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Ethylene dimerization by a homogeneous Ti-based three-component catalyst system: process evaluation and optimization of parametric performance

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Abstract

This research utilizes the design of experimental (DOE) methodology by Taguchi orthogonal array (OA) to optimize various operating parameters of a Ti-based homogeneous catalyst in presence of the mixture of two modifiers and triethylaluminum (TEA) as activator for production of 1-butene in the ethylene dimerization reaction. 2,5-dimethoxytetrahydrofuran (2,5-DMTHF) and tetrahydropyran (THP) were used as modifiers. L_9 OA of the Taguchi technique was implemented to evaluate the influence of four factors (i.e. reaction temperature, ethylene pressure, Al/Ti molar ratio, and mixed modifiers/Ti molar ratio) at three levels on the overall selectivity to 1-butene (wt. %). The process parameters were optimized and ranked using data obtained from mean S/N ratios for overall selectivity to 1-butene. Also, confirmation experiment was performed to prove effectiveness of the Taguchi technique and validity of the predicted results.

Keywords: Taguchi technique; S/N ratio; Ethylene dimerization; Overall selectivity to 1-butene; Optimum conditions

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1. Introduction

1-Butene, a versatile chemical intermediate involved in the production of a wide variety of industrial products, is the first member of the even-numbered linear 1-alkenes, and has diverse applications [1,2]. On the basis of a scientific report, the average annual increase in demand for 1-butene is 5.3% from 2006-2020 even more than estimated average annual growing rate for 1-hexene production (i.e. 4.7%) [3]. Dimerization of ethylene to 1-butene has been of great interest from both academic and technological viewpoints, since there are a number of different processes that can happen during the reaction, some of which lead to isomers of 1-butene, linear oligomer formation, and polymeric products [4–10]. Generally, the process of ethylene dimerization is conducted in liquid phase with the homogeneous catalytic system e.g. $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$–modifier (an electron donor compound) [3]. $Al(C_2H_5)_3$ (triethylaluminum (TEA)) serves as an activator, which can release free coordination sites in the titanate complex and generate one or more Ti-C bond(s) by exchanging its ethyl groups with the butoxide groups of the titanate complex [9]. The catalyst modifiers (electron donor ligands) are Lewis bases or polar organic compounds (such as tert-phosphine, phosphite, amine, and cyclic ether), which, when added to the catalyst system, provide better selectivity for the desired reaction [8–10].

Taguchi method is a form of design of experimental (DOE) with a special application principle and is a technique for designing and performing experiments to investigate processes where the output depends on many factors (variables, inputs) without having tediously and uneconomically run of the process using all possible combinations of values [11]. The Taguchi approach uses a system of specific orthogonal arrays (OA) to be chosen and applied in suitable conditions to describe a large number of experimental situations and provide a set of well-balanced experiments [12]. The Taguchi method employs signal to noise (S/N) ratio to quantify the present variation. The S/N ratio can be used to determine the product quality and to compare the product performance. There are several S/N ratios available depending on type of characteristics: (a) smaller is better, (b) nominal is best, and (c) larger is better [13]. The analysis of variance (ANOVA) statistical method is also used to analyze the influence of each controllable factor on the relevant responses [14]. Usually, in final step, a confirmation experiment is performed to verify the experimental conclusions. In fact, running confirmation experiment is necessary to show the optimum conditions and comparing the result with the expected performance and it provides direct proof of the methodology [15]. If the new design does not meet the specified requirement, the process must be reiterated using new systems until the criteria are met.

In our previous research work, we optimized the operating conditions of the ethylene dimerization with relevant homogeneous catalyst system using the one-variable-at-a-time (OFAT) approach [16]. The conventional approach of experimenting with OFAT method is labor-intensive and time-consuming. Therefore, it is clearly an important requirement to satisfy the design objectives with the least number of tests. In this study using Taguchi's experimental design methodology, we could rank the selected factors of the ethylene dimerization reaction and determine their optimum levels in order to maximize overall selectivity to 1-butene for a Ti-based homogeneous catalyst system in the presence of 2,5-dimethoxytetrahydrofuran (2,5-DMTHF) and tetrahydropyran (THP) as modifiers in the combination with TEA as activator.

2. Experimental

2.1. Material and apparatus

2,5-DMTHF and THP were purchased from Merck Co. TEA was obtained from Crompton Chemicals and was diluted to a 0.5 M solution in heptane before use. *n*-Heptane was distilled from anhydrous sodium

carbonate under dry nitrogen and stored over pre-activated molecular sieves (4 Å) until its water content was below 1 ppm. Polymerization grade ethylene was supplied by Arak Petrochemical Company (ARPC) and was checked for purity by gas chromatography (GC). Other chemicals were obtained commercially and were used without further purification.

A 1-L double-wall stainless steel Büchi pressure reactor equipped with an external circulation bath for temperature control, a magnetically driven mechanical stirrer for saturation of inlet gas in the liquid phase, an internal thermocouple, gas inlet and outlet ports, and a liquid sampling port was used. The reactor was set up with a Büchi multi channel data system (BDS MC) to display and record the temperature, pressure, and stirrer speed profiles with reaction time.

GC analyses of reaction products were carried out on a Varian 3800 chromatograph with a flame-ionization detector (FID) using a CP Sil 8 capillary column (25 m × 0.53 mm). The column oven temperature of the GC was programmed to run from 40 to 280 °C at 10 °C/min.

2.2. Ethylene dimerization procedure and product analysis

All manipulations involving air- and moisture-sensitive materials were handled under an atmosphere of dry nitrogen using standard Schlenk techniques. Before conducting a catalytic batch experiment, the reactor was heated to 100 °C for an hour to eliminate traces of water, air, and oxygenate impurities. It was then cooled to ambient temperature under dry nitrogen. Thereafter, the reactor was charged with 400 mL of *n*-heptane as solvent to provide sufficient liquid height to ensure successful operation of the gas entrainment stirrer for both mass and heat transfer. Subsequently, the calculated quantities of titanium catalyst, TEA, and mixture of modifiers were immediately injected into the reactor. The speed of the stirrer was initially set to 900 rpm to eliminate gas-to-liquid mass transfer limitations. The reactor then was heated to a temperature lower than the desired temperature. It is noteworthy that the internal temperature of the reactor was adjusted to a level 3−5 °C lower than the desired value because of the highly exothermic nature of ethylene dimerization. Ethylene was then introduced into the reactor to the desired pressure. The interior temperature of the reactor was controlled using cooling fluid, if required. The volume of ethylene introduced was measured using a Brooks mass-flow controller (MFC). After the dimerization was allowed to proceed for 0.5 h, the reaction was terminated by switching off the gas entrainment stirrer and quenching by the addition of methanol/HCl solution, and the products were withdrawn. The total volume of gaseous components was measured by means of a gas flowmeter.

A gas sample was collected in a 150 ml stainless steel bomb and then subjected to GC-FID analysis. A liquid sample was distilled in order to remove catalyst and TEA. Finally, the sample was analyzed with GC-FID. The polymers formed in certain runs were removed, washed with hexane, dried in a vacuum oven at 100 $^{\circ}$C, and ultimately weighed.

The mass balance of the experiments was determined via quantification for ethylene consumption based on measured values from the MFC, flowmeter, and also GC analyses of the gaseous and liquid products, the liquid product weight and the gas volume.

2.3. Taguchi design of experiments

This study considers four controllable factors in three levels. These factors include temperature, pressure, Al/Ti (mol/mol), and mixed modifiers/Ti (mol/mol) (see Table 1). L_9 (3^4) OA of the Taguchi technique was implemented to evaluate the influence of these factors.

Table 1. Design experiments in ethylene dimerization reaction

Factors	Levels		
	1	2	3
A Temperature (°C)	45	50	55
B Pressure (bar)	6	16	28
C Al/Ti (mol/mol)	2	3.5	4.5
D Mixed modifiers/Ti (mol/mol)	0.5	1	2

3. Results and discussion

3.1. S/N ratio calculations and optimal parameters of ethylene dimerization

The overall selectivities to 1-butene were obtained under nine sets of experimental conditions (see Table 2).

In this study, our aim was to maximize the overall selectivity to 1-butene in the ethylene dimerization reaction for the relevant homogeneous catalyst system. Therefore, the S/N ratios have been calculated by eq. (1) as logarithmic transformation of the loss function:

$$S/N = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \quad (1)$$

where n represents the number of repetitions under the same experimental conditions and Y_i represents the overall selectivity to 1-butene (wt. %) for each test.

The S/N ratios for the nine sets of experiments were listed in Table 2.

Table 2. Overall selectivities to 1-butene and S/N ratios for L_9 OA

Experiment No.	Parameters and their levels				$S_{1\text{-butene}}$ (wt. %)	S/N ratio (db)
	A	B	C	D		
1	1	1	1	1	56.20	34.99
2	1	2	2	2	69.84	36.88
3	1	3	3	3	75.36	37.54
4	2	1	2	3	80.50	38.11
5	2	2	3	1	65.44	36.31
6	2	3	1	2	73.90	37.37
7	3	1	3	2	72.62	37.22
8	3	2	1	3	74.15	37.40
9	3	3	2	1	70.78	37.00

The mean of S/N ratios of each factor in the ith level have been calculated and presented in Table 3. As reported in Table 3, the order of influence of the controllable factors of the homogeneous catalytic system presented in this study in term of overall selectivity to 1-butene was: D (mixed modifiers/Ti) > A (reaction temperature) > C (Al/Ti) > B (ethylene pressure).

Also, it was determined that the optimum levels of the factors were: A_2, B_3, C_2, D_3. It must be noted that the above combination of factor levels A_2, B_3, C_2, D_3 are not among the nine combinations tested for the experiment, therefore the confirmation test is required. This is expected due to the multifactor nature of the experimental design employed (9 from 3^4=81 possible combinations).

Table 3. Mean S/N ratios for overall selectivity to 1-butene and parameter ranking

Factor	Level	Mean S/N ratios	Difference (Maximum-Minimum)	Rank
A	1	36.470		
	2	37.263	0.793	2
	3	37.206		
B	1	36.773		
	2	36.863	0.530	4
	3	37.303		
C	1	36.586		
	2	37.330	0.744	3
	3	37.023		
D	1	36.100		
	2	37.156	1.583	1
	3	37.683		

3.2. Verification test

The estimated value of S/N ratio ($S/N_{predicted}$) using the optimal levels of the process factors can be calculated by following equation (eq. (2)) [11]:

$$S/N_{predicted} = \overline{S/N} + \sum_{i=1}^{j} (\overline{S/N}_{i-opt.} - \overline{S/N}) \quad (2)$$

where $\overline{S/N}$ is the overall mean S/N ratio of orthogonal array table, $\overline{S/N}_{i-opt.}$ are the multiple S/N ratios corresponding to optimum factor levels, and j is the number of process factors that affect the quality characteristic.

To confirm this prediction, a verification test was carried out by means of the optimal levels of the process factors i.e. A_2, B_3, C_2, and D_3. Table 4 shows the comparison of the predicted overall selectivity to 1-butene with the experimental results using the optimal control factors. A convincing agreement between the predicted and experimental rate was obtained.

Table 4. Results of the confirmation experiments for selectivity to 1-butene

	level	Overall selectivity to 1-butene	
		Value (wt. %)	S/N ratio (db)
Prediction	$A_2B_3C_2D_3$	85.50	38.639
Experiment	$A_2B_3C_2D_3$	85.90	38.680

4. Conclusion

In present research, the ethylene dimerization reaction was investigated to optimize and identify effect of the selected parameters of a three-component homogeneous catalyst system comprising a titanium compound, a mixture of two ethers as modifier, and TEA as activator in term of overall selectivity to 1-butene using the Taguchi DOE approach. In this regard, the Taguchi L_9 experimental layout was used to explore the effect of temperature, pressure, Al/Ti, and mixed modifier/Ti molar ratios. The process

parameters were ranked and screened using data obtained from mean S/N ratios for overall selectivity to 1-butene. The results showed that mixed modifiers/Ti molar ratio had the highest influence on the overall selectivity to 1-butene in the aforesaid catalytic system. Finally, in order to certify the orthogonal results of the applied technique, the predicted optimum levels of the selected parameters were monitored again and the used method reproducibility was confirmed. According to the Taguchi approach, after setting the controllable factors at optimum values, the overall selectivity to 1-butene for the relevant homogeneous catalyst system was almost enhanced to 85.90%.

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