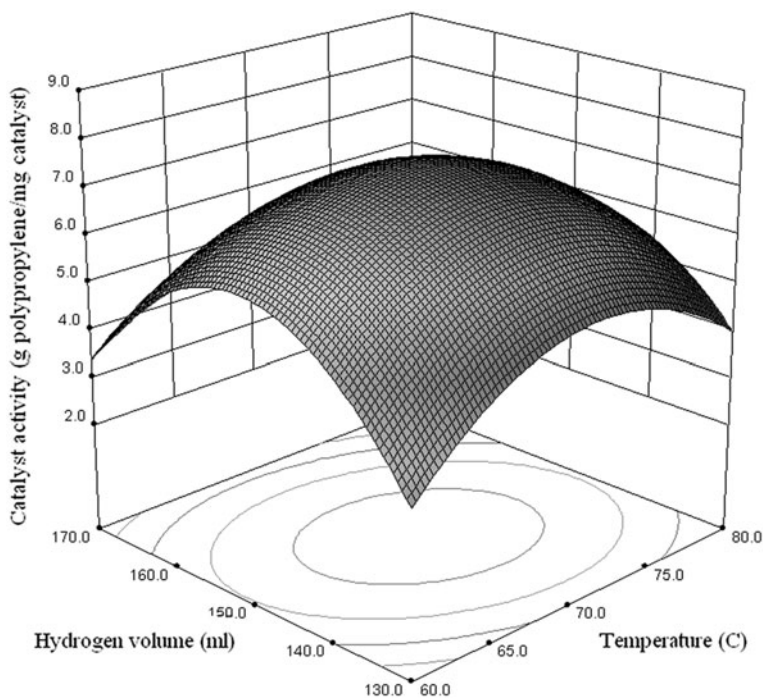


Fig. 5 Catalyst activity as a function of temperature and hydrogen volume

$$Y = \beta_0 + \sum_{i=1}^k \beta_i \chi_i + \sum_{i=1}^k \beta_{ii} \chi_i^2 + \sum_{i=1, i \leq j}^k \sum_j^k \beta_{ij} \chi_i \chi_j + \varepsilon \quad (1)$$

where Y is the response, k is the number of variables, β_0 is the constant coefficient, β_i represents the coefficients of the linear parameters, β_{ii} represents the coefficients of the quadratic parameter, β_{ij} represents the coefficients of the interaction parameters, χ_i represents the variables, and ε is the residual associated to the experiments.

Data were processed with Eq. 1 to obtain the interaction between the process variables and the responses including analysis of variance (ANOVA). The quality of fit of the polynomial model was expressed by the coefficient of determination (R^2), and its statistical significance was checked by the F test. The three-dimensional plots and their respective contour plots were obtained for responses based on effects of the four factors at three levels. Furthermore, the optimum region was identified based on the main parameters in the overlay plot.

Results and discussion

Statistical analysis

Twenty-nine tests were performed to locate the optimum conditions for maximum catalyst activity in the slurry polymerization of propylene with Ziegler–Natta

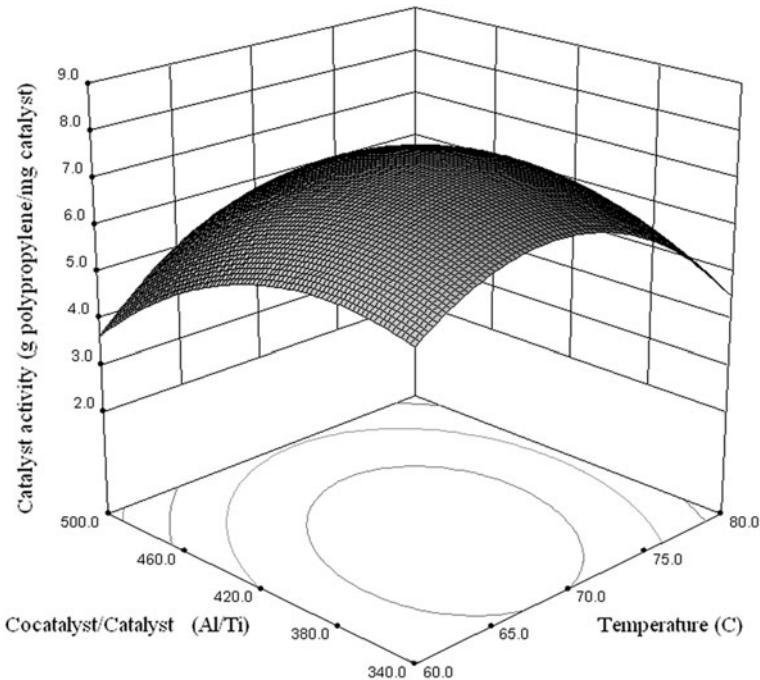


Fig. 6 Catalyst activity as a function of temperature and cocatalyst to catalyst ratio

catalyst. The experiments were carried out in random order as required in many design procedures. RSM was applied to build up an empirical model for modeling catalyst activity and MFR in terms of the operational parameters of temperature, pressure, hydrogen volume, and ratio of cocatalyst to catalyst. The quadratic equations for catalyst activity and MFR were developed as:

$$\begin{aligned} \text{Activity} = & -277.55561 + 2.48605 (T) + 0.30446 (P) + 2.30773 (H_2) \\ & + 0.11701 (Al/Ti) + 5.37536 \times 10^{-3} (T)(P) - 2.78754 \\ & \times 10^{-3} (T)(H_2) + 7.43266 \times 10^{-4} (T)(Al/Ti) + 0.010170 (P)(H_2) \\ & + 6.03612 \times 10^{-3} (P)(Al/Ti) - 4.23348 \times 10^{-4} (H_2)(Al/Ti) \\ & - 0.017331 (T^2) - 0.29658 (P^2) - 6.73899 \times 10^{-3} (H_2)^2 \\ & - 1.80578 \times 10^{-4} (Al/Ti)^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{MFR} = & +572.98364 - 1.87401 (T) - 27.82212 (P) - 4.14094 (H_2) \\ & - 0.59502 (Al/Ti) - 0.27521 (T)(P) + 3.57120 \times 10^{-3} (T)(H_2) \\ & + 1.73625 \times 10^{-3} (T)(Al/Ti) + 0.059102 (P)(H_2) + 0.033163 (P)(Al/Ti) \\ & + 9.03592 \times 10^{-4} (H_2)(Al/Ti) + 0.028340 (T^2) + 1.45406 (P^2) \\ & + 0.010297 (H_2)^2 + 1.52731 \times 10^{-4} (Al/Ti)^2 \end{aligned} \quad (3)$$

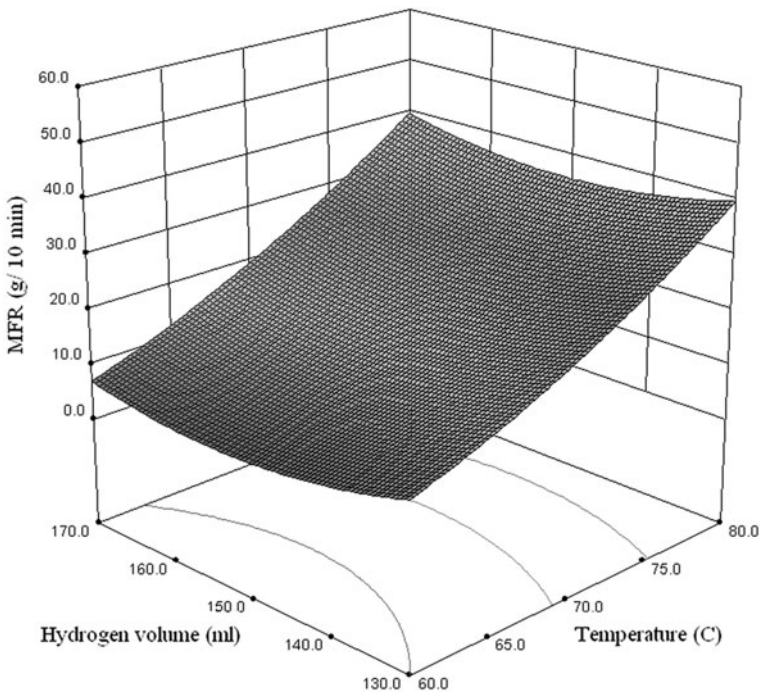


Fig. 7 MFR as a function of temperature and hydrogen volume

ANOVA results of the quadratic models in Tables 2 and 3 indicated that the model equations derived by RSM could adequately be used to describe the catalyst activity and MFR under a wide range of operating conditions. For the models, there was no lack of fit and a good coefficient of determination (R^2) was observed. This means that the quadratic polynomial models were sufficient to represent the actual relationship between the responses and significant variables. The R^2 coefficient gives the proportion of the total variation in the response predicted by the model, indicating ratio of sum of squares due to regression to total sum of squares. A high R^2 value, close to 1, is desirable and a reasonable agreement with adjusted R^2 is necessary [11].

Figures 1 and 2 show the observed catalyst activity and MFR versus corresponding one predicted from the empirical models (Eqs. 2 and 3). From these figures and statistical evaluation in Tables 2 and 3, the predicted empirical models precisely represent the catalyst activity and MFR over a wide range of operational parameters. Data given in these tables demonstrates that the models were significant at the 5% confidence level since P values were less than 0.05. The F value is a ratio of two mean squares. The numerator is the treatment mean square, or the variance due to the different treatments, and the denominator is the experimental error mean square, or the variance of the entire data set. Generally, the hypothesis that the variance due to treatments is significantly larger than the variance of the data set

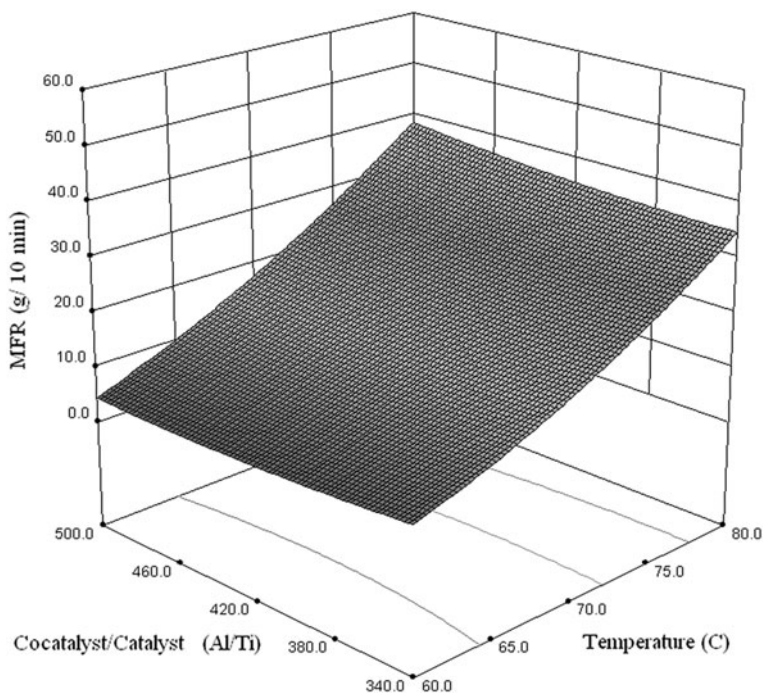


Fig. 8 MFR as a function of temperature and cocatalyst to catalyst ratio

(experimental error) is tested. If the F value exceeds the critical value, the null hypothesis is rejected and concluded that there is a significant effect due to the treatments. The lack of fit describes the variation of the data around the fitted model. If the model does not fit the data well, this will be significant. Adequate precision (AP) in Table 4 compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination [3, 11]. Diagnostic plots such as the predicted values versus corresponding actual (Figs. 1, 2) help us judge the models successfully. These plots indicate an adequate agreement between real data and the ones obtained from the models. The coefficient of variance (CV %) as the ratio of the standard error of estimate to the mean value of the observed response, defines reproducibility of the models. A model normally can be considered reproducible if its CV % is not greater than 10% [11].

Process analysis

Figures 3 and 4 show the response surface plots as a function of the pressure, temperature and their interaction on the catalyst activity and MFR at hydrogen volume of 140 mL and cocatalyst to catalyst ratio of 410. The catalyst activity increases with increase in the reaction pressure. This could be due to the increasing

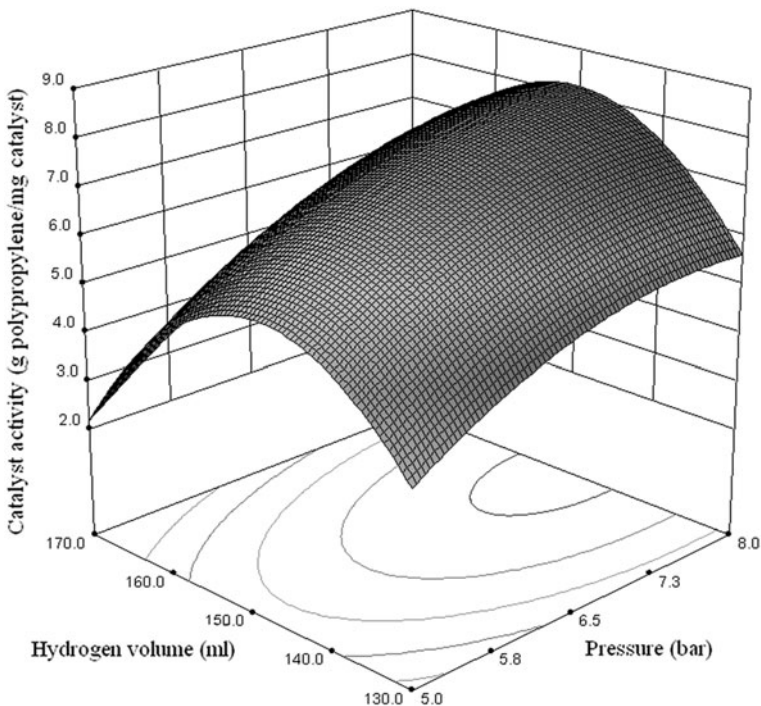


Fig. 9 Catalyst activity as a function of pressure and hydrogen volume

of the monomer solubility in the solvent and monomer concentration near the catalyst active centers [12, 13]. This plot implies that the operating conditions of 70 °C and 8 bar, lead to the maximum catalyst activity (over 7 g/mg). The catalyst activity also increases as the temperature increases from 60 to 70 °C and thereafter decreases further up to 80 °C. The increase in the catalyst activity is a clear indication of the conformational change indicating higher productivity at 70 °C than at 60 and 80 °C. By increasing of the reactor temperature, alkylation rate, active center formation, and polymerization rate increase, but irreversible deactivation of the active centers may also occur [10, 11]. It can be concluded that the rate of chemical reaction and monomer penetration are determining steps at low and high temperatures, respectively [12–14]. The MFR also decreases with the increase in the reaction pressure which is indicating the increase in the molecular weight of polymer chains by increasing the monomer concentration near the catalyst active centers. When temperature increases, relative amount of active centers in different center populations change and the average molecular weight of the polymer decreases (MFR increases) [12, 14].

The effect of varying the hydrogen volume and reaction temperature on the propylene polymerization at the constant reaction pressure (7 bar), and Al/Ti at 410 are shown in Figs. 5 and 7. Figures 6 and 8 represent the effect of varying the Al/Ti and reaction temperature on the propylene polymerization at the constant reaction

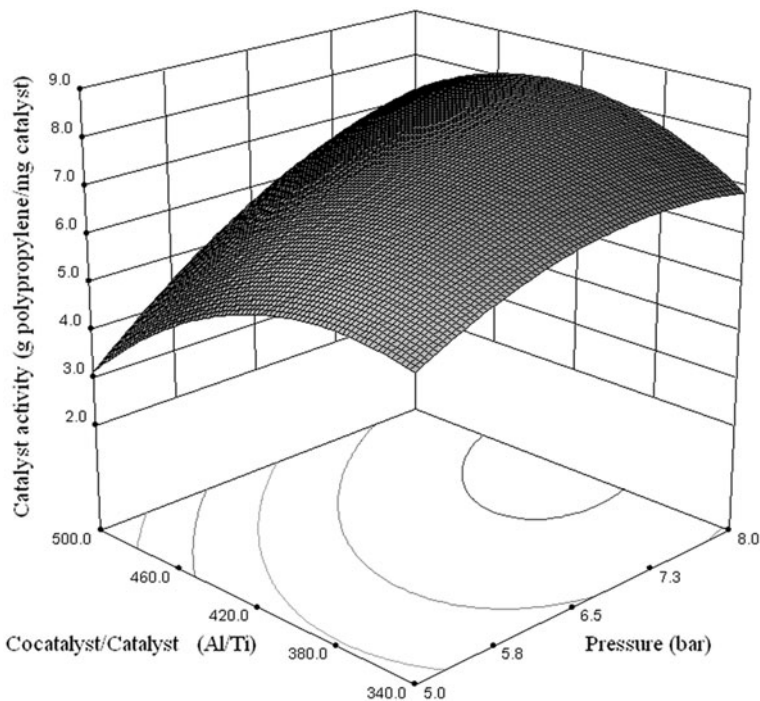


Fig. 10 Catalyst activity as a function of pressure and cocatalyst to catalyst ratio

pressure (7 bar), and hydrogen volume of 140 mL. The plots related to the catalyst activity response are more like semi-spherical shaped, and approximately symmetrical in shape with circular contours. They show clear peaks, implying the optimum conditions to get maximum value of the response. The semi-spherical response surface of the catalyst activity gradually increases with increasing the temperature from 60 to 70 °C at any hydrogen volume and cocatalyst to catalyst ratio. A similar trend is also observed for the hydrogen volume and Al/Ti ratio. The maximum value of the catalyst activity was about 7.5 g/mg at temperature of 70 °C, hydrogen volume of about 148 mL and Al/Ti of 410. The optimum amount of hydrogen in the polymerization reaction is determined by the need to produce polypropylene with the required molecular weight or MFR. At any temperature, the MFR decreases with increasing the hydrogen volume from 130 to 140 mL and thereafter increases further up to 170 mL. This can be clearly seen in corresponding contour plots of Fig. 7. A similar trend is also observed in Fig. 8 for the cocatalyst to catalyst ratio, but this is intangible.

Hydrogen acts as a chain transfer agent to control the polymer molecular weight in most of the olefin polymerization by Ziegler–Natta catalysts. Increasing the hydrogen concentration in the reaction medium results in a decrease of both the reaction rate and productivity [12, 13, 15–19] whereas MFR (which is reciprocal to the molecular weight of the polymer), increases.

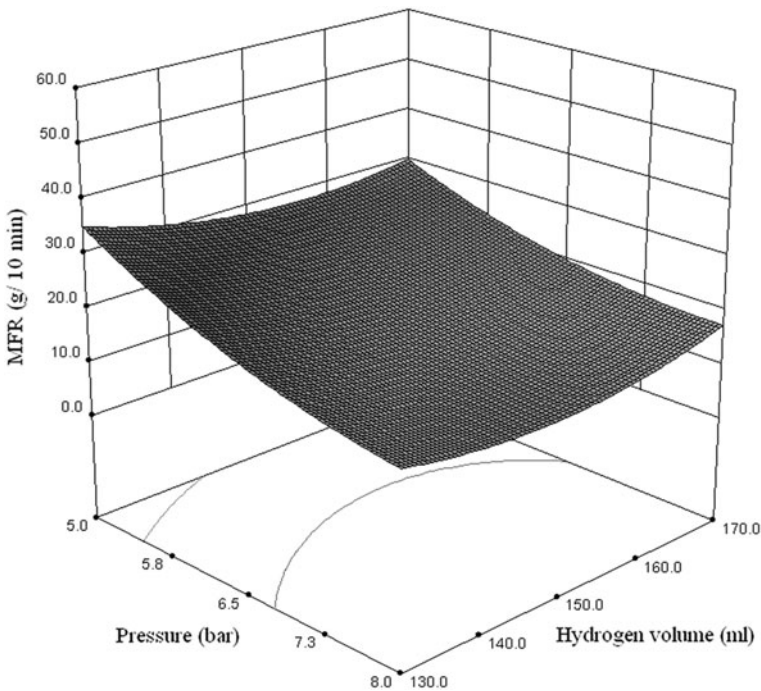


Fig. 11 MFR as a function of pressure and hydrogen volume

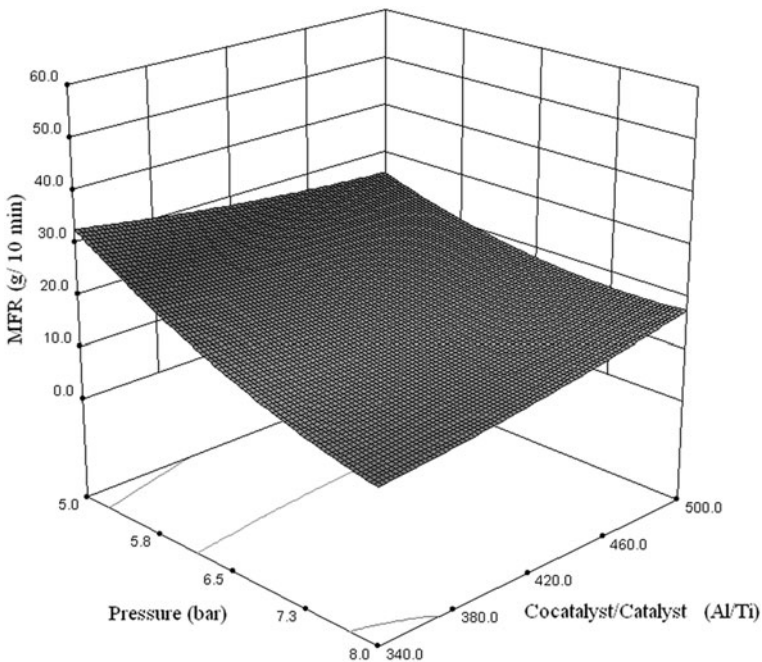


Fig. 12 MFR as a function of pressure and cocatalyst to catalyst ratio

One of the roles of TEA cocatalyst is alkylation of catalyst centers and making Ti–C bonds. In this way at low TEA concentrations and low temperatures, slow alkylation occurs and all the active centers maybe not participate in the alkylation reaction. High concentration of TEA also leads to further reduction of Ti^{+3} to Ti^{+2} which is not active to polymerize propylene anymore [12, 13].

Figures 9, 10, 11, and 12 depict the response surface plots of the catalyst activity and MFR as a function of the pressure, hydrogen volume, and Al/Ti, at temperature of 70 °C. The plots related to the catalyst activity response are more like dome shaped. In these types, in one axis there is a linear increase in the catalyst activity, while in the other axis there is an increase in the catalyst activity only up to the certain extent and decrease thereafter. This indicates that there are critical values for hydrogen volume and Al/Ti ratio in order to get the maximum catalyst activity.

Figures 13 and 14 represent the effect of varying the hydrogen volume and Al/Ti ratio on the catalyst activity and MFR at 70 °C, and 7 bar pressure. The plot of the catalyst activity response is a semi-spherical plot showing clear peak of optimum conditions to get the maximum catalyst activity. The maximum catalyst activity is about 7.5 g/mg at hydrogen volume of about 148 mL and Al/Ti of 410.

Process optimization

The optimal conditions for the propylene polymerization with Ziegler–Natta catalyst were predicted using the optimization function of the Design Expert

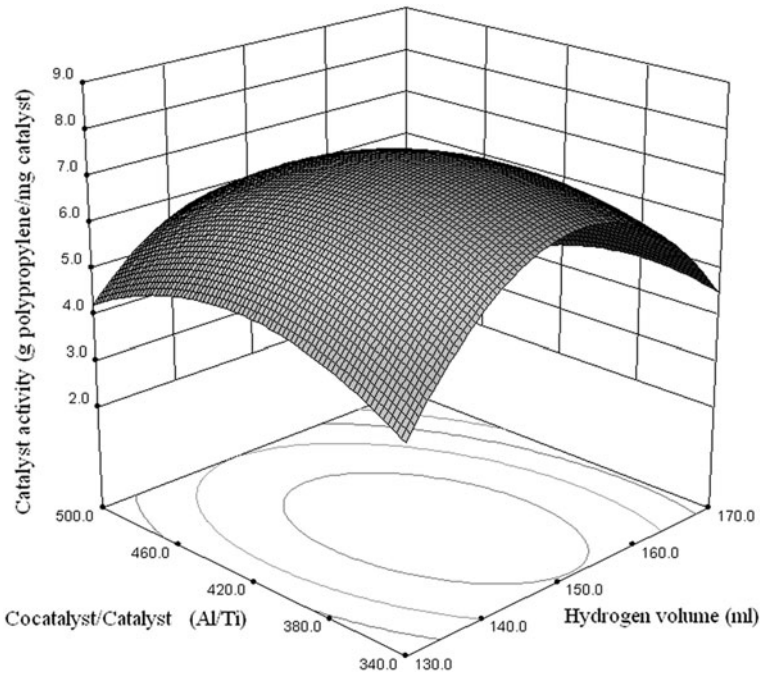


Fig. 13 Catalyst activity as a function of hydrogen volume and cocatalyst to catalyst ratio

Software. These are presented in Table 5 along with their responses. As it is known TEA is rather expensive material that was used in this polymerization. Therefore, the optimum conditions were chosen in order to use the minimum amount of Al/Ti ratio (experiment 10, Table 5).

Conclusions

Response surface methodology (RSM) was applied successfully for the optimization of operational conditions to the catalyst activity and MFR in the propylene polymerization with Ziegler–Natta catalyst. The effects of polymerization factors on the catalyst activity and MFR such as the temperature, pressure, hydrogen volume, and cocatalyst to catalyst ratio were also analyzed through Design-Expert 8 software. Two empirical models to simulate the catalyst activity and MFR were developed in terms of the polymerization conditions (factors) by Box–Behnken design and an ANOVA test was performed. The correlation coefficient for the models was evaluated quite satisfactorily. The pressure, hydrogen volume, and cocatalyst to catalyst ratio were found to be the factors with the greatest influence on the catalyst activity, and the temperature and pressure were found to be the factors with the greatest influence on the MFR. The optimum values for temperature,

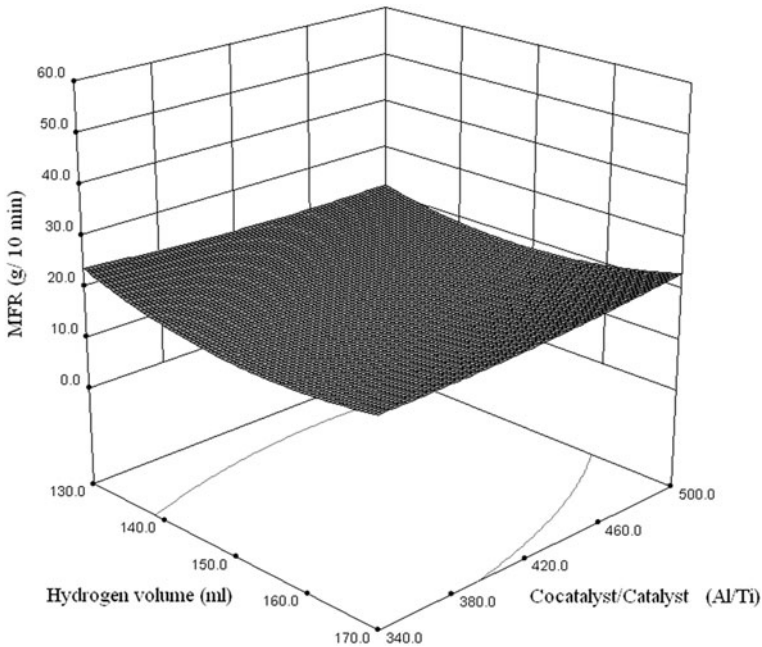


Fig. 14 MFR as a function of hydrogen volume and cocatalyst to catalyst ratio

Table 5 Solutions of the optimum conditions

Experiment	Temperature (°C)	Pressure (bar)	Hydrogen std. volume (mL)	Cocatalyst to catalyst ratio (Al/Ti)	Catalyst activity (g polypropylene/mg catalyst)	MFR (g/10 min)
1	70	8	153	420	8.1	12.7
2	70	8	146	457	8.0	14.5
3	70	8	148	396	8.0	11.1
4	70	8	153	394	8.0	11.2
5	70	8	154	407	8.1	12.0
6	70	8	148	416	8.2	12.2
7	70	8	146	408	8.1	11.8
8	70	8	144	417	8.0	12.3
9	70	8	143	434	8.0	13.3
10	70	8	151	390	8.0	10.9

pressure, hydrogen volume, and Al/Ti ratio were found to be at 70 °C, 8 bar, 151 mL, and 390, respectively. These optimum values were determined from the process cost point of view and offered better operational conditions.

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