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OPTIMIZATION OF ETHYLENE POLYMERIZATION CONDITIONS WITH METALLOCENE CATALYST USING EXPERIMENTAL DESIGN METHODOLOGY

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ABSTRACT

A study of ethylene polymerization was carried out using a 2^3 full factorial design in order to obtain a better understanding of the metallocene catalyst system. Three independent variables (reaction temperature, Al/Zr ratio and ethylene pressure) were evaluated at two levels. The observed responses were catalytic yield, average molecular weight, polydispersity, melt flow rate, density, melting temperature, enthalpy of fusion and crystallinity, the yield being of primary interest. The catalyst, co-catalyst and the solvent used were, respectively, $Et(Ind)_2ZrCl_2$, methylaluminoxane (MAO) and n-hexane. The statistical model was efficient in describing the effect of the variables on the yield and showed that the temperature was the variable of larger influence. The results permitted conclusions about the best polymerization conditions.

RESUMO

Buscando conhecer melhor os catalisadores metalocênicos realizou-se um estudo para otimização das condições de polimerização do etileno usando metodologia de delineamento experimental via plano fatorial completo 2^3. Relacionou-se as variáveis independentes temperatura de reação, razão Al/Zr e pressão de etileno com as respostas, principalmente o rendimento catalítico. Como catalisador, cocatalisador e solvente foram usados, respectivamente, $Et[Ind]_2ZrCl_2$, metilaluminoxana (MAO) e n-hexano. Analisando-se os dados foi possível concluir que o modelo estatístico utilizado foi eficiente e possibilitou a identificação da temperatura como variável de maior influência no rendimento das polimerizações na região testada. Demais respostas, como massa molar, polidispersidade, taxa de fluidez e densidade também foram estudadas, possibilitando conclusões a respeito das propriedades dos polímeros obtidos e das melhores condições de polimerização.

KEY WORDS: metallocene, ethylene polymerization, experimental design.

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INTRODUCTION

The thermoplastic industry is undergoing an innovation phase, particularly with respect to the development and use of metallocene/methylaluminoxane catalyst systems for polymerization of α-olefins[1,2]. They are distinctly different from Ziegler-Natta catalysts because they facilitate the production of polymers with oriented and diversified molecular structure and can be used in copolymerization with many monomers, offering great versatility in the copolymer formation. These polyolefins can substitute other materials, such as elastomers and engineering plastics, having the advantage that the facilitate recycling due to a smaller variety of materials in the reject[3,4,5].

There are big differences in the microstructure of the polymeric materials produced with these two types of catalysts. The metallocenes are soluble in hydrocarbon solvents and their active sites are all equivalent in reactivity. They behave in an identical way during polymerization and this results in a polymer with a narrow molecular weight distribution and high uniformity along the chain as far as ramifications and comonomer distribution are concerned. The physical properties (mechanical, thermal, electrical, optical and rheological) are better defined and can be controlled in a precise way, leading to a better performing final product. Thus, kinetic and molecular modelling of the polymer can be done for a wide variety of niches[6].

Chemometrics Considerations

According to Hunter[7], those involved with chemistry should be involved with statistics as well, simply because statistics tells you what your data mean. An important illustration of the influence of chemistry on statistics was the work of W. S. Gosset, under the pseudonym "Student" who empirically derived *t* distribution. The term chemometric was applied for the first time by chemists in order to formalize the study of the application of mathematical methods to chemical sciences. S. Wood appears to have been the first person who worked in pattern recognition methods. Although formally pattern recognition methods gave rise to the term chemometrics, the use of statistical methods for the study of chemical processes has been known for a long time[8].

Experimental Design, Analysis of Variance (ANOVA) and Tests of Hypothesis

The statistical experimental design had its origin in work of Ronald Fisher and is best exemplified in his two classical books, "Statistical Methods for Research Workers"[9] and "The Design of Experiments"[10]. He showed that, through the simultaneous combination of several factors it was possible to obtain information on separate effects from a large number of factors. Tests in wich each factor is varied separately may lead to wastes and false results. The grouping of a series of experiments in blocks can show better the influence of various factors as well as reduce the number of experiments. The planning of tests in random order may guarantee additional protection against bias caused by unknown or uncontrollable factors[7]. An important type of experimental design used in chemistry is the factorial design. In this case, m levels of k factors are worked in several combinations. Usually two levels are used (where the factors assume values of -1 and +1), giving a 2^k factorial design, that allows the estimation of the main effects of each factor (first order influence), coupled infuences (2^{nd}, 3^{rd} order) can also estimate interaction effects in the obtained answers. An empirical representation of how a group of factors can influence the answer is given by the polynomial model[7]:

$$y = B_0 + \sum_i B_i x_i + \sum_i B_{ii} x_i^2 + \sum_{i \neq j} \sum B_{ij} x_i x_j$$

Where y = predicted value, xi = controlled factors, Bo, Bi, Bii, Bij are coefficients of the constant term (independent), first order, second order, and cross-product coefficient, respectively.

Analysis of Variance (ANOVA) is a technique by which it is possible to isolate and estimate the variances that contribute to the total variation of an experiment. It allows the identification of variables that are important and it establishes means to estimate their effects[11]. When the effect of several factors on an answer variable is desired, an analysis of variance is made using more than one classification factor and a comparison of the variance of each factor in the study is done with respect to the relative variance to the residue or inherent error of the measure.

Tests of hypothesis, also called significance tests, are used a lot in analysis of variance. A test of hypothesis considers the H_0 hypothesis (null hypothesis) to be tested and the H_1 complementary hypothesis, also called alternative. These hypotheses are formulated on populational parameters, with their acceptance or rejection being based on sampling results[12]. The F test in the factorial model evaluation consists of the comparison of calculated F with controlled F for the significance level chosen for the test. The calculated F consists of the ratio between the variance of the terms of the model and the relative variance to the residue. The fatorial design is based on a first degree polynomial model, without quadratic terms that would give a second degree equation. For each answer a curvature test is necessary and it consists of comparison of factorial model points average with the central points average. The F test is, of course, applied also on this curvature[13].

In order to evaluate the significance of the coefficients, the t test is applied. This consists in comparing calculated t with controlled t for the significance level chosen for the test. Calculated t is the ratio of the estimated coefficient for each factor and the standardized error. The calculated t value actually represents the number of standard deviations of the coefficient from zero[13].

METHODOLOGY

The polymerizations were performed using a 1.5 L steel reactor. The experimental procedures were carried out under inert atmosphere, using the Schlenk technique. The ethylene, used as monomer, was provided by Companhia Petroquímica do Sul (COPESUL), Triunfo, RS, Brazil. The metallocene catalyst was supplied by Witco GmbH Polymer Chemicals Group, P.O.

Box 1620, D-59180, Bergkamen, Germany. It consist of 1,2-ethylene-bis-indenyl-zirconium dichloride, $Et[Ind]_2ZrCl_2$ (racemic mixture), with the trade name EURECEN®5036, code no. TA02677. The co-catalyst methylaluminoxane (MAO) was supplied by Albemarle Co., Florida Street, LA, USA. The catalyst was diluted with toluene supplied by Merck do Brasil, Rio de Janeiro. The solvent used for polymerization was n-hexane, polymeric grade, supplied by Phillips Co. The solvent was purified by drying for 12 hours with molecular sieve 10A - Grace 544, previously dried at 200°C for 4 hours, followed by fractional distillation in the presence of metallic sodium and benzophenone as indicator using a Vigreux column of 100 cm height, packed with glass.

A complete 2^3 factorial design was elaborated having three replicates in the central point, and three independent variables, temperature, Al/Zr ratio and ethylene pressure. They were evaluated at two levels (+ and -). All the design data is shown in Table 1.

Table 1. Full factorial design 2^3 for ethylene polymerization

Factors				Coded Factors		
Order*	**Temp.** (°C)**	**Al/Zr*** Ratio**	**Ethylene Pressure (bar)**	**Temp. (°C)**	**Al/Zr Ratio**	**Ethylene Pressure (bar)**
4	50.0	1000	1.00	-	-	-
9	80.0	1000	1.00	+	-	-
3	50.0	2500	1.00	-	+	-
10	80.0	2500	1.00	+	+	-
11	50.0	1000	4.00	-	-	+
8	80.0	1000	4.00	+	-	+
5	50.0	2500	4.00	-	+	+
7	80.0	2500	4.00	+	+	+
2	65.0	1750	2.50	0****	0	0
6	65.0	1750	2.50	0	0	0
1	65.0	1750	2.50	0	0	0

*Random order. **Temperature. ***Without dimension. ****Replicates in the central point.

The replicates in the central point are important because they can supply an estimate of the experimental error used in the ANOVA of the model. The central point is also useful for the evaluation of the presence of curvature. The DESIGN-EXPERT® software, version 5.0.9 supplied by STAT-EASE Inc., Minneapolis, MN, USA, was used to facilitate the statistical calculations, necessary for a consistent factorial model evaluation. Using the DESIGN-EXPERT® software each answer was analyzed according to the following sequence: selection of main effects, graphical visualization of the effects through normal probability plots[14,15], analysis of variance, evaluation of residues and detection of outliers. Once the existence of a valid predictive model was confirmed, a detailed interpretation of the results represented by a series of graphs was performed.

RESULTS AND DISCUSSION

The experiments for the factorial design (2^3), the yield and the activity of the polymerizations, as well as the results obtained for the characterization of the polymers are illustrated in Tables 2 and 3.

Table 2. General results obtained for the polymerization of ethylene – factorial design (2^3)

Experiments			Results					
Independent Variables			Dependent Variables					
T °C	Al/Zr Ratio	P ethylene bar	Yield g	Activity g/mmol cat	Mn* g/mol	Mw** g/mol	Mz*** g/mol	Pd****
-	-	-	**3.5**	7.46E+05	61500	185000	497000	3.0
+	-	-	**16.2**	3.45E+06	51000	155000	459000	3.0
-	+	-	**7.4**	1.58E+06	54400	152000	357000	2.8
+	+	-	**14.9**	3.18E+06	42000	126000	344000	3.0
-	-	+	**5.7**	1.22E+06	40900	120000	405000	2.9
+	-	+	**35.6**	7.59E+06	40800	127000	479000	3.1
-	+	+	**12.2**	2.60E+06	50200	133000	363000	2.6
+	+	+	**39.8**	8.49E+06	33700	98000	298000	2.9
0	0	0	**17.0**	3.62E+06	54400	160000	414000	2.9
0	0	0	**18.2**	3.88E+06	65500	198000	508000	3.0
0	0	0	**18.0**	3.84E+06	61200	163000	403000	2.7

*Number average molecular weight. **Weight average molecular weight. ***Z average molecular weight. ****Polydispersity = Mw/Mn.

Analysis of the Yield Results

The importance of the main effects, temperature (A), Al/Zr ratio (B) and ethylene pressure (C) is illustrated in Figure 1 in terms of half normal probability plots. This figure is useful for the selection of effects for the ANOVA.

Table 3. General results obtained for the polymerization of ethylene – factorial design (2^3)

Experiments			Results				
Independent Variables			Dependent Variables				
T °C	Al/Zr Ratio	P ethylene bar	MFR (190/21,6)* g/10 min	Dens.** g/cm^3	Tm*** °C	ΔH_f**** J/g	Crys.***** %
-	-	-	0.08	0.976	125	177	59
+	-	-	1.00	0.960	125	189	64
-	+	-	0.00	1.065	122	144	47
+	+	-	1.60	0.969	124	188	63
-	-	+	2.80	0.968	126	189	63
+	-	+	2.90	0.956	125	190	65
-	+	+	0.38	0.971	126	186	61
+	+	+	2.80	0.959	125	196	66
0	0	0	0.10	0.961	124	176	59
0	0	0	0.07	0.954	122	160	52
0	0	0	0.12	0.954	122	172	58

*Melt flow rate at 190°C and 21.6 kg, according to ISO 1133/97, ASTM D1238/95. **Density according to ASTM D792/98 method B, ISO 1183/87 method A. ***Melting temperature. ****Enthalpy of fusion. *****Crystallinity. The thermal analyses were carried out according to ASTM D3417/97, ASTM 3418/97.

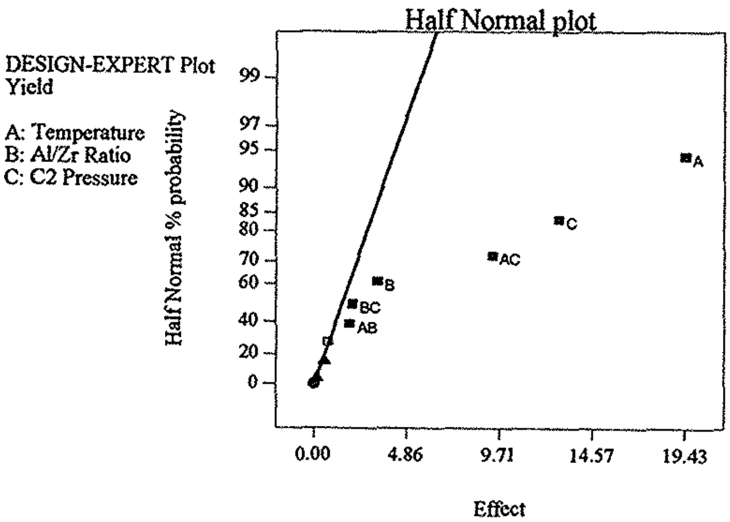

Figure 1. Half normal probability plot of effects

Values far from the straight line, which represents the error, have more significant effects, and values very close to the straight line are not considered significant. In the calculations, the effect of 3rd order (ABC) was not considered. Analysis of the ANOVA results for the polymerization yield (Table 4) shows that the terms of the model are not a consequence of population error. It is possible to reject the H_0 hypothesis (null hypothesis) considering a significance level of 0.0002 (99.98% of confiability). The *F* test of Snedecor was used in the evaluation.

The results of the *F* test for curvature, indicate that it is not possible to reject the hypothesis of the existence of curvature. The curvature presented by the model is significant and a 1st degree polynomial model is not adaptable for a significance level of 0.2226 or 77.74 % of confiability. However the predictions obtained through the equation were satisfactory, indicating a valid factorial model in spite of the existence of curvature. Analysis of the variance of the coefficients through the Student *t* test, considering a maximum significance level of 0.05 (95% of confiability), shows that is not possible to reject H_0 only for the central point. The results obtained for the yield are shown in Table 4.

Table 4. Analysis of variance (ANOVA) for the yield results

Model evaluation – F Test (Snedecor)		
	Calculated F Value	*Prob. > F (significance level)*
Model	347.6	0.0002
Curvature	2.35	0.2226
Coefficient evaluation – t Test (Student)		
	t for H_0 (coef. = 0)	*Prob. > |t| (significance level)*
A – temperature	34.86	< 0.0001
B - Al/Zr ratio	5.96	0.0095
C - C_2 pressure	23.02	0.0002
AB	3.37	0.0433
AC	16.74	0.0005
BC	3.62	0.0361
Central point	1.53	0.2226

Once the analysis of variance was concluded, an equation for factors was obtained. This equation can be used to predict yields under various independent variables values in the analyzed area, but in this case, it is necessary to use the equation for uncoded factors. The final equation for coded factors is as follows:

$$\mathbf{Yield = 16.9150 + 9.7150A + 1.6600B + 6.4150C - 0.9400AB + 4.6650AC + 1.0100BC}$$

The yield results representations are shown in Figures 2 and 3. The 2^3 factorial model is illustrated in Figure 2, while Figure 3 shows the surface answer of these results with respect to temperature and pressure of ethylene using a ratio of 1750 for Al/Zr. The temperature exhibits the main effect in the system studied, it showed better results in the *t* test and contributed the largest coefficient in the final equation of the coded factors.

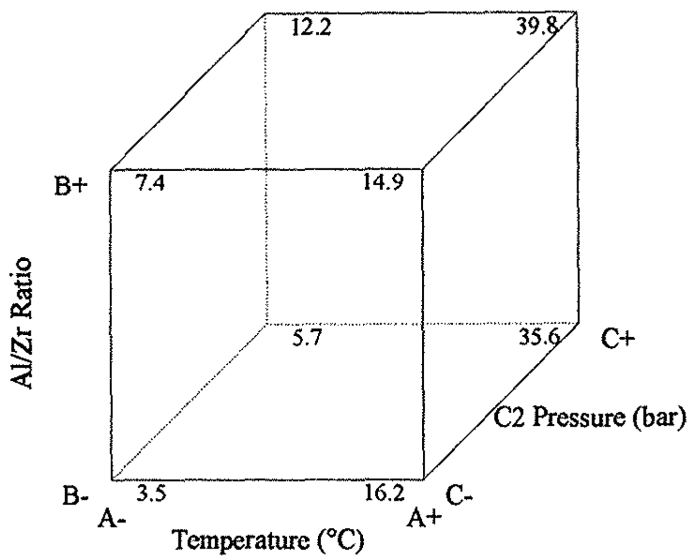

Figure 2. Yield results arranged in the vertexes of a cube

Analysis of the Characterization Tests

The ANOVA of the characterization results are shown in Table 5. As can be seen, the terms of the model are a result of the population error. This means that it is not possible to reject the null hypotesis (H_0) that affirms that the model terms are part of the population error considering a maximum significance level of 0.05 (95 % of confiability) and making use of the *F* test. The results of MFR (190/21.6) and density presented satisfactory results with respect to the validity of the model. However, the analysis of the coefficients estimated for the factors using the *t* test and considering a maximum significance level of 0.05 exhibited satisfactory results only for the density tests.

As far as the properties obtained for the polymers are concerned the results were in accordance with those reported in the literature and the best agreement was obtained for the polydispersity[1-5]. A more careful analysis of the results shown in Tables 2 and 3 showed some incoherences for some structure-property relationships.

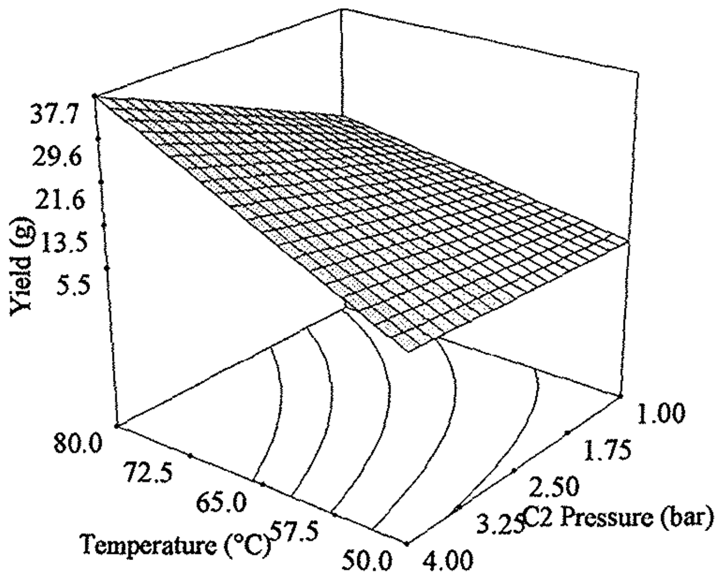

Figure 3. Surface answer of yield results with respect to temperature and pressure of ethylene using a ratio of 1750 for Al/Zr

Table 5. ANOVA for the characterization tests

Model evaluation – F Test (Snedecor)			
Characterization Tests		*Calculated F Value*	*Prob. > F (significance level)*
Mn	g/mol	2.74	0.2930
Mw	g/mol	1.57	0.4433
Mz	g/mol	1.54	0.4487
Pd	-	1.03	0.5745
MFR (190/21.6)	g/10 min	2502	**0.0004**
Density	g/cm^3	88.52	**0.0112**
Tm	°C	1.09	0.5583
ΔH_f	J/g	4.03	0.2134
Crystallinity	%	3.02	0.2715

A reduction in the melt flow rate (MFR) was not observed with the increase in the number average molecular weight (Mn) as expected. This may be due to the fact that hydrogen, that is a very important factor in molecular weight control was not used and, consequently, the polymers exhibited very high molecular weight and very low melt flow rate (MFR) and as a consequence difficulty was encountered in their material processing and characterization. The polydispersity showed very low values, confirming that polymerization occured at a single site. The low polydispersity values may be responsible for the low melt flow rate found. A narrow polydispersity range may be indicative of the lack of the short chain fraction that would act as lubricant during the processing, in this particular case, during the displacement of the polymer in the plastometer.

The values obtained for the density were quite high. A discrepancy was also noted between density and crystallinity. In some cases, materials with larger density (smaller free volume, closer molecules and a larger ordering of the lamelae) showed lesser crystallinity, contrary to what would be expected. These contradictory results may be explained in terms of an inadequate material morphology. Since the comonomer was absent, high density values were expected. The crystallinity had oscillations typical of values for high density polyethylene (HDPE). On the other hand, the values obtained for the melting temperature (Tm) were low and close to typical values of linear low density polyethylene (LLDPE) when compared to results of HDPE synthesized with Ziegler-Natta catalyst. This behavior was expected because lower Tm values are also usually observed for polypropylene (PP) and LLDPE synthesized with metallocenes[16]. A better evaluation of the structure-property relationship can be obtained using other analytical techniques such as X-ray diffraction, rheology and nuclear magnetic resonance.

CONCLUSIONS

The methodology of full factorial design (2^3) was efficient and satisfactory for the optimization of the ethylene polymerization conditions with metallocene catalyst. As expected, the temperature, the ethylene pressure and the Al/Zr ratio had important effects on the catalytic yield. The temperature was the most important variable, a small alteration in temperature resulting in an important alteration in the yield. The optimized polymerization condition was in the superior level tested (T = 80°C; P = 4 bar; Al/Zr = 2400). The Al/Zr ratio had a small influence on the yield results and it is possible to work with temperature and ethylene pressure in the superior levels using a smaller ratio of Al/Zr than the one mentioned above.

One important factor that needs considerable additional future investigation is the presence of hydrogen and its role in molecular weight control, polydispersity and material processing. The obtained knowledge regarding the statistical techniques and physical-chemistry of the analyzed area will be useful for future works with metallocene catalyst systems.

The statistical analysis of the results obtained for Mn (number average molecular weight), Mw (weight average molecular weight), Mz (Z average molecular weight), polydispersity (Mw/Mn), melt flow rate - MFR (190/21.6), Tm (melting temperature), ΔH_f (enthalpy of fusion) and crystallinity, did not permit the establishment of a satisfactory linear correlation between them and the independent variables (temperature, ethylene pressure and Al/Zr ratio) for the conditions tested. For the density results it was possible to establish a consistent statistical model. On the other hand, some inconsistences or incoherences were observed for the structure-property relationship. On the whole, the results were useful for the characterization for the synthesized polymers.

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