Investigation of Effective Factors on the 4th Generation Ziegler-Natta Catalyst Activity by Design of Experiments

Zahra Sekhavat Pour, Abbas Shockravi, and Ali Sabzevari Zadeh

Abstract—**This study presents the influence of triethylaluminium as cocatalyst, cyclohexylmethyldimethoxysilane as external electron donor, and interaction between these two factors on catalyst activity in propylene polymerization with a 4th generation Ziegler-Natta catalyst. The experiments were performed by a two factor factorial design (concentration of triethylaluminium and cyclohexylmethyldimethoxysilane) and the analysis of variance was used to evaluate the results by Minitab14 software. This experimental design enabled us to investigate the main effects or individual effects of each factor and determine whether the factors had interaction or not. It was found that triethylaluminium had significant effect on catalyst activity but cyclohexylmethyldimethoxysilane donor was not individually effective on catalyst activity.**

Index Terms—**Catalyst Activity, Cocatalyst, External Electron Donor, Design of Experiments.**

I. INTRODUCTION

Ever since its discovery in the 1950s, the Ziegler-Natta catalyst has played a fundamental role in the production of polyolefin plastics. Ziegler-Natta catalysts enabled the preparation of polyolefin plastics under conditions of low pressure and temperature. The conventional Ziegler-Natta polypropylene (PP) catalysts consist of $TiCl_4$ and microcrystals of $MgCl_2$ as support. $TiCl_4$ is very often used together with the cocatalyst which is usually an aluminium alkyl, such as triethylaluminium (TEA). Al/Ti mole ratio is an effective factor in propylene polymerization that can affect catalyst activity, polymerization rate and final property of products. Electron donors play a fundamental role in modern Ziegler-Natta catalyst systems for propylene polymerization. The internal donor is added during the catalyst preparation and the external donor, together with the cocatalyst, to polymerization reactor. Electron donors are used to control the stereospecificity. For the fourth generation Ziegler-Natta catalyst internal electron donor is an alkylphthalate and external electron donor is a silane compound.

Effect of cocatalyst and external electron donors with different structures on propylene polymerization with Ziegler-Natta catalyst was studied by many researchers [1-11]. Studies show that all types of external donors easily form complexes with cocatalyst [1], but these complexes are more stable with silane compound [2].

In studies on the complexation of different alkoxysilanes with triethylaluminium Iiskola et al. [12] found that, at room temperature, TEA and alkoxysilane instantly form a 1:1 complex independent of the number of alkoxy groups in the silane. The stability of the complex depends on the structure of the alkoxysilane, Al/Si mole ratio, temperature and time. Under typical polymerization conditions, the greatest part of the complex seems to persist in its original form. Spitz et al. [3] studied the effect of triethylaluminium and triethoxyphenylsilane concentration and Al/Si mole ratio on $MgCl_2$/dibutylphthalate/$TiCl_4$. It was found that at increasing silane content, the activity increased up to a maximum and then decreased. The rate of isotactic polymer production had the same behavior and the production of atactic polymer continuously decreased. Seppala and Harkonen [4] selected nineteen silane compounds of structure $R_nSi(OR')_{4-n}$ where n=1-4, R=C_6H_5, alkyl or H; and R'=C_{1-3}-alkyl as external donors. They reported decrease of catalyst activity with increase of silane external donor. Busico et al. [5] also reported this decreasing trend for catalyst activity with increase of triethoxyphenylsilane as external donor. Garrof et al. [6] did several polymerizations with increase of dicyclopentyldimethoxysilane/Ti mole ratio. Catalyst activity increased at first but at high donor/Ti mole ratio a gradual decrease in the activity was observed. Increase in the activity was explained by increased complexation of the external donor to the catalyst and hence decrease in the number of donor-free sites. Decrease in activity was demonstrated by exchange reaction between ethoxy and ethyl ligand.

In most publications, each effective factor such as cocatalyst or external electron donor has been investigated by one factor at a time approach. The major disadvantage of the one factor at a time strategy is that it fails to consider any possible interaction between the factors. Interactions between factors are very common, and if they occur, the one factor at a time strategy will usually produce poor results. The correct approach to deal with several factors is to conduct a factorial design. This is an experimental strategy in which factors are varied together instead of one at a time [13].

In this work we report effects of triethylaluminium as cocatalyst and cyclohexylmethyldimethoxysilane ((Cy)(Me)Si(OMe)$_2$ or CHMDS) as external donor on catalyst activity. A factorial design with two factors

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consisting of TEA and CHMDMS concentration was selected. Experiments were performed randomly and each test was repeated twice. The analysis of variance (ANOVA) was used for investigation of the tests' results by Minitab14 software.

II. EXPERIMENTAL PROCEDURE

A. Materials

In this study, a 4th generation Ziegler-Natta catalyst manufactured by Basell Company under the trade name GTF2 was used. This catalyst was donated by Navid Zar Petrochemical Company. Its concentration was 230 g catalyst per liter.

Hydrogen and propylene (donated by Bandar Imam Khomeini Petrochemical Company (BIPC)) were used with further purification. Hexane (donated by BIPC) was extra dried by passing through molecular sieve. Concentration of TEA solution (donated by BIPC) was determined by titration with 0.1 molar butanol solution in heptane. CHMDMS (Merck) was used as external electron donor.

B. Slurry polymerization of propylene

Propylene (10 bar) was polymerized in a Buchi stainless steel reactor with Ziegler-Natta catalyst (0.03 mol Ti) in hexane (1 liter) at 70 ˚C for 90 minutes. The conditions of each test from viewpoint of TEA and CHMDMS

concentrations are given in Table I. Hydrogen (100 ml) was introduced into the reactor as chain transfer agent [14]. After 90 minutes, residual gases were removed from the reactor and the reaction was stopped. The solid polymer was filtered and dried. Each test was repeated twice, so 24 slurry polymerizations were carried out in these test series. The catalyst activity for each test was calculated by measuring the total mass of polymer produced in the test divided in the amount of the catalyst used in each test.

III. RESULT AND DISCUSSION

A. Catalyst Activity

Table I shows the catalyst activities reached in the test series measured as g PP/g catalyst. A two factor factorial experiment with design factors at four different concentrations of TEA and three different concentrations of CHMDMS was considered. Analysis of results was difficult by means of Table I, and therefore the ANOVA and Minitab14 software were used for the analysis of experiments' results.

Before the conclusions from the ANOVA are adopted, the adequacy of the model was checked by residual analysis [13]. We evaluated the normality, the independence and equality of variances of residuals for model adequacy checking.

TABLE I: EFFECTS OF DIFFERENT CONCENTRATIONS OF TEA AND CHMDMS ON CATALYST ACTIVITY

[TEA]	[CHMDMS]	Catalyst activity	
(mmol/l)	(mmol/l)	(g PP/g Catalyst)	
4.35	0.2	5250	4530
4.35	0.4	4857.5	5260
4.35	0.6	5350	5030
6	0.2	5305	5965
6	0.4	6650	6215
6	0.6	5220	4500
10	0.2	5562.5	6250
10	0.4	5787.5	5000
10	0.6	6675	6387.5
13	0.2	5777.5	6350
13	0.4	6142.5	5937.5
13	0.6	5282.5	4975

A. Model adequacy checking

1) The normality assumption

The first assumption in model adequacy checking is normality of residuals. Residuals are differences between resulting amounts of response variable (catalyst activity) in experiments and fitted value by regression model. Normal probability plot of the residuals was obtained for effect of TEA and CHMDMS on catalyst activity by Minitab 14 software and it has been shown in Fig. 1. Since given points have considerable distance from the central line of the standard normal distribution, the normality assumption is not concluded. Hence, reciprocal transformation was used for increasing the accuracy of the ANOVA results. In the other word, 1/(g PP/g catalyst) was used instead of g PP/g catalyst. Fig. 2 shows normal probability plot of the residuals for the

transformed variable. In this figure, given points have short and admissible distance from the central line, so the normality assumption is confirmed for the transformed variable.
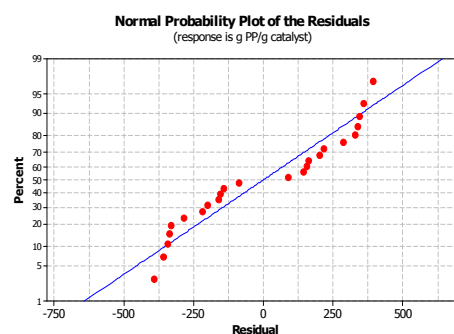

Fig. 1: Normal probability plot of the residuals for g PP/g catalyst

Normal Probability Plot of the Residuals
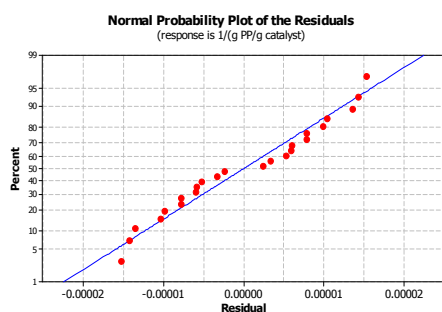(response is 1/(g PP/g catalyst)

Fig. 2: Normal probability plot of the residuals for 1/(g PP/g catalyst)

2) The independence assumption

Fig. 3 shows residuals versus the order of the data for the transformed variable. It is easy to see from this figure, there is not any special trend such as ascending, descending or sine trend. Thus, the residuals are structureless and independency of residuals is verified.

Residuals Versus the Order of the Data
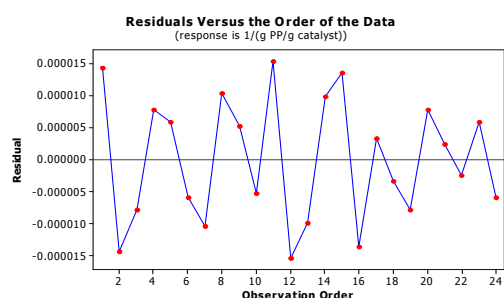(response is 1/(g PP/g catalyst))

Fig. 3: residuals versus the order of the data for 1/(g PP/g catalyst)

3) Equality of variances

The third assumption for using the ANOVA is equality of variances. Bartlett's test was used to check this assumption. Bartlett's test is sensitive to the normality assumption, so it can only be used for normal residuals. Fig. 4 depicts the equality of variances, because P_{value} of Bartlett's test is more than error type I (0.963>0.1). Note that, throughout this paper we considered 10 percent for error type I.
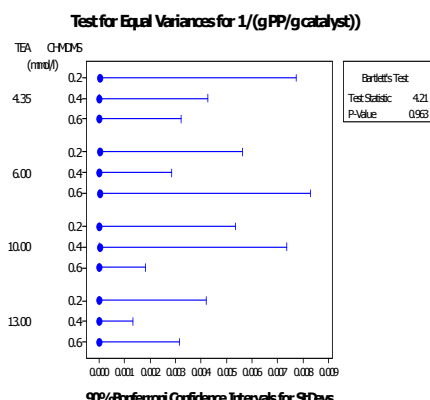
Test for Equal Variances for 1/(g PP/g catalyst))

Fig. 4: Equality of variances for 1/(g PP/g catalyst) using Bartlett's test.

B. The ANOVA results for catalyst activity

Table II shows the results of the ANOVA for TEA and CHMDMS effect and interaction between them on 1/(g PP/g catalyst). The results show that, TEA concentration and its interaction with CHMDMS have significant effect on catalyst activity, because of P_{value}(TEA)=0.014<0.1, and P_{value}(TEA×CHMDMS)=0.015<0.1. P_{value} of CHMDMS is 0.310, so this factor has no significant effect on catalyst activity.

TABLE II: MINITAB OUTPUT FOR 1/(G PP/G CATALYST)

Analysis of Variance for 1/(g PP/g catalyst), using Adjusted SS for Tests:

Source	DF	Seq SS	Adj SS	Adj MS	F	P
TEA	3	0.000	0.000	0.000	5.43	0.014
CHMDMS	2	0.000	0.000	0.000	1.29	0.310
TEA×CHMDMS	6	0.000	0.000	0.000	4.33	0.015
Error	12	0.000	0.000	0.000		
Total	23	0.000				

S = 0.0000133474   R-Sq = 78.90%   R-Sq(adj) = 59.56%

whereas these results are confirmable by the statistical concepts, do not actually occur in the real world. On the other hand, the low amount of R-Sq(adj) discloses that other unchecked factors (such as temperature, pressure, hydrogen and so on) might also be effective on catalyst activity and their effects could be appeared in interaction effect between TEA and CHMDMS. Hence, for investigation of TEA effect on catalyst activity, CHMDMS and its interaction with TEA are discarded and the one-way ANOVA is used. The result of the one-way ANOVA has been shown in Table III.

TABLE III: MINITAB OUTPUT FOR EFFECT OF TEA ON CATALYST ACTIVITY

One-way ANOVA: g PP/g catalyst versus TEA

Source	DF	SS	MS	F	P
TEA	3	2683544	894515	2.64	0.078
Error	20	6781215	339061		
Total	23	9464758			

S = 582.3 R-Sq = 28.35% R-Sq(adj) = 17.61%

According to Table III, TEA concentration has significant effect on catalyst activity because of P_{value}<0.1. Fig. 5 shows the box plot of TEA concentrations on catalyst activity. As this figure shows increase of TEA concentration initially causes to increase in catalyst activity, but there is a maximum in [TEA]=10 mmol/l, further addition of cocatalyst decreases catalyst activity.

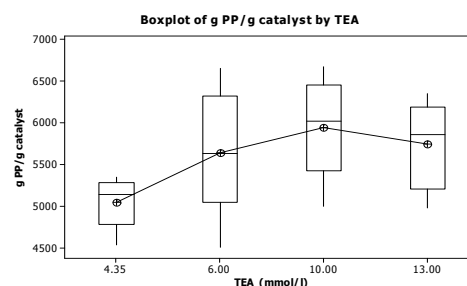**Boxplot of g PP/g catalyst by TEA**

Fig. 5: Box plot of TEA concentrations on catalyst activity

TEA needs for alkylation and activation of catalyst and transforms the catalyst site to active site. A little amount of TEA eliminates impurity and catalyst poisons such as H_2O and O_2 in the polymerization. There is no doubt that Ti^{4+} undergoes an extensive reduction whenever the catalyst is treated with TEA. According to scientist thought, Ti^{4+} and Ti^{3+} are active in propylene polymerization [11]. So catalyst activity increases with increasing TEA concentration because catalyst poisons are removed, Ti^{3+} species are increased and polymerization centers are activated. Increase of catalyst activity continues until all polymerization centers become active. Further increase in TEA decreases the catalyst activity because high TEA concentration causes further reduction of

Ti^{4+} even to Ti^{2+} species that aren't active for propylene polymerization. Some of authors agree in opinion that the main reason for the observed decrease of catalyst activity is the poisoning by $EtAlCl_2$ (ethylaluminiumdichloride), which is the product of interaction of catalyst with cocatalyst Et_2AlCl and TEA [15].

$$TiCl_3 + Et_2AlCl \leftrightarrow TiCl_2 - Et + EtAlCl_2 \qquad (1) \; [15]$$
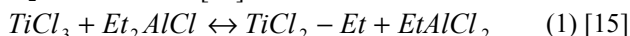
As a result of reaction (1), the gradual elimination of chlorine from the catalyst takes place. Extraction of Cl^- during the catalyst and TEA interaction and the decrease of the catalyst activity are correlated.

Response Surface Methodology (RSM) was used for three dimensional display of fluctuations in catalyst activity with respect to TEA and CHMDMS concentrations. [13,16]. Fig. 6 shows three dimensional response surface plot of TEA and CHMDMS effect on catalyst activity.
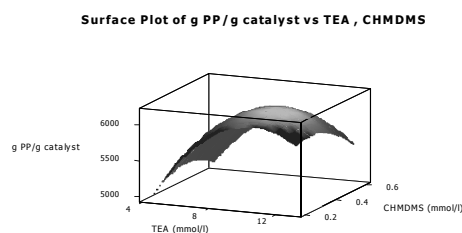

Fig. 6: three dimensional response surface plot of TEA and CHMDMS concentration on catalyst activity.

According to Fig. 6, change in TEA concentration affects catalyst activity since curvature of three dimensional plot is clearly observable with increase of this factor, whereas catalyst activity is almost constant with increase of CHMDMS concentration in certain amount of TEA and curvature along CHMDMS axis is low and it is negligible. There is a maximum in this three dimensional plot. This maximum almost includes all amounts of CHMDMS that illustrates catalyst activity is independent of CHMDMS concentration.

Fig. 7 exhibits a contour plot of catalyst activity versus TEA and CHMDMS concentration. This response surface indicates that maximum catalyst activity is obtained at [TEA]=9-12 mmol/l and [CHMDMS]=0.2-0.5 mmol/l. Note that this obtained range may only be valid for catalyst activity, so further research is necessary to determine the optimum range for other response variables [17].

Contour lines are parallel with CHMDMS concentration variations' axes. It illustrates that CHMDMS do not affect catalyst activity.
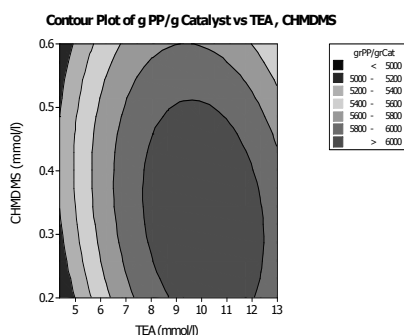

Figure 7: Contour plot of catalyst activity versus TEA and CHMDMS concentration.

IV. Conclusions

Effect of TEA as cocatalyst and CHMDMS as external electron donor on catalyst activity in propylene polymerization with a 4th generation Ziegler-Natta catalyst was investigated. A factorial design with two factors was selected. The analysis of variance and Minitab14 software were used for investigation of results. In this research, not only effect of each factor but also interplay between them was evaluated. Two factor factorial design revealed that TEA concentration and its interaction with CHMDMS have significant effect on catalyst activity and CHMDMS did not affect it. In the real world when one factor actually has not significant effect, its interaction with other factor is not also effective. So the one-way ANOVA was used for investigation of TEA effect on catalyst activity and ineffective CHMDMS was abandon.

Increase of TEA up to certain concentration in polymerization enhanced the yield of obtained polymers and catalyst activity because; TEA reduced Ti^{4+} to Ti^{3+} active species and activated the catalyst. Further increase of TEA caused to reduction of Ti^{4+} species even to Ti^{2+} that were inactive in propylene polymerization. Hence, TEA had an optimum concentration in polymerization.

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