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# Simultaneous multi-objective optimization of a new promoted ethylene dimerization catalyst using grey relational analysis and entropy measurement

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**Abstract**−A hybrid approach between the Taguchi method and grey relational analysis (GRA) with entropy measurement was applied to determine a single optimum setting for reaction factors of the proposed ethylene dimerization catalyst having overall selectivity to 1-butene ($S_{1\text{-}btn}$ (%)) and turnover frequency (TOF ($h^{-1}$)) as multiple quality characteristics. Titanium tetrabutoxide ($Ti(OC_4H_9)_4$) catalyst precursor in combination with triethyl aluminum (TEA) activator, 1,4-dioxane as a suitable modifier, and ethylene dichloride (EDC) as a novel promoter were used in the catalysis. Control factors of temperature, pressure, Al/Ti, 1,4-dioxane/Ti, and EDC/Ti mol ratios were investigated on three levels and their main effects were discussed. The effect of the binary interaction between temperature, pressure, and Al/Ti mol ratio was also examined. Weight of the responses was determined using entropy. Analysis of variance (ANOVA) for data obtained from GRA indicated that EDC/Ti mol ratio with 27.64% contribution had the most profound effect on the multiple quality characteristics. Development of the weighted Grey-Taguchi method used the Taguchi method as its basic structure, adopted GRA to deal with multiple responses, and entropy to enhance the reasonability of the comprehensive index produced by GRA to make the results more objective and accurate. Overall, these combined mathematical techniques improved catalytic performance for 1-butene production.

Keywords: Multi-objective Optimization, Grey Relational Analysis, Entropy Measurement, Ethylene Dimerization, EDC

## INTRODUCTION

The full-range processes for the production of linear $\alpha$-olefins (LAOs) typically rely on a mathematical Schulz-Flory distribution or Poisson ratios of nonselective ethylene oligomerization [1]. The global annual average growth for LAOs is estimated to be 3.3% (2012-2018) but depends largely on the specific region, with higher growth found in developing countries [2]. Since some end-markets are more profitable than others, a goal of industry is to develop technologies that can selectively target certain markets and make only one specific alpha olefin cut. The ability to produce the most economically viable LAOs, i.e., co-monomer grade 1-butene, 1-hexene and 1-octene, is therefore highly desirable. Accordingly, much academic and industrial effort has been devoted to study of di-, tri-, and tetramerization of ethylene [3-5]. Research has focused on improving the performance of the Ti and Ni catalysts, which are the preferred homogeneous catalysts for ethylene dimerization, because isomers of 1-butene, linear oligomers, and polymeric materials can form during the reaction [6-18]. Moreover, some studies have employed the metallacycle or Cossee-type catalytic pathway/mechanisms [19-22]. Dimerization reaction is currently conducted in a liquid phase using a titanium tetrabutoxide ($Ti(OC_4H_9)_4$)-triethyl aluminum (TEA)-modifier catalyst system. Modifiers (electron donor ligands) are Lewis bases or polar organic compounds (such as phosphine, amine, and cyclic ether) that provide better selectivity [15-17]. Researchers have reported that the addition of geminal chloro-compounds and halides as promoters to the homogeneous catalyst systems in ethylene trimerization and tetramerization has resulted in remarkable increase in selectivity to 1-hexene and 1-octene, respectively [23-25]. By contrast, few reports discuss the use of halides as catalyst promoters in the Ti-based ethylene dimerization [7,10].

One goal of this type of chemical reaction engineering is to optimize performance to achieve high efficiency by varying the parameters that affect the relevant process. Traditional optimization of chemical reaction processes for LAO production alters one factor at a time, keeping all other factors constant to assess the effect of each factor. This method usually cannot produce comprehensive understanding of the whole process in terms of which factor more significantly improves the results, how two factors interact, or in which pattern each factor affects the response. The disadvantages of the traditional method of varying each factor in turn to test all possibilities requires a more efficient and scientific approach, especially when a large number of factors are considered in a complicated process. Application of statistical techniques for the development of carefully-planned experimentation at the design stage is necessary for continual quality improvement of products and processes. This should be accompanied by reduction of variability and other failure costs using low cost efforts to maintain economic viability [26,27]. The Taguchi method is an effective methodology that achieves breakthrough improvements of quality characteristics that are robust under

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S.H.M. dedicates this paper to the memory of his late father, Mr. Seyed Hasan Mahdaviani, renowned professor of Persian literature.

environmental conditions through the application of statistical and engineering concepts [28]. It has been used extensively for experimentation and devising strategies for quality control in the production and manufacturing industries. Taguchi technique allows industries to greatly reduce product development cycle time for both design and production, thereby reducing costs and increasing profits [29]. In our previous work, we used this method to optimize homogeneous ethylene dimerization catalysis with the additives of tetrahydropyran and chloroethane to separately increase the yield of the reaction and decrease the weight of the polymer [6]. The conventional Taguchi method was designed to optimize a single performance characteristic that cannot satisfy the requirements of overall quality. Simultaneous optimal combination of responses was determined using engineering judgment and experience, which can often bring uncertainty into the decision-making process. In that study, the authors concluded that further optimization will be required for multiple quality analysis, particularly when responses are moderately or highly correlated [6]. An option for rectifying this problem is the use of a multi-criteria methodology applied to find optimal compromises between several responses.

In the present study, grey relational analysis (GRA) a computational method with extensive mathematical criteria proposed by Deng [30] was integrated with the Taguchi approach for simultaneous multi-objective optimization of overall selectivity to 1-butene ($S_{1\text{-}btn}$ (%)) and turnover frequency (TOF ($h^{-1}$)) for the Ti-based ethylene dimerization. The modifier of 1,4-dioxane was used with ethylene dichloride (EDC) as a novel promoter and triethyl aluminum (TEA) as an organometallic initiator to establish a new catalytic system. The effectiveness of the Taguchi-Grey hybrid approach to convert multi-objective problems into an equivalent single objective function was demonstrated to fulfill the goal of overall quality optimization. In this regard, a Taguchi $L_{27}$ orthogonal array (OA) was first used to plan the experiments for the ethylene dimerization reaction. The controllable factors of temperature, pressure, Al/Ti, 1,4-dioxane/Ti, and EDC/Ti mol ratios were selected with three levels for each factor. In the OA table, binary interactions between temperature, pressure, and Al/Ti mol ratio were considered and their effects on catalytic performance were investigated. GRA was then applied to simultaneously examine how the ethylene dimerization factors influence the quality targets of $S_{1\text{-}btn}$ and TOF. An optimal factor combination was obtained. To derive the equivalent objective function, different priority weights were assigned to different responses according to their relative importance, but no specific guidelines exist for assigning the response weights. So, entropy measurement [31] was implemented as a hybrid method with GRA to calculate the relative response weights from analysis of entropy of the entire process.

## METHODS

### 1. Taguchi Approach

The Taguchi method has been successfully applied in many US, Japan and European manufacturing firms, such as in automobile, electronics, food processing, and medical equipment industries [32]. Analysis of the main effects and interactions enables screening and ranking of individual factors using an OA to establish optimal settings and ensure that the experimental design is both straightforward and consistent [33]. Variability is expressed by signal-to-noise (S/N) ratio as a single indicator to jointly and simultaneously consider the average value and standard deviation of test results. The S/N ratio of mean to standard deviation can effectively consider the variation encountered in a set of trials. The experience and knowledge of the researcher is essential to the proper selection of variables and their levels. In other words, it is chosen using prior knowledge, expertise, and an understanding of process [34]. S/N ratios are log functions of desired output which serve as objective functions for optimization and aid data analysis and prediction of optimum results. The basic principle of this method is to develop an understanding of the individual and combined effects of various design parameters. In the current study, the target was maximizing both $S_{1\text{-}btn}$ and TOF; hence, the S/N ratio for the two responses was considered as 'the-higher-the-better' using Eq. (1):

$$S/N_H = -10.\log\frac{1}{m}\sum_{j=1}^{m}\frac{1}{y_j^2} \quad (1)$$

where m is the number of repetitions under the same test conditions and $y_j$ is the observed data for $S_{1\text{-}btn}$ and TOF at each test.

### 2. GRA

Any system between known and unknown limits is considered to be grey and contains primitive data providing poor, uncertainty, and discrete information. GRA is an extensive computational method in the grey system theory that can compensate for the shortcomings of statistical regression, and effectively analyze relationships between sequences in situations involving limited data. Grey is appropriate for pragmatic problems that occur in strategic industrial decision-making [30]. GRA can be used to consider multiple responses at the same time and provide a comprehensive index to represent the evaluation of responses [35]. Notably, it utilizes the mathematical method when analyzing correlations between series comprising a grey relational system, thereby determining the difference in contribution between a reference series and each compared series [36]. A review of the literature indicates that GRA has found applications for determining optimal parameters by different processes. This technique has been integrated with Taguchi method for reliable optimization of complicated multi-response processes. For example, Yan and Li [37] applied GRA to milling parameters for simultaneous optimization of energy, production rate and cutting quality. Kuram and Ozcelik [38] employed the Taguchi method and GRA to obtain optimal multiple response outputs in micro-milling. The GRA approach was used by Padhee et al. [39] to obtain optimum cutting parameters for multiple quality characteristics during laser drilling of metal-matrix composites (MMC). Siriyala et al. [40] applied Taguchi $L_{25}$ orthogonal design-based GRA to optimize dry sliding wear properties of aluminum MMCs. Mondal et al. [41] applied the GRA approach for the multi-objective optimization of the laser cladding process. Acherjee et al. [42] combined the Taguchi method and GRA to solve multi-criteria optimization problems in laser transmission welding. Jung and Kwon [43] combined GRA with the Taguchi method to determine the single optimal setting for multiple quality characteristics of electrical discharge machining (EDM). Chen et al. [44] applied the Grey-Taguchi method to optimize gallium-doped zinc oxide thin film deposition on the

polyethylene terephthalate substrate with multiple performance characteristics. Tzeng et al. [45] reviewed optimization of turning operations having multiple performance characteristics using the Taguchi method and GRA. Caydas and Hascalik [46] presented an effective approach for optimizing laser cutting for St37 steel using multiple performance characteristics based on GRA. Pan et al. [47] combined the Taguchi method with GRA to investigate the optimal design of cutting parameters for Nd:YAG laser welding titanium alloy plates. Kuo et al. [48] integrated the GRA and Taguchi methods to determine the optimal processing parameters for multiple quality characteristics of needle punching of nonwoven fabrics. Singh et al. [49] outlined multi-response optimization of process parameters on the electrical discharge machining (EDM) of Al-10%SiCp as cast metal matrix composites using Taguchi OA combined with GRA. Fung et al. [50] studied the GRA to obtain the optimal factors for injection molding for the mechanical properties of yield stress and elongation in polycarbonate/acrylonitrile butadiene-styrene (PC/ABS) composites. Kao and Hocheng [51] developed a method of applying GRA to optimize electropolishing of 316L stainless. Tarng et al. [52] applied Grey-based Taguchi method to optimize submerged arc welding process parameters in hardfacing. Lin and Lin [53] proposed a new technique for optimizing EDM with multiple performance characteristics based on Taguchi OA combined with GRA.

The procedure for GRA is as follows:

*Step 1* - Grey relational generation and data pre-processing: The experimental results are normalized from 0 to 1 by transforming into a comparable dimensionless sequence. The types of data normalization are [40]:

(i) The-higher-the-better

$$[x_i^*(k)]_H = \frac{y_i(k) - \min y_i(k)}{\max y_i(k) - \min y_i(k)} \tag{2}$$

(ii) The-nominal-the-best

$$[x_i^*(k)]_N = 1 - \frac{y_i(k) - y_{ob}(k)}{\max y_i(k) - y_{ob}(k)} \tag{3}$$

(iii) The-lower-the-better

$$[x_i^*(k)]_L = \frac{\max y_i(k) - y_i(k)}{\max y_i(k) - \min y_i(k)} \tag{4}$$

where i=1, 2, ..., n; k=1, 2, …, p, $x_i^*(k)$ is the normalized value of the $k^{th}$ quality characteristic in the $i^{th}$ sequence (test), $y_{ob}(k)$ is the desired value of the performance, max $x_i^*(k)$ is the largest value of $y_i(k)$, min $x_i^*(k)$ is the smallest value of $y_i(k)$, n is the number of tests, and p is the number of quality characteristics.

Step 2 - Determination of the absolute value of the difference sequence ($\Delta_i(k)$), the minimum value ($\Delta_{min}$), and maximum value ($\Delta_{max}$) of the difference sequence:

$$\Delta_i(k) = \left| x_0^*(k) - x_i^*(k) \right| \tag{5}$$

$$\Delta_{min} = \min_k \min_i \left| x_0^*(k) - x_i^*(k) \right| \tag{6}$$

$$\Delta_{max} = \max_k \max_i \left| x_0^*(k) - x_i^*(k) \right| \tag{7}$$

*Step 3* - Setting the identification or distinguishing coefficient $\zeta$ ($\zeta \in [0, 1]$): The value of $\zeta$ is adjusted according to actual system requirements and is usually equal to 0.5 because there is good stability of outcomes [44].

*Step 4* - Calculation of grey relational coefficient: This coefficient displays relationship between the optimal and actual normalized experimental results. It is expressed as:

$$\xi_i(k) = \xi(x_0^*(k), x_i^*(k)) = \frac{\Delta_{min} + \zeta\Delta_{max}}{\Delta_i(k) + \zeta\Delta_{max}} \tag{8}$$

*Step 5* - Determination of grey relational grade (GRG): Overall evaluation of the multi-performance characteristics is based on GRG, which fluctuates from 0 to 1. It is computed by averaging the grey relational coefficients for each quality characteristic; however, importance of each response could differ. Accordingly, GRG values for each test ($\Gamma_i$) were computed as following formula [53] based on the weights ($w_k$) obtained from the entropy measurement:

$$\Gamma_{0,i} = \sum_{k=1}^{p} w_k \xi_{0,i}(k) \qquad i=1, \ldots, n \tag{9}$$

## 3. Entropy Measurement

To propose the relative priority among synchronously-occurring multiple quality characteristics, a weight factor was given to each using the concept of entropy. Wen et al. [31] defined $w_e(x)$ as a mapping function as follows:

$$w_e(x) = xe^{(1-x)} + (1-x)e^x - 1 \tag{10}$$

The maximum value of this function is x=0.5, and $e^{0.5} - 1 = 0.6487$. To produce a mapping result in the range of [0, 1], Wen et al. defined:

$$W \equiv \frac{1}{(e^{0.5} - 1)n} \sum_{i=1}^{n} w_e(x_i) \tag{11}$$

Assume sequence $\in_i = \{\xi_i(1), \xi_i(2), \ldots, \xi_i(n)\}$ where i=1, …, n.

Entropy measurement is used when researchers cannot determine which quality characteristic is most important. It has been used with the Taguchi-GRA method in different fields as reported in the literature [54-60]. Weight calculation requires:

(a) Calculation of the sum of grey relational coefficients

$$D_k = \sum_{i=1}^{n} \xi_i(k), \quad k=1, 2, \ldots, p \tag{12}$$

(b) Evaluation of the normalized coefficient

$$s = \frac{1}{(e^{0.5} - 1) \times n} = \frac{1}{0.6487 \times n} \tag{13}$$

(c) Calculation of the entropy of each quality characteristic

$$e_k = s \sum_{i=1}^{n} w_e\left(\frac{\xi_i(k)}{D_k}\right), \quad k=1, 2, \ldots, p \tag{14}$$

(d) Calculation of the sum of entropy

$$E = \sum_{k=1}^{p} e_k \tag{15}$$

(e) Calculation of the weight of each quality characteristic

$$w_k = \frac{1/p - E(1 - e_k)}{\sum_{k=1}^{p} [1/p - E(1 - e_k)]}, \quad k=1, 2, \ldots, p \tag{16}$$

**4. Analysis of Variance (ANOVA) for GRG Values**

After the GRG values were calculated, ANOVA was performed to determine which factors significantly affect catalytic performance. ANOVA was used to statistically analyze the variation caused by each factor relative to the total variation in the results. Using GRA and ANOVA, the optimal combination of the experimental parameters were predicted. This was accomplished by separating the total variability of the GRG values as measured by the sum of the squared deviations from the total mean of the GRG ($\Gamma_m$), into contributions by each ethylene dimerization factor and the error. The total sum of squared deviations ($SS_T$) based on the total mean of GRG was calculated as [53]:

$$SS_T=\sum_{i=1}^{n}(\Gamma_i-\Gamma_m)^2 \tag{17}$$

where n is the number of tests and $\Gamma_i$ represents GRG value for the $i^{th}$ test. Total and factor sums of squares are basic calculations needed for ANOVA [61]. For factor A, sum of square ($SS_A$), DOF ($df_A$), total DOF ($df_T$), mean square (variance) ($V_A$), pure sum of square ($SS'_A$), percentage of influence ($P_A$), error sum of square ($SS_e$), error variance ($V_e$), and $F_A$-ratio are used in ANOVA [62-65] and defined as:

$$SS_A=\sum_{x=1}^{L_A}\frac{1}{n_{A_x}}\left[\left(\sum_{i=1}^{n}\Gamma_{A_i}\right)^2\right]_x-\text{C.F.} \tag{18}$$

$$\text{C.F.}=\frac{\left(\sum_{i=1}^{n}\Gamma_i\right)^2}{n} \tag{19}$$

$$SS_{A\times B}=\sum_{x=1}^{L_A}\sum_{y=1}^{L_B}\frac{1}{r_{A_xB_y}}G^2_{A_xB_y}-\text{C.F.}-SS_A-SS_B \tag{20}$$

$$G_{A_xB_y}=\sum_{i=1}^{n}\Gamma_i\Big|_{\text{in levels } x,\,y}^{\text{for } A,\,B} \tag{21}$$

$$V_A=SS_A/df_A \tag{22}$$

$$df_A=L_A-1 \tag{23}$$

$$SS'_A=SS_A-V_e\times df_A \tag{24}$$

$$V_e=SS_e/df_e \tag{25}$$

$$df_e=df_T-(df_A+df_B+df_C+\ldots+df_{A\times B}+df_{A\times C}+\ldots) \tag{26}$$

$$df_T=N-1 \tag{27}$$

$$SS_e=SS_T-\sum_{F=A}^{Z}SS_F \tag{28}$$

$$F_A\text{-ratio}=V_A/V_e \tag{29}$$

$$P_A=SS'_A/SS_T\times 100 \tag{30}$$

where N represents the number of all experiments (N=m×n), $L_A$ is the number of levels of factor A, $n_{A_x}$ is the number of observations in which level x of A is present, $r_{A_xB_y}$ is the number of tests for $A_xB_y$ when factors A and B are at levels x and y, respectively, and $\sum_{i=1}^{n}\Gamma_i\Big|_{\text{in levels } x,\,y}^{\text{for } A,\,B}$ represents the sum of GRG values for situations (runs) in which A and B have been set at levels x and y.

**5. Confirmation Experiment Step**

In the final step, a confirmation test verified the results to control the accuracy of analysis in the predicted optimal conditions. Estimated GRG ($\Gamma_{predicted}$) was calculated as [57]:

$$\Gamma_{Predicted}=\Gamma_m+\sum_{x=1}^{L_F}(\overline{\Gamma}_{F_{x\text{-}opt.}}-\Gamma_m) \tag{31}$$

where $\Gamma_m$ is equal to its value in Eq. (17), $\overline{\Gamma}_{F_{x\text{-}opt.}}$ is the mean GRG at the optimum level of the individual factors that significantly affect the multiple quality characteristics.

## EXPERIMENTAL

**1. Materials**

EDC (99.8%) and 1,4-dioxane (>99%), and *n*-butanol (>99%) were obtained from Merck (Germany). TEA (Crompton) was diluted to a 0.5 M solution in *n*-heptane. The *n*-heptane was refluxed and distilled from anhydrous sodium carbonate under dry nitrogen and stored over pre-activated molecular sieves (4 Å). $TiCl_4$ (99%) was obtained commercially. Ethylene (99.98%) was supplied by Arak Petrochemical (Iran). Nitrogen for purging (>99.99%) was purchased from Roham Gas (Iran). $TiCl_4$ and *n*-butanol were used for the synthesis of $Ti(OC_4H_9)_4$ catalyst precursor.

**2. Instruments**

The Fourier transform infrared (FTIR) spectrum of the synthesized Ti catalyst was determined from a pressed KBr pellet of a sample using a Nicolet 550 spectrometer.

The proton-nuclear magnetic resonance ($^1$H-NMR) spectrum was recorded on a Bruker Avance 300 spectrometer operating at room temperature at 300 MHz. Tetramethylsilane (TMS) and deuterated solvent ($CDCl_3$) were used as an external standard and the internal lock, respectively. The splitting patterns were designated as singlet (s), triplet (t), or multiplet (m).

Elemental (CHN) analysis of the synthesized Ti catalyst was performed with a Leco-600.

A 1-L double-walled stainless steel Büchi reactor equipped with an external circulation bath for temperature control, a magnetically driven mechanical stirrer using a two-blade impeller and an overhead engine, an internal thermocouple, gas inlet and outlet ports, and a liquid sampling port were used.

Gas chromatography (GC) of gas phase sample involved a Varian 3800 with a flame-ionization detector (FID) equipped with a 250 μL gas sample loop and a PLOT fused silica capillary column (50 m in length×0.53 internal diameter, 10 μm film thickness) with a stationary phase based on CP-$Al_2O_3$/KCl.

Liquid phase sample GC-FID analysis used a Varian 3800 equipped with a WCOT Fused Silica capillary column (50 m in length×0.32 mm internal diameter, 1.2 μm film thickness) with a stationary phase based on CP-Sil 8 CB.

**3. Catalyst Preparation and Characterization**

$Ti(OC_4H_9)_4$ was synthesized according to the procedure reported in the literature [66,67]. $^1$H-NMR ($\delta$, $CDCl_3$, TMS): $\delta$=1.02 (t, 3H, $CH_3$), 1.46 (m, 2H, $CH_2$), 1.70 (m, 2H, $CH_2$), 4.42 (t, 2H, $CH_2O$). Anald. Calcd. for $Ti(OC_4H_9)_4$: C, 56.47; H, 10.59. Found: C, 55.82; H, 10.86. The main bands and relevant functional groups of FTIR were: 1) 1040 $cm^{-1}$ (C-O), 2) 1375 $cm^{-1}$ (Ti-O) with symmetric stretching vibrations, 3) 1464 $cm^{-1}$ (Ti-O) with asymmetric stretching vibrations, and 4) 2870 $cm^{-1}$ (C-H) with stretching vibrations. In addition, a broad peak at 3350 $cm^{-1}$ was observed due to the

presence of free butanol in the catalyst which could be attributed to its (O-H) functional group.

**4. Ethylene Dimerization and Product Analysis**

All procedures using solvents and catalyst components were under nitrogen atmosphere using standard Schlenk techniques. Prior to each experiment, the reactor was heated to 100 °C for 1 h to eliminate all traces of moisture. It was then cooled to ambient temperature under dry nitrogen. After evacuation and flushing with nitrogen, the reactor was charged with 400 mL of *n*-heptane as solvent to provide sufficient height for the liquid to ensure successful operation of the gas entrainment stirrer. In a typical run, $Ti(OC_4H_9)_4$ (1.46 mmol Ti), 1,4-dioxane (0.50 mL; 1,4-dioxane/Ti mol ratio of 4), a 0.5 M solution of TEA (8.76 mL; Al/Ti mol ratio of 3), and EDC (0.29 mL; EDC/Ti mol ratio of 2.5), in sequence, were immediately added into the autoclave under an ethylene atmosphere. Precautions were taken to avoid catalyst deactivation. The order in which the additives and Al-reagent are added to the Ti-based precursor catalyst can significantly alter the reactivity with the transition metal-initiator component. The reactor was then heated to 2 °C below the desired running temperature to conform to the exothermic nature of the reaction. The speed of the stirrer was initially set at 900 rpm. The ethylene pressure was then increased to the run value and ethylene was fed on demand for the duration of the experiment. The interior temperature of the reactor was controlled using an external circulation bath set at the reaction run temperature. The amount of ethylene required to reach the reaction pressure and the amount added during the course of a run were measured using a Brooks mass-flow controller (MFC). After 0.5 h, the reaction was terminated by switching off the stirrer and allowing it to cool to room temperature. The gas product phase from the reactor headspace was then quantified using a gas flow meter; a small fraction was then collected in a purged and evacuated stainless steel bomb for GC-FID analysis. Because butanes have low boiling points and are volatile, a $C_4$ fraction was detected in the gas phase at room temperature during sampling and analysis. We previously [6] observed that this affords accurate quantification of the 1-butene formed during catalysis. The reaction solution was then discharged through the bottom valve into the liquid sampling chamber. A small sample was quenched with HCl followed by deionized water to remove the catalyst, TEA, and HCl. The organic layer was dried over anhydrous sodium sulfate and then analyzed by GC-FID. Under such conditions, <0.5 wt% 1-butene and its isomers remained in the liquid sample. The 1-butene content dissolved in the liquid phase could be influenced during post-catalysis quenching by evaporation of the liquid phase before analysis. Nevertheless, a deviation of >0.5 wt% is consistently negligible and the analysis was considered reliable and correct. The remaining solution was poured into a 5% HCl-acidified ethanol mixture and the precipitated solid by-product was filtered, washed with hexane, dried in an oven at 100 °C for 1 h, and weighed.

Injections of 20 μL gas samples were done using a type 1041 middle injector at 150 °C. The carrier gas was helium at 1.4 mL/min in constant flow mode. The column was held at 45 °C for 4 min and then ramped to 200 °C at 15 °C/min; this value was held constant for 30 min. A gaseous mixture of ethylene, *n*-butane, *i*-butane, 1-butene, *i*-butene, *trans*-2-butene, and *cis*-2-butene as a standard gas was used to calibrate the GC. 1-Butene was as the balance gas.

Injections of 1 μL liquid samples were done using a type 1177 front split/splitless injector at 240 °C with a split ratio of 200 : 1. The carrier gas was helium at 1.4 mL/min in constant flow mode. For all separations the column oven was held at 40 °C for 5 min and then ramped to 280 °C at 10 °C/min and held constant for 40 min. This made it to separate the olefins in the $C_4$-$C_{12}$ range. The retention times for the different compounds were determined by injecting pure compounds as calibration reagents under identical GC conditions.

TOF and product selectivity were evaluated from the mass balance for ethylene consumption based on the measurements from the MFC, gas flow meter, GC analysis of the separate gaseous and liquid products. $S_{1\text{-}btn}$ was calculated as moles of 1-butene produced in gas phase divided by the total numbers of moles of ethylene converted to gaseous and liquid products (oligomers of $C_6$, $C_8$, $C_{10}$, and $C_{12+}$) multiplied by 100. TOF was expressed as moles of converted ethylene per mol of Ti per hour.

**5. Taguchi Experimental Design**

The reaction was optimized by evaluating the simultaneous effects of parameters for the EDC-promoted [$Ti(OC_4H_9)_4$/1,4-dioxane/TEA] catalyst system using the Taguchi method. The factors were temperature (A), pressure (B), Al/Ti mol ratio (C), 1,4-dioxane/Ti mol ratio (D), and EDC/Ti mol ratio (E). The factors and their levels are shown in Table 1. The levels of the factors were selected according to the factor setting provision used in the set-up and knowledge of the characteristics. In the Taguchi method, the effect of uncontrollable factors is nullified by proper selection of the levels for combination of controllable factors [28].

The appropriate choice of OA depends on the degree of freedom (DOF) required to study the main and interaction effects. The OA selected must satisfy the following inequality [34]: total DOF of OA≥total DOF required for experiment. Herein, an $L_{27}$ ($3^{13}$) OA was used to configure the processing factors with the same number of levels and binary interactions between temperature and pressure (A×B), temperature and Al/Ti mol ratio (A×C), and pressure and Al/Ti mol ratio (B×C), because a three-level factor has 2 DOF and each two-parameter interaction term has 4 DOF; thus, using five factors at three levels and three second-order interactions, the $df_T$ required is 22. Minitab (15.2) software was employed to determine the operating conditions for each set of 27 experimental runs (Table 2).

## RESULTS AND DISCUSSION

To the best of our knowledge, no study has been reported on

**Table 1. Processing factors and their values**

| Symbol | Factor | Units | Level | | |
|---|---|---|---|---|---|
| | | | 1 | 2 | 3 |
| A | Temperature | °C | 53 | 55 | 57 |
| B | Pressure | MPa | 1.5 | 2.2 | 2.9 |
| C | Al/Ti | mol/mol | 3 | 5 | 7 |
| D | 1,4-Dioxane/Ti | mol/mol | 2 | 4 | 6 |
| E | EDC/Ti | mol/mol | 0.5 | 2.5 | 4.5 |

**Table 2. Experimental layout using $L_{27}$ ($3^{13}$) OA with five control factors and three second-order interactions and experimental response values for ethylene dimerization and S/N ratios**

| Run | A | B | A×B | A×B | C | A×C | A×C | B×C | D | E | B×C | Quality characteristics | | $S/N_{H_1}$ [a] (db) | $S/N_{H_1}$ [b] (db) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | $S_{1\text{-}btn}$ (%) | TOF ($h^{-1}$) | | |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 87.7 | 5425 | 38.86 | 74.69 |
| 2 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 96.1 | 9640 | 39.65 | 79.68 |
| 3 | 1 | 1 | 1 | 1 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 78.0 | 4875 | 37.84 | 73.76 |
| 4 | 1 | 2 | 2 | 2 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 92.0 | 7945 | 39.27 | 78.00 |
| 5 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 1 | 81.1 | 4120 | 38.18 | 72.30 |
| 6 | 1 | 2 | 2 | 2 | 3 | 3 | 3 | 1 | 1 | 1 | 2 | 87.6 | 9880 | 38.85 | 79.89 |
| 7 | 1 | 3 | 3 | 3 | 1 | 1 | 1 | 3 | 3 | 3 | 2 | 82.9 | 2970 | 38.37 | 69.45 |
| 8 | 1 | 3 | 3 | 3 | 2 | 2 | 2 | 1 | 1 | 1 | 3 | 90.5 | 5885 | 39.14 | 75.39 |
| 9 | 1 | 3 | 3 | 3 | 3 | 3 | 3 | 2 | 2 | 2 | 1 | 86.8 | 7030 | 38.77 | 76.94 |
| 10 | 2 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 85.5 | 2850 | 38.64 | 69.10 |
| 11 | 2 | 1 | 2 | 3 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 84.0 | 5450 | 38.48 | 74.72 |
| 12 | 2 | 1 | 2 | 3 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 86.5 | 9745 | 38.74 | 79.77 |
| 13 | 2 | 2 | 3 | 1 | 1 | 2 | 3 | 2 | 3 | 1 | 3 | 83.3 | 3960 | 38.41 | 71.95 |
| 14 | 2 | 2 | 3 | 1 | 2 | 3 | 1 | 3 | 1 | 2 | 1 | 94.8 | 9860 | 39.54 | 79.88 |
| 15 | 2 | 2 | 3 | 1 | 3 | 1 | 2 | 1 | 2 | 3 | 2 | 83.7 | 7875 | 38.45 | 77.92 |
| 16 | 2 | 3 | 1 | 2 | 1 | 2 | 3 | 3 | 1 | 2 | 2 | 91.7 | 7845 | 39.25 | 77.89 |
| 17 | 2 | 3 | 1 | 2 | 2 | 3 | 1 | 1 | 2 | 3 | 3 | 86.0 | 7050 | 38.69 | 76.96 |
| 18 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 2 | 3 | 1 | 1 | 81.0 | 6730 | 38.17 | 76.56 |
| 19 | 3 | 1 | 3 | 2 | 1 | 3 | 2 | 1 | 3 | 2 | 1 | 82.1 | 4145 | 38.29 | 72.35 |
| 20 | 3 | 1 | 3 | 2 | 2 | 1 | 3 | 2 | 1 | 3 | 2 | 82.5 | 3940 | 38.33 | 71.90 |
| 21 | 3 | 1 | 3 | 2 | 3 | 2 | 1 | 3 | 2 | 1 | 3 | 80.5 | 6100 | 38.11 | 75.70 |
| 22 | 3 | 2 | 1 | 3 | 1 | 3 | 2 | 2 | 1 | 3 | 3 | 82.6 | 4050 | 38.34 | 72.15 |
| 23 | 3 | 2 | 1 | 3 | 2 | 1 | 3 | 3 | 2 | 1 | 1 | 87.9 | 5990 | 38.88 | 75.55 |
| 24 | 3 | 2 | 1 | 3 | 3 | 2 | 1 | 1 | 3 | 2 | 2 | 77.9 | 5850 | 37.83 | 75.34 |
| 25 | 3 | 3 | 2 | 1 | 1 | 3 | 2 | 3 | 2 | 1 | 2 | 86.4 | 6650 | 38.73 | 76.45 |
| 26 | 3 | 3 | 2 | 1 | 2 | 1 | 3 | 1 | 3 | 2 | 3 | 80.0 | 5100 | 38.06 | 74.15 |
| 27 | 3 | 3 | 2 | 1 | 3 | 2 | 1 | 2 | 1 | 3 | 1 | 77.0 | 6000 | 37.73 | 75.56 |

[a]Represents the S/N ratios for $S_{1\text{-}btn}$
[b]Represents the S/N ratios for TOF

the application of the hybrid Taguchi-GRA method with entropy measurement to improve multiple quality characteristics of homogeneous olefin oligomerization catalysis. This is the first report on this efficient integrated approach to optimize the operating parameters of ethylene dimerization catalyzed by a promoted Ti-based compound with correlated multi-performance characteristics that has an industrial significance. This study applied the Taguchi method to reduce the number of experiments and combined it with the GRA to determine the optimal processing parameters for multiple quality characteristics. An $L_{27}$ OA design was used to deal with factors that could affect the production of 1-butene in ethylene dimerization. GRA was then applied to resolve the deficiencies in the Taguchi method to focus on a single quality characteristic. Entropy measurement was integrated with GRA to determine the exact weights of the responses. Next, a response table for the GRG values was constructed to obtain the optimal combination of factors for the multiple quality characteristics. ANOVA was used to examine the most significant factors for ethylene dimerization. A confirmation experiment was conducted within the 95% confidence interval to verify experimental reliability.

**1. Analysis of Mean S/N Ratios, Main Effects and Interactions**

A total of 27 groups of tests were conducted randomly in accordance with OA. It is noteworthy that the variability of the test results can be determined by increasing the number of repetitions for each experiment, which increases the sensitivity to detection of small changes in the average responses. If the OA selected is of a higher order, such as $L_{16}$, $L_{27}$ or $L_{32}$, then repetition of conditions does not affect sensitivity [29,68]. A previous study by the authors [6] selected an $L_{16}$ OA with two repetitions per each experimental run under the same conditions for the ethylene dimerization catalysis. The values obtained for each response in each set of operating conditions were similar, demonstrating the very small effect of variability in the results. It has been reported that an $L_8$ OA with two repetitions per experimental run or $L_{16}$ OA with one repetition obtains 90% certainty of detecting changes of approximately 1.5 standard deviations [29,68]. Economy must always be considered when conducting repeated tests with the same experimental run; otherwise the design of experimental approach may be difficult or infeasible.

**Table 3. Main effects for raw and S/N data: (a) $S_{1\text{-}btn}$, (b) TOF**

| | Raw data, average value | | | Main effects (raw data) | | S/N data, average value | | | Main effects (S/N data) | | Max - Min (S/N data) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $L_1$ | $L_2$ | $L_3$ | $L_2$-$L_1$ | $L_3$-$L_2$ | $L_1$ | $L_2$ | $L_3$ | $L_2$-$L_1$ | $L_3$-$L_2$ | |
| (a) $S_{1\text{-}btn}$ | | | | | | | | | | | |
| A | 86.96 | 86.28 | 81.88 | −0.68 | −4.40 | 38.77 | 38.71 | 38.25 | −0.06 | −0.46 | 0.52 |
| B | 84.76 | 85.65 | 84.70 | 0.89 | −0.95 | 38.55 | 38.64 | 38.54 | 0.09 | −0.10 | 0.10 |
| C | 86.02 | 86.99 | 82.11 | 0.97 | −4.88 | 38.68 | 38.77 | 38.27 | 0.09 | −0.50 | 0.50 |
| D | 86.76 | 87.21 | 81.14 | 0.45 | −6.07 | 38.75 | 38.80 | 38.18 | 0.05 | −0.62 | 0.62 |
| E | 85.43 | 87.54 | 82.14 | 2.11 | −5.40 | 38.62 | 38.82 | 38.28 | 0.20 | −0.54 | 0.54 |
| A×B | 85.33 | 84.70 | 85.10 | −0.63 | 0.40 | 38.60 | 38.54 | 38.59 | −0.06 | 0.05 | 0.06 |
| A×C | 84.83 | 85.20 | 85.09 | 0.37 | −0.11 | 38.55 | 38.59 | 38.58 | 0.04 | −0.01 | 0.04 |
| B×C | 84.71 | 85.45 | 84.95 | 0.74 | −0.50 | 38.55 | 38.61 | 38.57 | 0.06 | −0.04 | 0.06 |
| (b) TOF | | | | | | | | | | | |
| A | 6418.9 | 6818.3 | 5313.9 | 399.4 | −1504.4 | 75.56 | 76.08 | 74.35 | 0.52 | −1.73 | 1.73 |
| B | 5796.6 | 6614.4 | 6140.0 | 817.8 | −474.4 | 74.63 | 75.88 | 75.48 | 1.25 | −0.40 | 1.25 |
| C | 5093.3 | 6337.2 | 7120.5 | 1243.9 | 783.3 | 73.56 | 75.61 | 76.82 | 2.05 | 1.21 | 3.26 |
| D | 6958.9 | 6792.2 | 4800.0 | −166.7 | −1992.2 | 76.34 | 76.25 | 73.40 | −0.09 | −2.85 | 2.94 |
| E | 6230.0 | 7462.2 | 4858.9 | 1232.2 | −2603.3 | 75.65 | 77.11 | 73.23 | 1.46 | −3.88 | 3.88 |
| A×B | 6491.1 | 6416.4 | 5643.6 | −74.7 | −772.8 | 75.92 | 75.64 | 74.44 | −0.28 | −1.20 | 1.48 |
| A×C | 6242.8 | 6171.6 | 6136.6 | −71.2 | −35.0 | 75.46 | 75.30 | 75.23 | −0.16 | −0.07 | 0.23 |
| B×C | 5900.5 | 6380.3 | 6270.3 | 479.8 | −110.0 | 74.93 | 75.59 | 75.47 | 0.66 | −0.12 | 0.66 |

In the current study, an $L_{27}$ OA was selected with one repetition per experiment taking into account the economy and the sensitivity of tests. The results of $S_{1\text{-}btn}$ and TOF are presented in Table 2. The experimental data was used to calculate the S/N ratio for each group of tests based on Eq. (1) at decibel scale (db). The calculated S/N ratios for two quality characteristics are shown in Table 2. After the collection of raw data, average effect response values were calculated. The average effect for level one of factor A (temperature) was computed using data from experiments 1-9 of Table 2. The average effects for levels 2 and 3 of temperature were computed using data from experiments 10-18 and 19-27 of Table 2, respectively. The average effects of other factors and interactions at all levels and the results are given in Table 3.

Product design or process optimization consistent with the highest S/N ratio always yields optimal quality with minimum variance, whatever the nature of the quality characteristics [28]. Here, analysis of the mean S/N ratio for each factor was used to obtain an optimum setting for each response. The effect of each ethylene dimerization factor on the S/N ratio at different levels can be determined because the experimental design is orthogonal. To obtain the effect of each experimental factor on each quality characteristic for each level, S/N ratios having same level of experimental factor were averaged over the 27 experiments. Taking factor A on $S_{1\text{-}btn}$ as an example, the mean S/N ratio of three levels was calculated as follows:

$$(\overline{S/N}_{H_1,A})_{L_1}=(38.86+39.65+37.84+39.27+38.18+38.85+38.37+39.14+38.77)/9=38.77$$

$$(\overline{S/N}_{H_1,A})_{L_2}=(38.64+38.48+38.74+38.41+39.54+38.45+39.25+38.69+38.17)/9=38.71$$

$$(\overline{S/N}_{H_1,A})_{L_3}=(38.29+38.33+38.11+38.34+38.88+37.83+38.73+38.06+37.73)/9=38.25$$

where $(\overline{S/N}_{H_p,F})_{L_x}$ is the effect of experimental factor F (F=A, B, C, D, E) on the $S/N_H$ ratio of quality characteristic p (p represents $S_{1\text{-}btn}$ (1) and TOF (2)) at level x.

The main effects for the interactions A×B, A×C, and B×C for each response were similarly calculated. The main effects for A×B in level 1 were calculated by averaging the values of $S_{1\text{-}btn}$ from experiments in which A×B was in level 1. This was done using the two columns of Table 2 ($L_{27}$ OA design) for A×B for each run: Experiments 1-3 for the first A×B column, again these experiments for A×B column 2, experiments 13-15 for column 2 (A×B) and 16-18 for column 1 (A×B), experiments 22-24 for column 1 (A×B) and 25-27 for column 2 (A×B). The value of 85.33 reported in Table 3, which is main effect for A×B in level 1 for $S_{1\text{-}btn}$, was computed as follows:

$$\{\text{Main effect for A×B in level 1 for } S_{1\text{-}btn}\}=(87.7+96.1+78.0+87.7+96.1+78.0+83.3+94.8+83.7+91.7+86.0+81.0+82.6+87.9+77.9+86.4+80.0+77.0)/18=85.33$$

The calculations were similarly conducted for S/N ratios reported in Table 2 for the responses. Average values of both the raw data and calculated S/N ratios of $S_{1\text{-}btn}$ and TOF for each parameter and also the interactions at levels 1, 2, and 3 are reported in Table 3. Factors A, B, C, D, and E had the highest influence at levels 1, 2, 2, 2, and 2, respectively, for $S_{1\text{-}btn}$. Fundamentally, the difference between S/N ratios for two levels of one factor indicates the relative influence of that factor. The larger the difference, the stronger the effect. As shown in Table 3, the highest (max - min) value of the average value of S/N data for $S_{1\text{-}btn}$ was 0.62 in case of factor D, the 1,4-dioxane/Ti mol ratio, indicating the strongest influence on $S_{1\text{-}btn}$. For catalyst TOF, factors A, B, C, D, and E had the highest impact at levels 2, 2, 3, 1, and 2, respectively. The highest (max - min) average value of the S/N data was 3.88 for factor E, the EDC/Ti mol ratio and hence the strongest effect on TOF. Table 3 also shows that

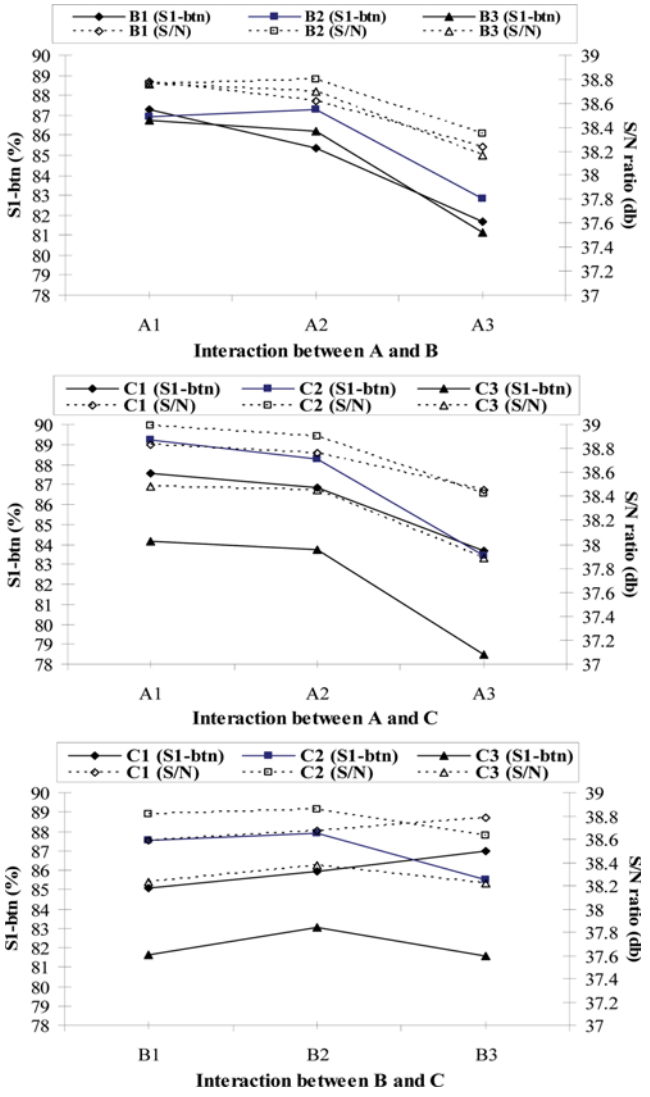


**Fig. 1. Binary interactions between factors A, B, and C at three levels on $S_{1\text{-}btn}$ and S/N ratios.**

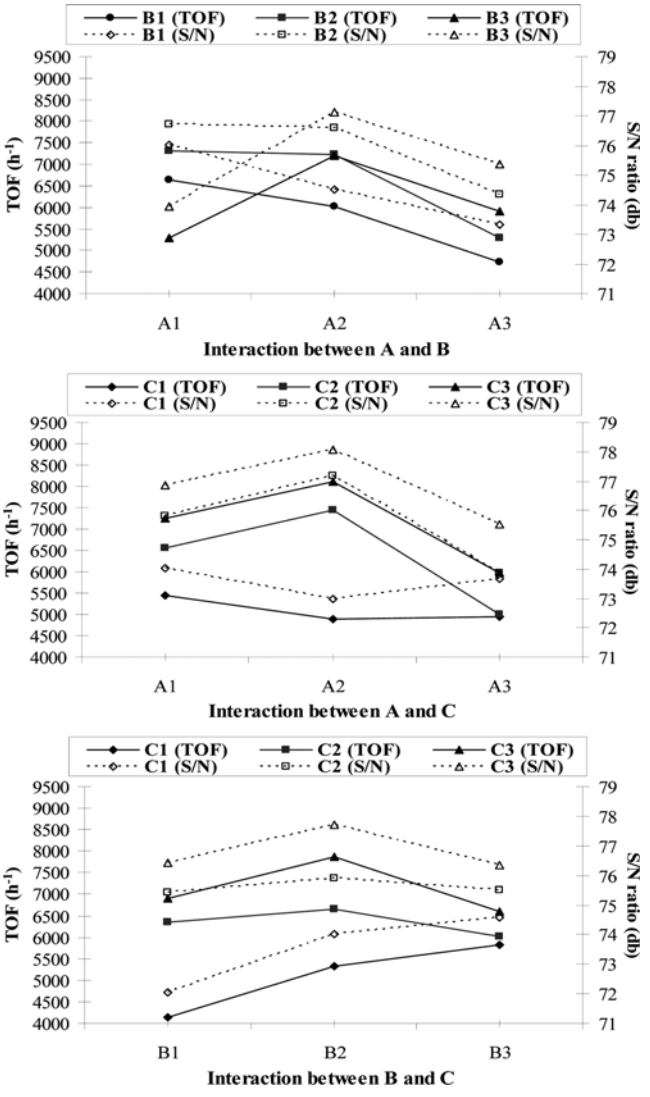


**Fig. 2. Binary interactions between factors A, B, and C at three levels on TOF and S/N ratios.**

interactions A×B and B×C were equally significant for $S_{1\text{-}btn}$. By contrast, A×B significantly affected catalyst TOF.

In Ti-based ethylene dimerization catalysis, the binary interactions between process factors are a concern from the industrial standpoint. Understanding the interaction between two factors provides better insight into overall process analysis.

The interactions for both the experimental data and S/N ratios of $S_{1\text{-}btn}$ and TOF were calculated and the results are presented in Figs. 1 and 2. The non-parallelism of the plots indicates that some amount of interaction existed between the two factors, and intersecting lines are an indication of strong interaction; the greater the difference between the slopes of the lines of the two factors, the greater the interaction [69].

Fig. 1 shows that the difference in the slope of the lines for A×B is greater in the lower levels of the factors. This indicates that the effect of the interaction of temperature and pressure at lower levels was more pronounced for both $S_{1\text{-}btn}$ and its S/N ratios. The graphs for A×C and B×C show that the difference in the slopes of the lines was greater at higher levels of the factors. This indicates that the effect of the interaction of temperature and Al/Ti mol ratio and also between pressure and Al/Ti mol ratio at higher levels was more pronounced for both $S_{1\text{-}btn}$ and its S/N ratios. A similar interpretation could be considered for the effect of the interactions of A×B, A×C, and B×C on TOF and its S/N ratios (Fig. 2).

From the mean S/N ratio responses in Table 3, the best set of combination parameter was determined by selecting the level with the highest value of each factor. Thus, optimum factor levels for $S_{1\text{-}btn}$ and TOF were $A_1B_2C_2D_2E_2$ and $A_2B_2C_3D_1E_2$, respectively. It is obvious that there is great inconsistency between two optimal conditions. When the results conflict for multiple quality characteristics, it is necessary to rely on the subjective experience of engineers to attain a compromise; however, experience and engineering knowledge is subjective and an optimal setting cannot fully ensure a compromise between multiple quality characteristics because of the possibility of error. The validity and robustness of results cannot be simply assured when the multiple quality characteristics are correlated

because it can add a degree of uncertainty to the decision-making process. This is of concern for safe operation in real production environments. GRA was used to optimize $S_{1\text{-}btn}$ and TOF simultaneously with reproducibility and feasibility. The importance of each quality characteristic can differ, and using the same weight for all quality characteristics can cause yield loss. To overcome this problem, entropy was applied as a hybrid method to GRA to make the results more objective and accurate.

**2. GRA Results**

The average values of the responses were calculated and substituted into Eq. (2) and the data normalized for $S_{1\text{-}btn}$ and TOF as $x_i^*(S_{1\text{-}btn})$ and $x_i^*(\text{TOF})$, respectively. The best-normalized average value for each response was unity. The absolute values of the difference sequence for each response ($\Delta_{0,i}(S_{1\text{-}btn})$ and $\Delta_{0,i}(\text{TOF})$) were evaluated using Eq. (5). The results are shown in Table 4. The grey relational coefficients were calculated for the experimental runs with a distinguishing coefficient of $\zeta$=0.5 using Eq. (8). These coefficients are reported in Table 4. The terms for $D_{S_{1\text{-}btn}}$ and $D_{TOF}$ (sum of the grey relational coefficients for $S_{1\text{-}btn}$ and TOF, respectively) were obtained using Eq. (12) as:

$$D_{S_{1\text{-}btn}}=\sum_{i=1}^{27}\xi_i(S_{1\text{-}btn})=13.4617$$

$$D_{TOF}=\sum_{i=1}^{27}\xi_i(\text{TOF})=14.5975$$

The normalized coefficient was calculated using Eq. (13) where n=27. It was obtained as s=0.0571. The $w_e(\xi_i(S_{1\text{-}btn})/D_{S_{1\text{-}btn}})$ and $w_e(\xi_i(\text{TOF})/D_{TOF})$ for each experimental run are also shown in Table 4. Eq. (14) was used to calculate the entropy for $S_{1\text{-}btn}$ as 0.14772 and for TOF as 0.14749. Eq. (15) was used for the sum of entropy (E=0.29521). Finally, using Eq. (16), the weights of $S_{1\text{-}btn}$ and TOF were obtained as 0.500068 and 0.499932, respectively. The weights for each quality characteristic were used to calculate the GRG by inserting them into Eq. (9).

Fig. 3 reports the GRG values for $S_{1\text{-}btn}$ and TOF based on the $L_{27}$ OA. Generally, the sequence with the largest GRG indicates the closest desired value for the performance characteristics. Accordingly, experiment 2 (the highest peak value in Fig. 3) showed the best performance for $S_{1\text{-}btn}$ and TOF. This GRG value (0.968) was not guaranteed to be the optimum of all possible mixtures. Overall optimum combination should be determined using the main effects table. The dashed line in Fig. 3 denotes $\Gamma_m$ which was calculated as 0.51961. Because the experimental design was orthogonal, a response table was generated to separate the effect of each level of processing parameter for the GRG. In other words, the re-

**Table 4. Data pre-processing, grey relational coefficients and weights for each deviation sequence vs. experimental runs for $S_{1\text{-}btn}$ and TOF**

| Run | $x_i^*(S_{1\text{-}btn})$ | $x_i^*(\text{TOF})$ | $D_{0,i}(S_{1\text{-}btn})$ | $D_{0,i}(\text{TOF})$ | $\xi_i(S_{1\text{-}btn})$ | $\xi_i(\text{TOF})$ | $w_e(\xi_i(S_{1\text{-}btn})/D_{S_{1\text{-}btn}})$ | $w_e(\xi_i(\text{TOF})/D_{TOF})$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.5602 | 0.3663 | 0.4398 | 0.6337 | 0.5320 | 0.4410 | 0.1024 | 0.0792 |
| 2 | 1.0000 | 0.9658 | 0.0000 | 0.0342 | 1.0000 | 0.9360 | 0.1846 | 0.1613 |
| 3 | 0.0523 | 0.2880 | 0.9477 | 0.7120 | 0.3454 | 0.4125 | 0.0675 | 0.0741 |
| 4 | 0.7853 | 0.7247 | 0.2147 | 0.2753 | 0.6996 | 0.6449 | 0.1325 | 0.1139 |
| 5 | 0.2146 | 0.1806 | 0.7854 | 0.8194 | 0.3890 | 0.3789 | 0.0759 | 0.0682 |
| 6 | 0.5550 | 1.0000 | 0.4450 | 0.0000 | 0.5291 | 1.0000 | 0.1019 | 0.1714 |
| 7 | 0.3089 | 0.0170 | 0.6911 | 0.9830 | 0.4198 | 0.3371 | 0.0817 | 0.0611 |
| 8 | 0.7068 | 0.4317 | 0.2932 | 0.5683 | 0.6303 | 0.4680 | 0.1202 | 0.0837 |
| 9 | 0.5131 | 0.5946 | 0.4869 | 0.4054 | 0.5066 | 0.5522 | 0.0977 | 0.0982 |
| 10 | 0.4450 | 0.0000 | 0.5550 | 1.0000 | 0.4739 | 0.3333 | 0.0917 | 0.0603 |
| 11 | 0.3665 | 0.3698 | 0.6335 | 0.6302 | 0.4411 | 0.4424 | 0.0855 | 0.0794 |
| 12 | 0.4974 | 0.9808 | 0.5026 | 0.0192 | 0.4987 | 0.9630 | 0.0962 | 0.1657 |
| 13 | 0.3298 | 0.1579 | 0.6702 | 0.8421 | 0.4273 | 0.3725 | 0.0829 | 0.0672 |
| 14 | 0.9319 | 0.9971 | 0.0681 | 0.0029 | 0.8801 | 0.9942 | 0.1643 | 0.1705 |
| 15 | 0.3508 | 0.7148 | 0.6492 | 0.2852 | 0.4351 | 0.6368 | 0.0845 | 0.1125 |
| 16 | 0.7696 | 0.7105 | 0.2304 | 0.2895 | 0.6845 | 0.6333 | 0.1299 | 0.1120 |
| 17 | 0.4712 | 0.5974 | 0.5288 | 0.4026 | 0.4860 | 0.5539 | 0.0940 | 0.0984 |
| 18 | 0.2094 | 0.5519 | 0.7906 | 0.4481 | 0.3874 | 0.5274 | 0.0756 | 0.0940 |
| 19 | 0.2670 | 0.1842 | 0.7330 | 0.8158 | 0.4055 | 0.3800 | 0.0789 | 0.0685 |
| 20 | 0.2879 | 0.1550 | 0.7121 | 0.8450 | 0.4125 | 0.3717 | 0.0802 | 0.0670 |
| 21 | 0.1832 | 0.4623 | 0.8168 | 0.5377 | 0.3797 | 0.4818 | 0.0741 | 0.0862 |
| 22 | 0.2932 | 0.1707 | 0.7068 | 0.8293 | 0.4143 | 0.3761 | 0.0807 | 0.0677 |
| 23 | 0.5707 | 0.4466 | 0.4293 | 0.5534 | 0.5380 | 0.4746 | 0.1034 | 0.0850 |
| 24 | 0.0471 | 0.4267 | 0.9529 | 0.5733 | 0.3441 | 0.4658 | 0.0672 | 0.0835 |
| 25 | 0.4921 | 0.5405 | 0.5079 | 0.4595 | 0.4961 | 0.5211 | 0.0957 | 0.0930 |
| 26 | 0.1570 | 0.3200 | 0.8430 | 0.6800 | 0.3723 | 0.4237 | 0.0726 | 0.0761 |
| 27 | 0.0000 | 0.4481 | 1.0000 | 0.5519 | 0.3333 | 0.4753 | 0.0652 | 0.0850 |

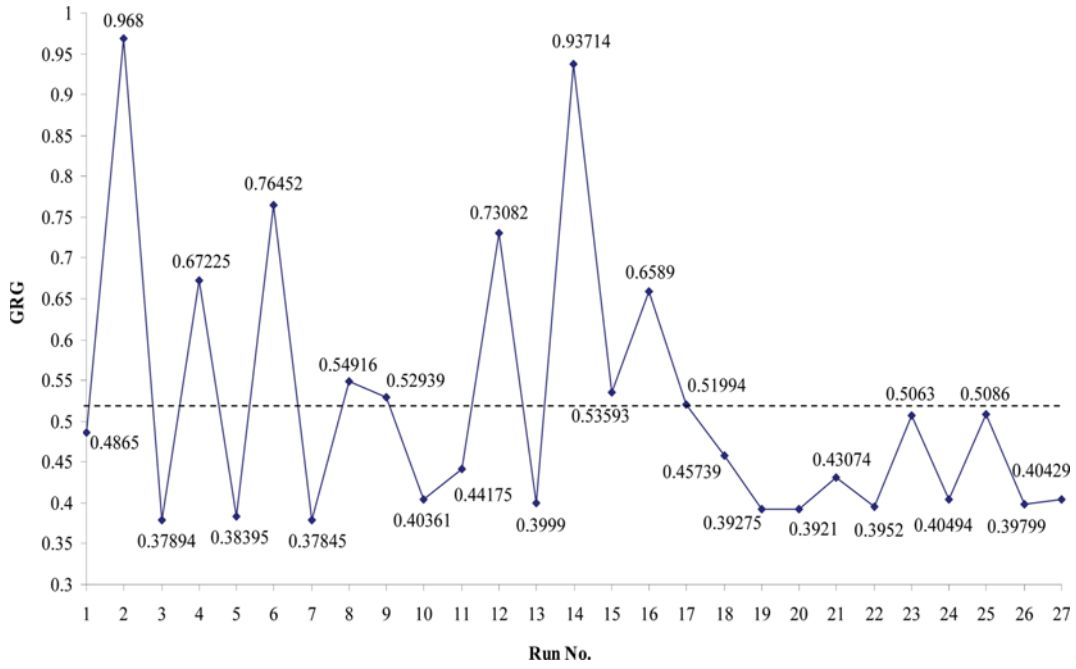


**Fig. 3. Variation in the GRG vs. experimental run.**

**Table 5. GRG response table**

| Factor | Level 1 | Level 2 | Level 3 | Max - Min |
|---|---|---|---|---|
| A | 0.56790* | 0.56504 | 0.42588 | 0.14202 |
| B | 0.51391 | 0.55557* | 0.48934 | 0.06623 |
| C | 0.47735 | 0.56626* | 0.51522 | 0.08891 |
| D | 0.59096* | 0.56386 | 0.40400 | 0.18696 |
| E | 0.50498 | 0.63246* | 0.42138 | 0.21108 |
| $\Gamma_m$=0.51961 | | | | |

sponse table of the Taguchi method was employed to calculate the average GRG for each ethylene dimerization parameter level.

This was obtained by calculating the average value of each input parameter on the GRG at its corresponding level. For example, the mean GRG for factor A (temperature) at levels 1 (53 °C), 2 (55 °C), and 3 (57 °C) were calculated by averaging the GRG values for the experiments 1 to 9, 10 to 18 and 19 to 27, respectively. The calculations were performed for each ethylene dimerization factor level by using the same method.

Table 5 is the response table. The optimum level combination of the factors for the multiple quality characteristics was considered based on analysis of the main effect of each parameter on the GRG. Since the GRG represents the level of correlation between the reference sequence and the comparability sequence, its greater value means that the comparability sequence has a stronger correlation to the reference sequence. In fact, regardless of the category of the quality characteristics, a greater GRG corresponds to better performance. As seen in Table 5, an asterisk (*) has been designated to the levels with the greatest GRG value for each factor, which indicates these factor levels have resulted in a better performance of the catalytic system. On the other hand, the optimum level based on the maximum average GRG was the first level of factors A and D, the second level of factors B, C and E which could be shortly given as $A_1B_2C_2D_1E_2$ namely temperature=53 °C, pressure=2.2 MPa, Al/Ti=5 mol/mol, 1,4-dioxane/Ti=2 mol/mol, and EDC/Ti=2.5 mol/mol. Moreover, Table 5 shows that the difference between maximum and minimum average GRG for each factor was as follows: 0.14202 for temperature, 0.06623 for pressure, 0.08891 for Al/Ti mol ratio, 0.18696 for 1,4-dioxane/Ti mol ratio, and 0.21108 for EDC/Ti mol ratio. The factors were compared to give the level of significance of the factors over the multiple quality characteristics. The maximum value was for EDC/Ti mol ratio (factor E) at 0.21108. This represented that the EDC/Ti mol ratio had the most profound effect on the multiple quality characteristics. The effects of the factors were, in order: E (0.21108), D (0.18696), A (0.14202), C (0.08891), and B (0.06623).

**3. Main Effects of the Factors on Multiple Quality Characteristics**

Table 5 shows that increasing factor A (temperature) decreased the GRG, which represents a decrease in the multiple performance characteristics. This could be ascribed to decreased solubility of ethylene in the heptane and to insufficient stability and a higher deactivation rate in the dimerization sites at elevated temperatures. These could cause co-dimerization of the ethylene molecules with the produced dimer, giving rise to the formation of significant amounts of linear and branched higher oligomers and heavy compounds and finally decreasing the selectivity and productivity for 1-butene [6].

Increasing factor B (pressure) to level 2 (2.2 MPa) had a suitable effect on the GRG. As observed in Table 5, a further increase of pressure resulted in a decrease in the GRG.

The optimum level of factor C (Al/Ti mol ratio) was 2 (Al/Ti= 5) to achieve the maximum GRG value (0.56626) and the best performance characteristics. When Al/Ti mol ratio was further increased,

the GRG decreased (0.51522). The detrimental effect of high mol ratio of Al/Ti results from the presence of free TEA, which prohibits its stability of the Ti species responsible for dimerization and caused rapid deactivation of the active sites in the reaction [10].

The optimum level (maximum GRG of 0.59096) for factor D (1,4-dioxane/Ti mol ratio) was 1 (1,4-dioxane/Ti=2), which provided the best multiple performance characteristics. As seen in Table 5, increasing 1,4-dioxane/Ti mol ratio decreased the GRG. This suggests that a further increase in 1,4-dioxane as a suitable Lewis basic oxygen donor additive produces coordinative binding of the sites by more than one ligand per metal atom, which shields the free coordination site and blocks ethylene access to the active sites, affecting the reaction performance.

For factor E (EDC/Ti mol ratio), the optimum level was determined to be 2 (EDC/Ti=2.5), which showed the highest GRG value (0.63243). Further augmentation of the EDC/Ti mol ratio (level 3= 4.5) had a negative effect on catalytic performance as evidenced by the decrease in the GRG (0.42138). This trend can be explained by the excessive interference of the promoter with the formation of the active Ti species or possibly preventing coordination of ethylene at the active dimerization sites [6].

**4. ANOVA Table**

An increase in the GRG, improves the multiple quality characteristics. The relative importance of the ethylene dimerization process parameters for multiple performance characteristics must be known so that the optimal combination of the ethylene dimerization parameter levels can be determined more accurately. ANOVA was performed to determine the effect of individual factors and the interactions on the GRG using Eqs. (17) to (30). The results are given in Table 6(a). For example, $SS_{A\times B}$ was calculated as follows:

$$SS_{A\times B}=\frac{1}{3}\sum_{x=1}^{3}\sum_{y=1}^{3}G_{A_xB_y}^2-\text{C.F.}-SS_A-SS_B$$

$$SS_{A\times B}=\frac{1}{3}(G_{A_1B_1}^2+G_{A_1B_2}^2+G_{A_1B_3}^2+G_{A_2B_1}^2+G_{A_2B_2}^2+G_{A_2B_3}^2+G_{A_3B_1}^2+G_{A_3B_2}^2+G_{A_3B_3}^2)+\text{C.F.}-SS_A-SS_B$$

$G_{A_1B_1}=\Gamma_1+\Gamma_2+\Gamma_3=0.48650+0.96800+0.37894=1.83344$

$G_{A_1B_2}=\Gamma_4+\Gamma_5+\Gamma_6=0.67225+0.38395+0.76452=1.82072$

$G_{A_1B_3}=\Gamma_7+\Gamma_8+\Gamma_9=0.37845+0.54916+0.52939=1.45700$

$G_{A_2B_1}=\Gamma_{10}+\Gamma_{11}+\Gamma_{12}=0.40361+0.44175+0.73082=1.57618$

$G_{A_2B_2}=\Gamma_{13}+\Gamma_{14}+\Gamma_{15}=0.39990+0.93714+0.53593=1.87297$

$G_{A_2B_3}=\Gamma_{16}+\Gamma_{17}+\Gamma_{18}=0.65890+0.51994+0.45739=1.63623$

$G_{A_3B_1}=\Gamma_{19}+\Gamma_{20}+\Gamma_{21}=0.39275+0.39210+0.43074=1.21559$

$G_{A_3B_2}=\Gamma_{22}+\Gamma_{23}+\Gamma_{24}=0.39520+0.50630+0.40494=1.30644$

$G_{A_3B_3}=\Gamma_{25}+\Gamma_{26}+\Gamma_{27}=0.50860+0.39799+0.40429=1.31088$

$$\text{C.F.}=\frac{\left(\sum_{i=1}^{n}\Gamma_i\right)^2}{n}=\frac{(14.02945)^2}{27}=7.28983$$

$$SS_A=\sum_{x=1}^{L_A}\frac{1}{n_{A_x}}\left[\left(\sum_{i=1}^{n}\Gamma_{A_i}\right)^2\right]_x-\text{C.F.}=\frac{1}{n_{A_1}}\left[\left(\sum_{i=1}^{9}\Gamma_{A_i}\right)^2\right]_1+\frac{1}{n_{A_2}}\left[\left(\sum_{i=10}^{18}\Gamma_{A_i}\right)^2\right]_2+\frac{1}{n_{A_3}}\left[\left(\sum_{i=19}^{27}\Gamma_{A_i}\right)^2\right]_3-7.28983=\frac{1}{9}(5.11116)^2+\frac{1}{9}(5.08538)^2+\frac{1}{9}(3.83291)^2-7.28983=0.11864$$

$$SS_B=\sum_{x=1}^{L_B}\frac{1}{n_{B_x}}\left[\left(\sum_{i=1}^{n}\Gamma_{B_i}\right)^2\right]_x-\text{C.F.}=\frac{1}{9}(4.62521)^2+\frac{1}{9}(5.00013)^2+\frac{1}{9}(4.40411)^2-7.28983=0.02017$$

$$SS_{A\times B}=\frac{1}{3}((1.83344)^2+(1.82072)^2+(1.45700)^2+(1.57618)^2+(1.87297)^2+(1.63623)^2+(1.21559)^2+(1.30644)^2+(1.31088)^2)-7.28983-0.11864-0.02017=0.02864$$

The F-values showed which processing factors had significant effects on the multi-performance characteristics. Generally, a larger F-value indicates that the variation of the process parameter makes a marked change on the quality characteristics [64]. The F-test examines the relationships between the variances generated from experimental error in the tests and the variance in individual factors. Table 6(a) shows the contribution of individual factors in increasing order as EDC/Ti mol ratio ($F_E$=47.297), 1,4-dioxane/Ti mol ratio ($F_D$=42.725), temperature ($F_A$=27.590), Al/Ti mol ratio ($F_C$=8.330), and pressure ($F_B$=4.688). Using the Fisher table [70] at a 95% confidence level, $df_e$=31 and $df_F$=2 for individual factors gave an F-value of 3.30. As seen in Table 6(a), the F-values of all individual factors were greater than the values from the Fisher table. This indicated that the variance of all individual factors was significant for $V_e$ at

**Table 6. (a) ANOVA for the GRG, (b) Pooled ANOVA for the GRG**

| Factor | (a) | | | | (b) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | DOF | SS | V | F | DOF | SS | V | SS' | F | P (%) |
| A | 2 | 0.11864 | 0.05932 | 27.590 | 2 | 0.11864 | 0.05932 | 0.11372 | 24.114 | 15.83 |
| B | 2 | 0.02017 | 0.01008 | 4.688 | 2 | 0.02017 | 0.01008 | 0.01525 | 4.097 | 2.12 |
| C | 2 | 0.03583 | 0.01791 | 8.330 | 2 | 0.03583 | 0.01791 | 0.03091 | 7.280 | 4.30 |
| D | 2 | 0.18372 | 0.09186 | 42.725 | 2 | 0.18372 | 0.09186 | 0.17880 | 37.341 | 24.90 |
| E | 2 | 0.20339 | 0.10169 | 47.297 | 2 | 0.20339 | 0.10169 | 0.19847 | 41.337 | 27.64 |
| A×B | 4 | 0.02864 | 0.00716 | 3.330 | 4 | 0.02864 | 0.00716 | 0.01880 | 2.910 | 2.62 |
| A×C | 4 | 0.01959 | 0.00490 | 2.279 | | | POOLED | | | |
| B×C | 4 | 0.04145 | 0.01036 | 4.818 | 4 | 0.04145 | 0.01036 | 0.03161 | 4.211 | 4.40 |
| Error/Pooled error | 31 | 0.06668 | 0.00215 | - | 35 | 0.08627 | 0.00246 | - | - | 18.19 |
| Total | 53 | 0.71811 | - | - | 53 | 0.71811 | - | - | - | 100 |

**Table 7. Performance of ethylene dimerization for the starting and optimum level factors**

| | Starting parameter setting | Optimum parameter setting | |
|---|---|---|---|
| | | Prediction | Experiment |
| Combination of testing parameters | $A_1B_1C_1D_1E_1$ | $A_1B_2C_2D_1E_2$ | $A_1B_2C_2D_1E_2$ |
| $S_{1\text{-}btn}$ (%) | 87.7 | | 95.8 |
| TOF ($h^{-1}$) | 5425 | | 9800 |
| GRG | 0.48650 | 0.83471 | 0.97360 |

the 95% confidence level. Statistically, all high and low factors had an effect on the performance characteristics. For the interactions A×B, A×C, and B×C, F-values were obtained as $F_{A\times B}$=3.330, $F_{A\times C}$= 2.279, and $F_{B\times C}$=4.818. Using the Fisher table at a 95% confidence level, $df_e$=31, and $df_{interaction\ between\ two\ factors}$=4, the F-value was determined as 2.68.

Table 6(a) shows that the F-value of interactions A×B and B×C were greater than their Fisher table values meaning that these interactions had a significant effect on the responses. Since the F-value of A×C ($F_{A\times C}$=2.279) was smaller than its Fisher table value (F= 2.68), this interaction could be ignored. It is reasonable to consider this interaction as the one which has not displayed statistically significant predictive ability when the other variables are present. Disregarding a parameter once it is appeared non-significant is known as pooling. The effect of A×C was pooled with the error to improve the percentage of contribution of the factors. The $V_{A\times C}$ and $V_e$ were combined to calculate a new pooled error. The improved contribution of the individual factors and interactions A×B and B×C were calculated after pooling A×C. The results of pooled ANOVA are shown in Table 6(b). The F-ratios changed slightly after the pooling process. According to Table 6(a), (b), the change in F-ratio of A was 27.590 to 24.114, B was 4.688 to 4.097, C was 8.330 to 7.280, D was 42.725 to 37.341, E was 47.297 to 41.337, A×B was 3.330 to 2.910, and B×C was 4.818 to 4.211. The last column of Table 6(b) shows the $P_F$ for total variation, thus exhibiting the degree of influence on the results. From the $P_F$ values for both the individual factors and interactions, it could be concluded that E ($P_E$=27.64%) was the most dominant factor followed, in order, by D ($P_D$=24.90%), A ($P_A$=15.83%), B×C ($P_{B\times C}$=4.40%), C ($P_C$=4.30%), A×B ($P_{A\times B}$=2.62%), and B ($P_B$=2.12%).

Table 6(b) shows that DOF of the pooled error, the sum of $df_e$ and $df_{A\times C}$, was 35. An increase in DOF for error as a result of pooling increases the confidence level of the significant factors. The sum of square of the pooled error was obtained as $SS_{A\times C}$+$SS_e$. The total variation in response was decomposed into variation due to both the various controllable factors/interactions and error involved in the experimentation. The percentage of error is used to evaluate the feasibility and sufficiency of a test, because it reflects uncertain or uncontrollable factors. Based on experience, a test is acceptable without regard to pooling technique if the percentage of error is less than 15%. It is unacceptable if significant factors are lost and the percentage of error is greater than 50% [33]. In this study, the percentage of error for pooling A×C (pooled error) was 18.19% as shown in Table 6(b), indicating that the proposed method and the outcome was proven to be acceptable. This implied that important factors could be effectively controlled in the experiment and the test results had good accuracy.

**5. Confirmation Experiment**

Once the optimum level of the individual factors was found to be $A_1B_2C_2D_1E_2$, the final step was to predict and verify the increase in the performance characteristics. Validation testing was done to determine if improvements in the results could be obtained by optimal parameter analysis for comparison with the initial conditions and to demonstrate the effectiveness of the Grey-Taguchi method. The $\Gamma_{predicted}$ was calculated using Eq. (31) as follows:

$$\begin{aligned}\Gamma_{predicted}&=\Gamma_m+((\overline{\Gamma}_{A_1}-\Gamma_m)+(\overline{\Gamma}_{B_2}-\Gamma_m)+(\overline{\Gamma}_{C_2}-\Gamma_m)+(\overline{\Gamma}_{D_1}-\Gamma_m)\\&\quad+(\overline{\Gamma}_{E_2}-\Gamma_m))=0.51961+((0.56790-0.51961)\\&\quad+(0.55557-0.51961)+(0.56626-0.51961)\\&\quad+(0.59096-0.51961)+(0.63246-0.51961))=0.83471\end{aligned}$$

The results are summarized in Table 7. A comparison of the grey theory prediction design ($A_1B_2C_2D_1E_2$) with the initial parameter setting ($A_1B_1C_1D_1E_1$) showed that $S_{1\text{-}btn}$ and TOF increased from 87.70% to 95.80% and from 5425 $h^{-1}$ to 9800 $h^{-1}$, respectively. Therefore, an overall improvement in the multiple quality characteristics was achieved. A further investigation in Table 7 revealed that a considerable improvement (0.4871) in the GRG at the optimum level had been obtained.

Table 7 also compares the predicted GRG with the actual GRG obtained using the optimum process factors. The estimated and experimental values were in good agreement, meaning the experimental results showed satisfactory reproducibility. It is noteworthy that the obtained GRG value (0.97360) at the optimal parameter setting ($A_1B_2C_2D_1E_2$) was higher than the GRG value (0.96800) corresponding to the experiment 2 ($A_1B_1C_2D_2E_2$), the highest value among the 27 experiments (Fig. 3). Consequently, the processing factors were successfully optimized for the improvement of the catalytic performance of the ethylene dimerization. This integrated method can also be recommended for multi-performance optimization of a range of similar chemical reaction engineering problems.

## CONCLUSIONS

For financial and environmental reasons, there is a perpetual need to optimize operating conditions for industrial process systems to improve their performance, energy efficiency, profitability and safety. Consequently, operation optimization can affect determination of appropriate settings for control variables of a production process more concerned with producing high quality products at lower cost from the competitive global market prevailing today. Most chemical engineering application problems have many variables with complex inter-relationships; meeting these optimization

objectives can be challenging. Simultaneous multi-objective optimization methods have been introduced as a solution to this problem. The following key conclusions can be drawn from the results of this study:

1) The practicability of the hybrid approach of Grey-Taguchi with the entropy concept was demonstrated using ethylene dimerization catalyzed by Ti-based compound under two suitable additives with different structure/composition to assess a single optimum setting for the multiple correlated responses. The entropy measurement was used to increase GRA ability and to make the results more objective and accurate. Instead of using engineering guesswork to resolve the problem of simultaneous multi-objective optimization, a more structured and rigorous methodology was used that delivered more convincing results.

2) By developing this reliable optimization method and exercising control over parameters, the optimum value of the factors for the overall improvement in the multiple quality characteristics of new efficient [$Ti(OC_4H_9)_4$/1,4-dioxane/TEA/EDC] catalyst system was determined as temperature=53 °C, pressure=2.2 MPa, Al/Ti= 5 mol/mol, 1,4-dioxane/Ti=2 mol/mol, and EDC/Ti=2.5 mol/mol.

3) Through ANOVA on the GRG values, the EDC/Ti mol ratio (with 27.64% contribution) was found to have the most profound impact on the multiple quality characteristics. The influence order of other individual factors and the interactions was determined to be: 1,4-dioxane/Ti mol ratio (24.90%), temperature (15.83%), interaction between pressure and Al/Ti mol ratio (4.40%), Al/Ti mol ratio (4.30%), interaction between temperature and pressure (2.62%), and pressure (2.12%). It was observed that the interaction between temperature and Al/Ti did not significantly affect the multi-performance characteristics and hence was pooled with error to improve the percentage of contribution of the factors. The contribution of the pooled error was found to be 18.19%, which was in a reasonable error range.

4) The confirmation test verified the robustness of the GRA predicted optimal configuration and showed that the targeted multiple quality characteristics were improved. The computed GRG corresponding to the optimum setting was 0.97360, namely, greater than the highest value of GRG (0.968) among the 27 experiments. This indicated that the reaction factors have been successfully optimized for the better performance of the ethylene dimerization process. The outstanding predictions of this mathematical optimization method are based on only 27 experimental runs, which proves that it is practicable for achieving the best results through the design of experimental approach. In general, this avoids the time-consuming procedure of large data collection, especially when a large number of reaction parameters are being considered in a complicated process.

5) Under plant conditions, additives can be introduced into the 1-butene reactor either prior to feeding the catalyst or during the course of the process. Control of the co-production of polymers constitutes a major part of systems associated with the use of additives and can form complexes with the catalyst. Consequently, establishment of the best set of factors to reach optimal performance is important for this catalytic system. The approach proposed in this study can be useful for processing on an industrial scale to achieve maximum economic benefit. The difficulty of achieving optimum settings for the variables disturbs smooth running of 1-butene production and causes reactor fouling that prevents adequate reaction heat removal, reduces the working time of the equipment, and could possibly result in the need to shut down the process.

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## NOMENCLATURE

ANOM : analysis of means
ANOVA : analysis of variance
$D_k$ : sum of grey relational coefficients in all sequences for each quality characteristic
$df_A$ : DOF of factor A
$df_e$ : error DOF
$df_T$ : total DOF
DOF : degree of freedom
E : sum of entropy
EDC : ethylene dichloride
$e_k$ : entropy of each quality characteristic
$F_A$-ratio : ratio of variance of factor A to error variance
FID : flame-ionization detector
FTIR : Fourier transform infrared
GC : gas chromatography
GRA : grey relational analysis
GRG : grey relational grade
$^1$H-NMR : proton-nuclear magnetic resonance
$L_A$ : number of levels of factor A
LAO : linear $\alpha$-olefin
m : number of repetitions under the same test conditions
MFC : mass flow controller
n : number of tests
N : number of all experiments
$n_{A_x}$ : number of observations in which level x of A is present
OA : orthogonal array
p : number of quality characteristics
$P_A$ : percentage of influence of factor A
$r_{A_xB_y}$ : number of tests for $A_xB_y$ when factors A and B are at levels x and y, respectively
s : normalized coefficient
$S_{1\text{-}btn}$ : overall selectivity to 1-butene [%]
S/N : signal to noise ratio [db]
$(S/N_{H_p,F})_{L_x}$ : effect of factor F on the $S/N_H$ ratio of quality characteristic p at level x
$SS_A$ : sum of square of factor A
$SS'_A$ : pure sum of square of factor A
$SS_e$ : error sum of square
$SS_T$ : total sum of square
TEA : triethyl aluminum
TOF : turnover frequency [$h^{-1}$]

$V_A$ : mean square of factor A
$V_e$ : error variance
$w_k$ : weight of each quality characteristic
$x_i^*(k)$ : normalized value of the $k^{th}$ quality characteristic in the $i^{th}$ sequence (test)
$y_j$ : observed data for $S_{1\text{-}btn}$ and TOF at each test

**Greek Symbols**

$\Gamma_i$ : GRG value for $i^{th}$ test
$\overline{\Gamma}_{F_{x\text{-}opt.}}$ : mean GRG at the optimum level of factors
$\Gamma_m$ : total mean of the GRG
$\xi_i$ : grey relational coefficient of each quality characteristic at each test
$\zeta$ : distinguishing coefficient

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