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## Comparative Study Of Ethylene Polymerization: Using Different Ziegler-Natta Catalysts On An Optimal Condition Obtained By Experimental Design



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### ABSTRACT

Various parameters including temperature, pressure, and Al/Ti molar ratio were used to evaluate the polymerization of ethylene using an  $L_{27}$  taguchi experimental design. Response surface method was employed to analyze the catalyst activity and polymerization yield. The results reveal that polymerization yield and catalyst activity are increased by pressure and Al/Ti molar ratio. However, raising temperature results in a decrease in both above-mentioned responses. According to results obtained in this work, pressure and temperature have synergistic effects on both polymerization yield and catalyst activity. A synthesized and two commercial catalysts were used to consider the effect of different catalysts on the polymer properties. The downward trend of catalyst activity in the presence of hydrogen can be easily seen for all the catalysts. Despite a decrease in weight- and number-average molecular weight in the presence of hydrogen, the polydispersity index remains approximately unchanged. The SEM results clearly show the various morphologies of the obtained polyethylenes, which are referred to the morphologies of the catalysts used.

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### KEYWORDS

Polyethylene;  
Polymerization;  
Ziegler-natta catalysts;  
 $L_{27}$  taguchi experimental  
design.

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### INTRODUCTION

Although polyethylenes are commercially produced by using free radical and catalyst-based systems, those based on catalyst systems, especially Ziegler-Natta catalysts, are the most common in industrial practice, which is due to their wide range of applications. These catalyst systems have been used to synthesize high density polyethylene, polypropylene, and other  $\alpha$ -olefins applying different polymerization processes.

The number of combinations of compounds that fits into the category of Ziegler-Natta catalysts are far too numerous to describe here. However, a Ziegler-Natta catalyst may roughly be defined as a combination of two components: (1) a transition metal compound of an element from group IVB to VIIB, and (2) an organometallic compound of a metal from group I to III of periodic table. Taking the solubility of catalysts into consideration, they can be delivered in different forms: homogeneous, heterogeneous, and colloidal forms. From industrial standpoint, most commonly, the catalyst systems are based on the titanium salts and aluminum alkyls<sup>[1,2]</sup>. This picture could be referred to the insufficient catalytic stability and stereochemical control of conventional soluble Ziegler-Natta catalysts<sup>[3-7]</sup>.

Since the discovery of Ziegler-Natta catalysts, extensive research endeavors have been directed towards a comprehensive understanding of their structure and kinetic behavior<sup>[8-9]</sup>. In spite of their scientific and industrial importance, there is still a lack of thorough knowledge of their mechanism and associated reactions.

In spite of various types of Ziegler-Natta catalysts, most of them show similar characteristic: they resemble each other in producing polymers with broad molecular weight distributions and copolymer composition in the case of copolymerization. There is a general agreement that they are consisted of several catalytic sites, known as multi-site catalysts; these sites differ in the rate of propagation and transfer reactions; they also have different abilities in comonomer incorporation. Due to this multi-site characteristic, the produced polymer is really a mixture of dissimilar grades at molecular level. On the

other hand, homogeneous species usually show the behavior of a single-site catalyst and follow Flory's most probable distribution<sup>[10]</sup>.

The peculiarities of ethylene polymerization with heterogeneous Ti-based Ziegler-Natta catalysts have been reported by different authors<sup>[11-13]</sup>. Here we consider different Ziegler-Natta catalysts to polymerize ethylene in an optimum condition achieved by Taguchi experimental design. Experimental design helps one to take the synergistic and antagonistic effects into consideration as well as to reduce the number of experiments<sup>[14-16]</sup>. Application of experimental design as a powerful tool in polymer engineering has been reported by different authors<sup>[17-19]</sup>. In the present work, an  $L_{27}$  orthogonal array was used to lessen the number of experiments and consider the interaction of reaction parameters. The response of different catalysts to hydrogen was studied by measuring molecular weight and molecular weight distribution.

### EXPERIMENTAL

Ethylene homopolymerization reactions were carried out in a 1600 cm<sup>3</sup> stainless steel reactor (Buchi Autoclave) with a pressure gauge, a mechanical-drive stirrer, an external oil-circulating heating jacket, and several ports for delivering liquids, gases, and catalyst component. All gases and liquid feeds to the reactor (n-hexane, ethylene, hydrogen, and nitrogen) were purified by passing them through three columns containing 3 Å molecular sieves. Polymerization experiments were carried out in two sets of reactions: (1) elementary reactions that were carried out according to Taguchi experimental design to find an optimal condition and study the effect of reaction parameters, (2) comparative reaction that were carried out to investigate the effect of different catalysts. The same procedure was used for both elementary and comparative reactions:

1. A clean reactor was dried in a flow of purified nitrogen at 80°C for 70 min and was cooled to ca. 45°C.
2. A solvent (n-hexane) was added to the reactor under nitrogen flow, so that the solvent volume reaches 800 cc. The solvent was vigorously

stirred at 1000-1100 rpm for 10 min, and then the speed of stirrer reduced to ca. 650 rpm.

- Required amount of cocatalyst,  $\text{AlEt}_3$  (Fluka, diluted in n-heptane) was added directly into the reactor (under slow flow of ethylene) by using a glass syringe with a long needle; cocatalyst was stirred for 10 min.
- Pre-measured amount catalyst was also delivered to the reactor using the same way applied for the cocatalyst.
- Hydrogen, if necessary, was added to the reactor using Buchi Pressflow Gas Controller to satisfy pre-determined pressure.
- Finally, ethylene was added to the reactor to the specified pressure.
- After a desired time (120 min) the ethylene was rapidly vented from the reactor and its contents was quickly cooled to  $25^\circ\text{C}$ . The polymer powder was dried at  $25^\circ\text{C}$  for 24 hr; the dried powder was treated under vacuum at  $75^\circ\text{C}$  for 1.5 hr.

It should be mentioned that the amount of cocatalyst and reaction parameters including pressure and temperature were set according to experimental design for elementary reactions; no hydrogen was added to the polymerization media during the elementary reactions. Typical reaction conditions for comparative reactions were obtained by experimental design. The catalyst was added as a diluted slurry mixture in n-heptane; the amount of the catalyst was equal to 2 cc for all of the reactions.

Temperature, pressure, and molar ratio of Al/Ti were chosen as independent variables for the design of experiment; the yield of polymerization and activity of catalyst were considered as response parameters. Using an  $L_{27}$  design of experiment array enabled us to take the binary interactions of three independent variables into consideration; the desired confidence limit for analysis of variance was supposed to be 0.05. The analysis of experimental design results was carried out with MINITAB program.

GPC method was applied to measure molecular weight and molecular weight distribution of samples. The GPC analysis of samples was carried out at  $135^\circ\text{C}$  with Waters 2000 ALLIQNCE liquid chromatograph equipped with four columns of crosslinked polystyrene (2 columns  $10^6$ ,  $10^4$ , and  $10^3$  Å); the sol-

vent was 3-chlorobenzene. SEM method was used to study the morphology of polymer powder. The microscopic scanning of samples was carried out with Philips XL Series at 12KV intensity and 40X zoom; the SEM analyses for different catalyst types were carried out at the same amount of hydrogen.

## CATALYSTS ANALYSIS

TABLE 1 shows the analysis of catalysts used for the polymerization. This table includes the amount of Ti and Mg elements as well as the BET and porosity values for each catalyst.

**TABLE 1: Analysis of the catalysts used for the polymerization**

Attribute Catalyst	Ti (%)	Mg (%)	Area BET ( $\text{m}^2 \text{gr}^{-1}$ )	Porosity (Å)
A	6.68	19.3	178.4	24.1
B	5.52	18.16	152.6	19.5
C	1.8	11.3	143.1	16.2

## RESULTS AND DISCUSSION

A general comment is required with respect to the present work; presented here is consisted of two relevant parts: experimental design and the effect of various catalysts. Experimental design was used to study the effect of typical reaction conditions (pressure and temperature) and molar ratio of Al/Ti; it was used to find an optimum condition in which the reactions that are required to investigate the effect of hydrogen and catalyst type were carried out.

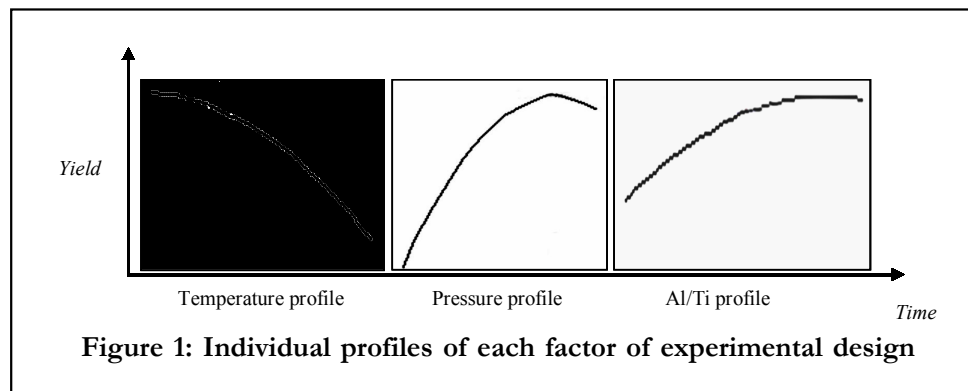
### Taguchi experimental design

The experimental design factors and their levels are summarized in TABLE 2. As can be seen the independent variables, so-called factors, are tempera-

**TABLE 2: Experimental design factors and their levels**

Independent variables (unit)	High level (1)	Middle level (0)	Low level (-1)
Temperature ( $^\circ\text{C}$ )	90	80	70
Pressure (bar)	10	8	6
Al/Ti (molar ratio)	150	100	50

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TABLE 3: Applied  $L_{27}$  orthogonal array

Experiments	Al/Ti (molar ratio)	Pressure (bar)	Temperature (°C)
1	-1	-1	-1
2	0	-1	-1
3	1	-1	-1
4	0	-1	0
5	1	-1	0
6	-1	-1	1
7	0	-1	1
8	1	-1	1
9	-1	0	-1
10	0	0	-1
11	1	0	-1
12	-1	1	-1
13	0	1	-1
14	1	1	-1
15	-1	1	0
16	0	1	0
17	1	1	0
18	-1	1	1
19	0	1	1
20	-1	0	0
21	1	1	1
22	0	0	0
23	-1	0	1
24	0	0	1
25	1	0	0
26	1	0	1
27	-1	-1	0

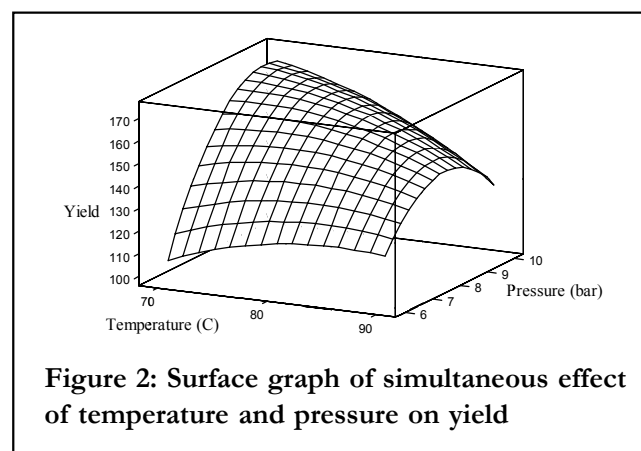
ture, pressure, and Al/Ti molar ratio. TABLE 3 shows the  $L_{27}$  orthogonal array used in this experimental design in a coded form; according to TABLE 3, 27 experiments must be accomplished. In order to

reduce the error of experiments and distribute this error among all reactions, one needs to carry out these experiments randomly.

The individual profiles of each factor, obtained with MINITAB program, are shown in figure 1. In accordance with this figure, increasing pressure and Al/Ti molar ratio continually increase the yield of polymerization, while increasing temperature result in a decrease in the yield of polymerization.

### 1. Simultaneous effect of temperature and pressure on yield

The simultaneous effect of temperature and pressure is shown in figure 2. As one can see, increasing temperature in low pressures causes a little reduction in the yield of polymerization while this effect can be sensible in high pressures. This dramatic reduction of the yield in high pressures could be attributed to destruction of catalyst particles. Increasing pressure lead to higher values of the yield of polymerization, this is ascribed to higher monomer concentration. It is worth mentioning that maximum yield of polymerization is achieved when the tem-



perature takes its minimum value and pressure is maximum; this is also known as 'synergistic effect'.

## 2 Simultaneous effect of temperature and Al/Ti on yield

Figure 3 shows the simultaneous effect of temperature and Al/Ti molar ratio. In this case like temperature-pressure case, increasing the temperature causes the yield of polymerization to decrease, and increasing Al/Ti molar ratio increases the yield of polymerization. This positive effect of Al/Ti molar ratio on the yield of polymerization is ascribed to the activation of more potential catalytic sites, which, in fact, results in more active sites in the catalyst particles. The synergism could be observed for high values of Al/Ti molar ratio and low temperatures.

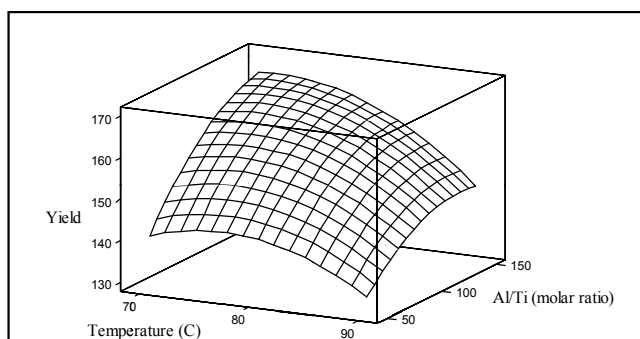


Figure 3: Surface graph of simultaneous effect of temperature and Al/Ti on yield

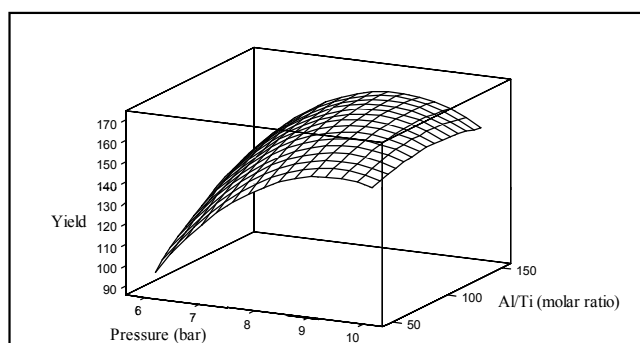


Figure 4: Surface graph of simultaneous effect of pressure and Al/Ti on yield

## 3. Simultaneous effect of pressure and Al/Ti on yield

Figure 4 depicts the variations of yield with pres-

sure and Al/Ti molar ratio. In accordance with this figure, increasing either pressure of ethylene or Al/Ti molar ratio raises the yield of polymerization. As mentioned before, this upward trend of the yield could be referred to more potential site activation and higher ethylene concentration.

Using response surface method, an equation, defining the correlation of the yield (response) and the independent parameters (factors), was derived:

$$\text{Yield} = -1210.20 + 156.226 X + 15.9184 Y + 1.79129 Z - 5.14056 X^2 - 0.0649889 Y^2 - 0.00200089 Z^2 - 0.703583 XY - 0.0862500 XZ - 0.00625000 YZ \quad (1)$$

Where, X, Y, and Z are considered variables for pressure, temperature, and Al/Ti molar ratio respectively. Dropping the less important factors, one may reach:

$$\text{Yield} = -1210.20 + 156.226 X + 26.9184 Y + 1.79129 Z - 5.14056 X^2 - 0.703583 XY \quad (2)$$

According to equation 2, there is only temperature-pressure interaction that could be considered as an efficient interaction.

## 4. Simultaneous effect of temperature and pressure on activity

As can be seen from figure 5, increasing either temperature or pressure causes a dramatic decrease in the activity of catalyst. This effect is greatly increased in high pressure and temperature values, as the catalyst particles fracture- as a destructive factor- has been amplified. It should be mentioned that although, increasing pressure results in higher monomer concentration, it causes catalyst particles to fracture in high temperatures.

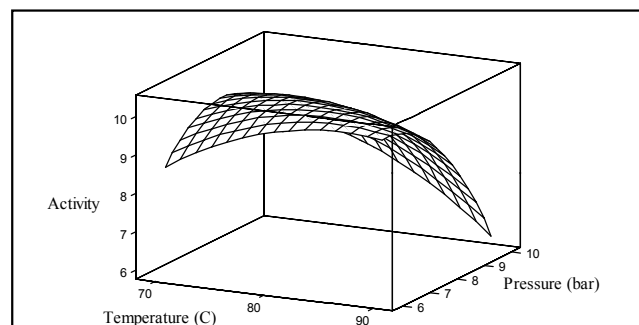
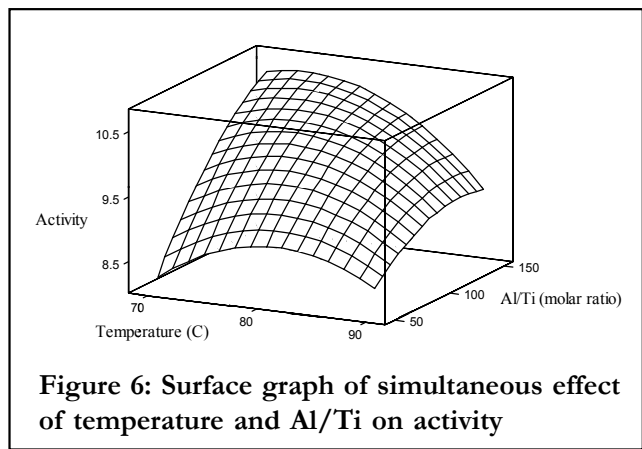


Figure 5: Surface graph of simultaneous effect of temperature and pressure on activity

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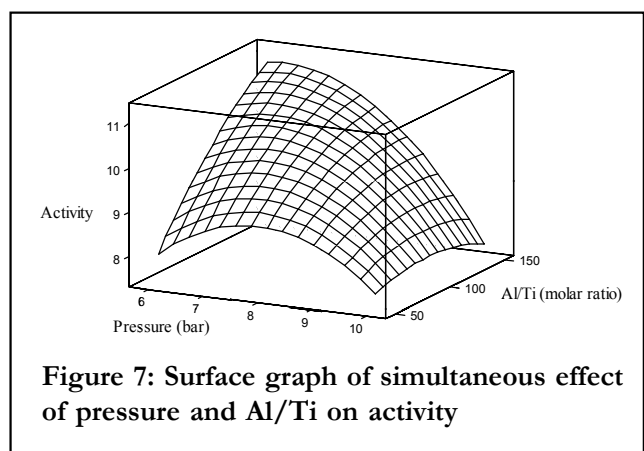
### 5. Simultaneous effect of temperature and Al/Ti on activity

Figure 6 portrays the simultaneous variation of the activity with temperature and Al/Ti. As can be seen, increasing Al/Ti raises activity of catalysts thanks to higher activation of potential catalyst sites.

### 6. Simultaneous effect of pressure and Al/Ti on activity

Variation of activity with pressure and Al/Ti molar ratio is shown in figure 7. it could be observed that increasing the pressure of ethylene causes activity to go through a maximum. This event is also referred to catalyst particles fracture in high pressures.

Applying response surface method, similar to what applied to the yield of polymerization, one can obtain an equation describing the relation between the activity of catalyst and reaction parameters (known as factors):



$$\text{Activity} = -83.7856 + 8.51347 X + 1.33909 Y + 0.168965 Z - 0.261667 X^2 - 0.00554167 Y^2 - 0.00012208 Z^2 - 0.0500208 XY - 0.00802083 XZ - 0.00814236 YZ \quad (3)$$

Where, X, Y, and Z are considered variables for pressure, temperature, and Al/Ti molar ratio respectively. Dropping the less important factors, one may obtain:

$$\text{Activity} = -83.7856 + 8.51347 X + 1.33909 Y + 0.168965 Z - 0.261667 X^2 - 0.0500208 XY \quad (4)$$

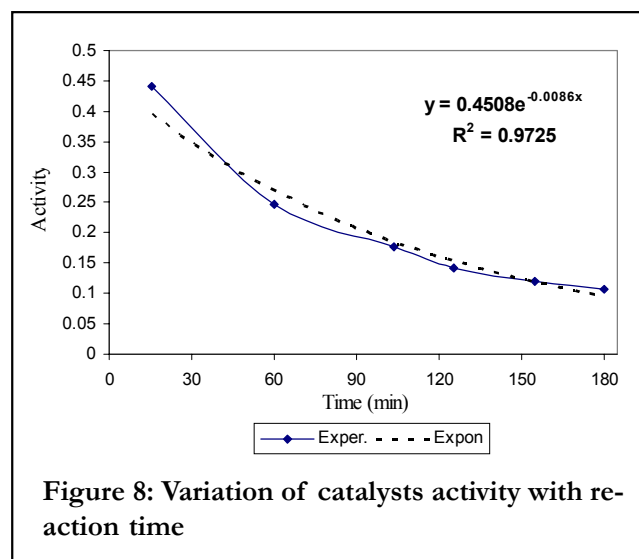
Similar to Equation 2, here, there is only an interaction between pressure and temperature.

### Effect of time on catalyst activity

Variation of catalyst activity with polymerization reaction time was separately investigated. Figure 8 shows that during the course of polymerization reaction there is deterioration in the catalyst activity. This drop in catalyst activity could be attributed to the formation of dormant sites during polymerization reaction.

### Comparative study of different catalysts

Considering the experimental design data, an optimal condition was set to study the comparative reactions in. Although different optimum conditions were possible to be obtained with MINITAB program, the used condition was set as close to industrial plant reaction conditions as possible. The pressure of ethylene, temperature, Al/Ti molar ratio, and reaction time were set for 8.5 bar, 75°C, 100, and 120 min respectively. Al/Ti molar ratio was consid-



ered greater than what is common in commercial plants, as more cocatalyst is required to scavenge unknown impurities in a laboratory batch reactor. The used catalysts are labeled as catalyst A, catalyst B and catalyst C; both catalysts A and C are commercial catalysts while catalyst B was synthesized in laboratory.

Considering the above-mentioned reaction conditions, the effect of hydrogen on the activity of catalyst, molecular weight, molecular weight distribution, and polyethylene morphology was studied.

### 1. Variation of catalyst activity versus amount of hydrogen used

Figure 9 depicts the variation of catalyst activity with the amount of hydrogen. According to this figure, different catalysts show different trends in activity deterioration. Catalyst A tends to show a continuous decrease in activity, while catalysts B and C tend to pass through a maximum. The amount of hydrogen required to bring about catalyst deterioration in catalyst B is more than what is needed in catalyst C. Reversible depression of the catalyst activity is due to a more frequent generation of Ti-H bond that, after ethylene insertion, forms the stable Ti-C<sub>2</sub>H<sub>5</sub> group. The unusual stability of this group is attributed to a relatively strong  $\beta$ -agostic interaction between the hydrogen atom of its methyl group and the Ti atom.

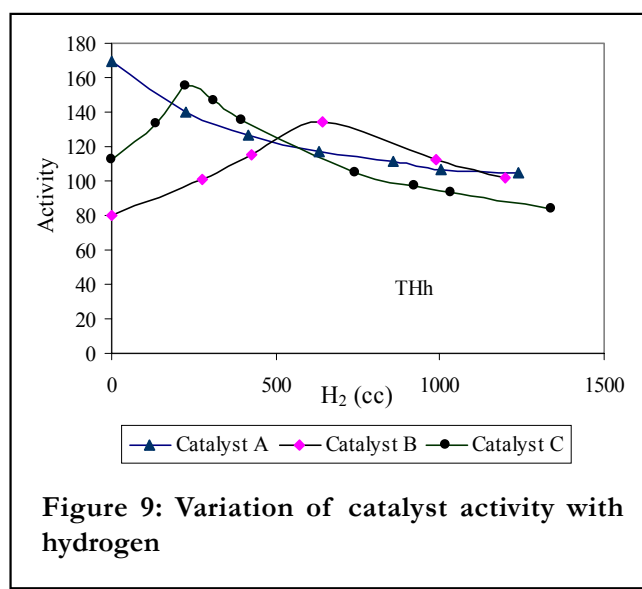


Figure 9: Variation of catalyst activity with hydrogen

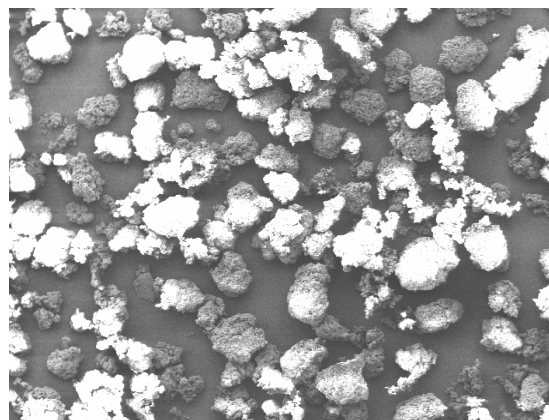


Figure 10: SEM image of sample produced by catalyst A

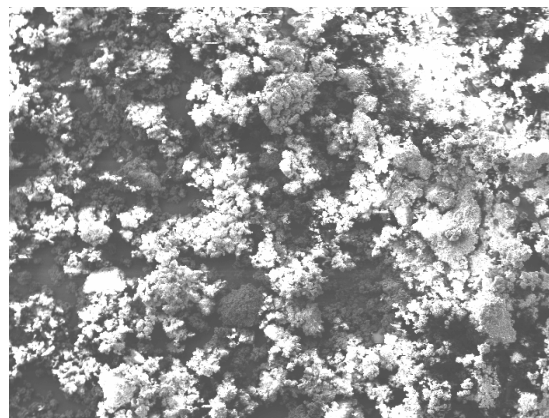


Figure 11: SEM image of sample produced by catalyst B

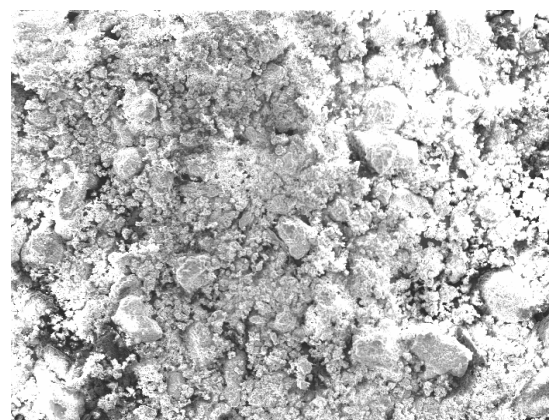


Figure 12: SEM image of sample produced by catalyst C

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### 2. Morphology of polyethylene powder

The SEM images of polymer powders from catalysts A, B, and C are shown in Figures 10, 11, and 12 respectively. As can be seen the morphology of catalyst A is more spherical than catalysts B and C. Intra-connection between powder grains could be clearly observed for catalysts B and C, while in catalyst A the powder grains are separately distributed. This intra-connection between grains in catalysts B and C is referred to the morphology of the catalysts used.

### 3. Molecular weight and molecular weight distribution

The effect of hydrogen, as a chain transfer agent, on  $M_n$  and  $M_w$  is shown in figure 13 and 14. As one may expect, because of transfer reaction to hydrogen, increasing the amount of hydrogen causes both  $M_n$  and  $M_w$  to decrease. However, according to figure 15, the polydispersity index remains approximately constant for all catalysts. According to the GPC analysis results, catalyst A shows bigger  $M_n$  and  $M_w$  rather than catalysts B and C. It could be interpreted that the active centers of catalyst A have less tendency to undergo transfer reaction to hydrogen; this catalyst shows higher activity than other catalysts in the presence of hydrogen, which indicates the same theory.

### CONCLUSION

Various reaction parameters were used to study the reaction condition and cocatalyst effect on ethylene polymerization using an  $L_{27}$  Taguchi design. Applying experimental design, an optimal condition was proposed for polymerization reaction. The influence of different catalysts was considered by using a synthesized and two commercial catalysts. According to the GPC analyses, the polydispersity index remains nearly unchanged in the presence of various amounts of hydrogen, whereas  $M_n$  and  $M_w$  decrease continuously. The SEM results show that, due to the morphologies of catalyst B and C used herein, powder produced by these catalysts is more intra-diffused with less separate grains. Finally, there

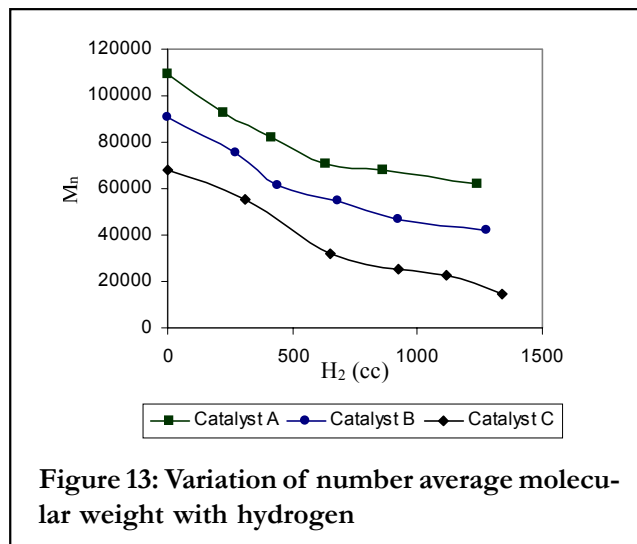


Figure 13: Variation of number average molecular weight with hydrogen

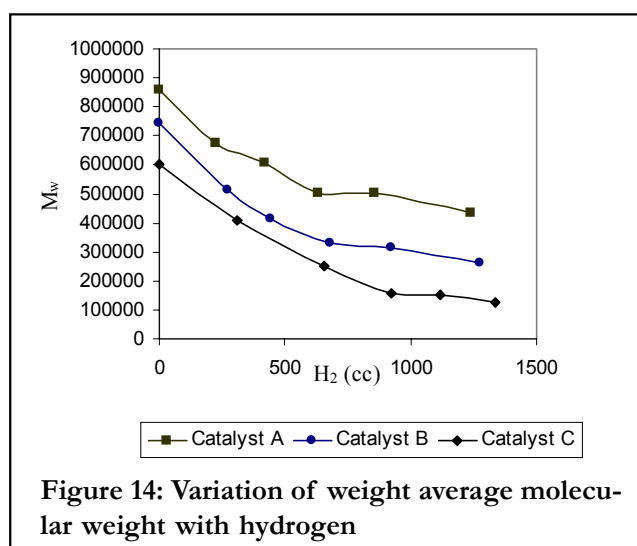


Figure 14: Variation of weight average molecular weight with hydrogen

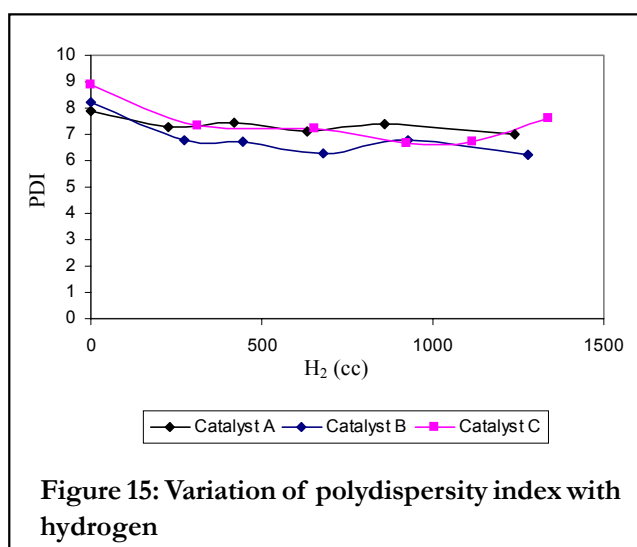


Figure 15: Variation of polydispersity index with hydrogen



is a tendency toward decreasing of catalyst activity in the presence of hydrogen, which is caused by formation of stable  $\text{Ti-C}_2\text{H}_5$  species.

## REFERENCES

- [1] M.Chanda; 'Advanced Polymer Chemistry', Marcel Dekker, New York (2000).
- [2] M.P.Stevens; 'Polymer Chemistry', Oxford University Press, New York, 2<sup>nd</sup> Ed., (1990).
- [3] Y.V.Kissin, R.I.Mink, T.E.Nowlin; J.Polym.Sci., Part A: Polym.Chem., **37**, 4255 (1999).
- [4] Y.V.Kissin, A.J.Brandolini; J.Polym.Sci., Part A: Polym.Chem., **37**, 4273 (1999).
- [5] Y.V.Kissin, R.I.Mink, T.E.Nowlin, A.J.Brandolini; J. Polym.Sci., Part A: Polym.Chem., **37**, 4281 (1999).
- [6] J.B.P.Soaes, A.E.Hamielec; J.Polym.Reac.Eng., **3**, 325 (1995).
- [7] J.B.P.Soaes, A.E.Hamielec; Polym., **36**, 2257 (1995).
- [8] P.C.Barbe, G.Cecchin, L.Noristi; Adv.Polym., **81**, 1 (1986).
- [9] J.J.A.Dusseault, C.C.Hsu; J.Appl.Polym.Sci., **50**, 431 (1993).
- [10] P.J.Flory; 'Principle of Polymer Chemistry', Cornell University Press, Ithaca (1953).
- [11] G.C.Han-Adebekun, W.H.Ray; J.Appl.Polym.Sci., **65**, 1037 (1997).
- [12] Y.V.Kissin; Macromol.Theory Simul., **11**, 67 (2002).
- [13] T.Garoff, S.Johansson, K.Pesonen, P.Waldvogel, D. Lindgren; Euro.Polym.J., **38**, 121 (2002).
- [14] D.C.Montgomery; 'Design, and Analysis of Experiments', 3<sup>rd</sup> ed., Wiley, New York (1991).
- [15] R.G.Launsby, D.L.Weese; 'Straight Talk on Designing Experiments', 2<sup>nd</sup> ed., Launsby Consulting, Colorado Springs, Co. (1995).
- [16] S.R.Schmidt, R.G.Launsby; 'Understanding Industrial Designed Experiments', 4<sup>th</sup> ed., Air Academy Press, Colorado Springs Co. (1994).
- [17] M.M.C.Forte, F.O.V.Cunha, J.H.Z.Santos, J.J.Zacca; Polymer, **44**, 1377 (2003).
- [18] S.S.Bafna, A.M.Beall; J.Appl.Polym.Sci., **65**, 277 (1997).
- [19] S.M.B.Nachtigall, R.B.Neto, R.S.Mauler; Polym.Eng. Sci., **39**, 630 (1999).