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Investigating the effect of key factors, their interactions and optimization of naphtha steam cracking by statistical design of experiments

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ABSTRACT

The effect of temperature, steam-to-naphtha ratio, and residence time and their quadratic and cubic interactions on the yield of light olefins (ethylene and propylene) in naphtha steam cracking has been investigated. The temperature, steam-to-naphtha ratio, and residence time were varied in the range 1053–1153 K, 0.5–0.9 g/g, and 0.15–0.4 s, respectively. Based on the experimental results, naphtha steam cracking was modeled by use of statistical design of experiments (DoE). The results for the successful multiobjective optimization (MOO) of the naphtha steam cracking have also been reported. The new developed model is employed for the optimization purposes. Two MOO problems are solved; these problems involved maximization of ethylene, propylene and selectivity and minimization of severity. The response defined by the three most significant parameters was obtained from full factorial design and the optimal parameter set was found. The superiority of the DoE method over the conventional change one separate factor at a time approach is shown by the fact that we were able to study the higher interactions and optimize three individual factors with only 27 runs.

1. Introduction

Ethylene and propylene are the two most important light olefins. They are important reaction intermediates in industrial organic synthesis and being staple feedstocks in petrochemical industry. They are used in production of plastics, fibers, lubricants, etc. Their production process, steam cracking, has the backbone status for the sector. Naphtha is still the most important feedstock in production of ethylene, especially in Asia. Most of the propylene consumed in the production of petrochemicals is produced as a byproduct of ethylene production. On the other hand, the demand for propylene has increased significantly in recent years. Therefore adjusting the operation conditions in order to satisfy the demand of both products (ethylene and propylene) is essential.

The usual experimental strategy for synthesis optimization is the change one separate factor at a time approach: all variable but one are fixed at predetermined values, and the response of the system is studied as a function of the changing variable. Each variable is scanned this way, and the combination of their optimum values is accepted as the global optimum. The two major shortcomings of this approach are (i) the amount of necessary experiments grows very fast with the number of variables, thus, the complete optimization of real systems is rather unfeasible, and (ii) it is very unlikely that the global optimum can be found this way. The reason for this is that it assumes that the effects of the variables are completely independent, whereas the response of a real system to a change in any single parameter appears often as the gross effect of several parameter alternations (that is, real life multi-dimensional parameter spaces are seldom orthogonal). Statistical design of experiments (DoE) is the science of obtaining the largest possible amount of information about a system with smallest number of experiments [1,2].

There have been a number of studies on investigating the main effects and optimization of thermal cracking plants. Effect of temperature, residence time and weight ratio of steam to naphtha has been reported by Basu and Kunzaru [3]. Yields of methane and ethylene increased with temperature, whereas the yield of propylene passes through maxima with increasing temperature. Ethylene yield tended to level off at higher residence times and propylene showed a maximum with increasing the residence time. The yield of ethylene increased with steam ratio, whereas the decrease in the partial pressure of the reacting components does not have an appreciable effect on the yields of methane and propylene. The influence of the reactor material, the temperature, the ratio of steam to hydrocarbon, the residence time, and the presence of sulfur compounds in terms of coke formation and yields of various reaction products was carried out by Bajus et al.

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[4]. Pinter et al. [5] showed that the optimal yields of ethylene and propylene are achievable at intermediate pyrolysis temperatures and residence times. It was found that the behaviour of the laboratory reactor is very similar to that of commercial furnaces, although some yield differences were identified. Abghari et al. [6] used central composite design to generate systematic experimental data and based on the results, a semi-mechanistic model was developed. The effect of main factors was investigated by Kumar and Kunzru [7] and similar results were presented.

In all the above cases, only the influence of main effects (not their interactions) was discussed on the yield of major products. Motivated by the limited number of studies on the quadratic and cubic interactions of main parameters of the industrially important thermal crackers, the first aim of this study is to investigate the key factors and their interactions affecting steam cracking yield with naphtha as the feed. Unlike in the previous works, the model is based on experimental data that fit the response surface using a full factorial design. The potential for employing DoE in data treatment is especially high in the case of systems presenting nonlinearities and interactions, since DoE possess the ability to be developed from a set of experimental data (e.g., processing conditions and corresponding responses) without actual knowledge of the physical and chemical laws that govern the system. The same trend can be seen in artificial neural network that was proved to be better than mathematical model [8,9]. In the present model study we prove that the DoE approach can be utilized successfully for the rapid optimization of naphtha steam cracking. Albeit DoE is rapidly gaining popularity in various fields related to material science [10,11] and catalysis [12], it is a new approach for naphtha steam cracking that has been reported.

Unlike the other researches that focused on optimization of steam crackers based on mathematical [13–15] or trained artificial neural network model [16] as an optimization function, we optimize the naphtha steam cracker for multiple objectives after developing a reliable model in much simpler way based on our statistical design of our experimental data. The goal of the optimization is to achieve the best compromise between ethylene yield and propylene yield for one case and maximization of ethylene selectivity index and minimization of severity index for another one.

2. Experimental set-up

Experiments were performed using a one zone tubular furnace. The reactor vessel consisted of a stainless steel tube 45 cm in length and 1.35 cm in diameter. Liquids, naphtha and water, were injected into a vaporizer using two pumps. Properties and composition of naphtha is shown in Table 1. Steam, which was used as an inert, was generated in a vaporizer and mixed with the naphtha before the preheater. To avoid cracking in the preheat section the temperature of the preheated mixture was kept below 550 °C and this mixture was then fed to the reactor. The effluent from the reactor was quenched in ice bath followed by two water-cooled condensers placed in series. The gas-phase components were analyzed online using a Hewlett-Packard 5890 Flame Ionization Detector (FID) gas chromatograph (GC) equipped with Agilent J&W GS-alumina column (30 m × 0.53 mm × 30 μm). The schematic of this pilot is shown in Fig. 1.

3. Results and discussion

3.1. Initial screening of the parameter space

Efficient optimization requires the early identification of key process parameters. Based on previous experience [5,17–19] with steam cracking we consider the following process variables in the optimization: (i) temperature, (ii) residence time and (iii) steam-to-naphtha ratio. They were varied in the range 1053–1153 K, 0.5–0.9 g/g, and 0.15–0.4 s, respectively.

Table 1
Properties and composition of naphtha.

Physical properties				
Specific gravity (g/cm^3)				0.655
Initial boiling point (°C)				60.7
Final boiling point (°C)				120.3
Chemical composition (wt%)				
Carbon no.	n-Paraffin	i-Paraffin	Naphthene	Aromatics
C_4	2.16	0.12	0	0
C_5	27.34	21.38	3.58	0
C_6	10.19	12.29	3.84	1.58
C_7	3.29	3.82	4.34	1.57
C_8	1.04	1.2	0.92	0.55
C_9	0.26	0.5	0	0.03
Sum	44.28	39.31	12.68	3.73

3.2. Full factorial design

The full factorial design can find the influences of each process variable as a variety of other variable levels, as well as the interactions among these variables on the yield of olefins. In order to investigate the quadratic interactions and higher orders, we should develop 3 level factorial design with 3 key variables. Therefore the total runs are limited to 27. Effects of the following process variables on the yields of ethylene and propylene were investigated in full factorial design study: (*A*) reaction temperature; (*B*) residence time; (*C*) steam-to-naphtha ratio. Fixed levels of these three variables are given in Table 2. The observation of the yields (wt%) of ethylene and propylene with the design matrix in the 3^3 full factorial experiments are shown in Table 3.

A cubic polynomial equation was developed to represent the responses as a function of independent variables involving their quadratic and cubic interactions and squared terms.

The variables X_i were coded by linear transformation of the factor space coordinates with the coordinate beginning in the experimental center and defining the coordinate axes ratio in units of the factor variation interval [20]. The arithmetic of this transformation is given in Eq. (1):

$$x_i = \frac{X_i - X_{i0}}{\Delta X}; \quad i = 1, 2, 3, \ldots, k \tag{1}$$

where x_i is the coded value of *i*th factor, X_i is the uncoded factor value, X_{i0} is the uncoded factor value at center point, and ΔX is the uncoded value of the factor-variation interval.

Data of the light olefin yields shown in Table 3 were subjected to regression analysis to estimate the effects of process variables. The analysis of variance (i.e., ANOVA) on the yields of ethylene and propylene in wt% is summarized in Tables 4 and 5, respectively. The test statistic, *F*, is defined as *F* = MSF/MSE, where MSF and MSE were the mean squares of factors or interactions, and errors, respectively. If the calculated value of *F* is greater than the value in the *F* table at a specified probability level (e.g., $F_{0.05}(1,8) = 5.32$), a statistically significant factor or interaction is obtained.

After the test, factors *A*, *B*, *C*, and interactions $A \times B$, A^2, A^2B exhibit statistically significant effects on the yield of ethylene and factors *A*, *B* and interactions $A \times B$, $B \times C$, A^2, B^2, $A \times B \times C$ exhibit statistically significant effects on the yield of propylene. From a combination of estimates for the process variables and the ANOVA results, a polynomial model with statistical significance can be generated. This model, quantitatively elucidating the effects of process variables with statistical significance, is presented as

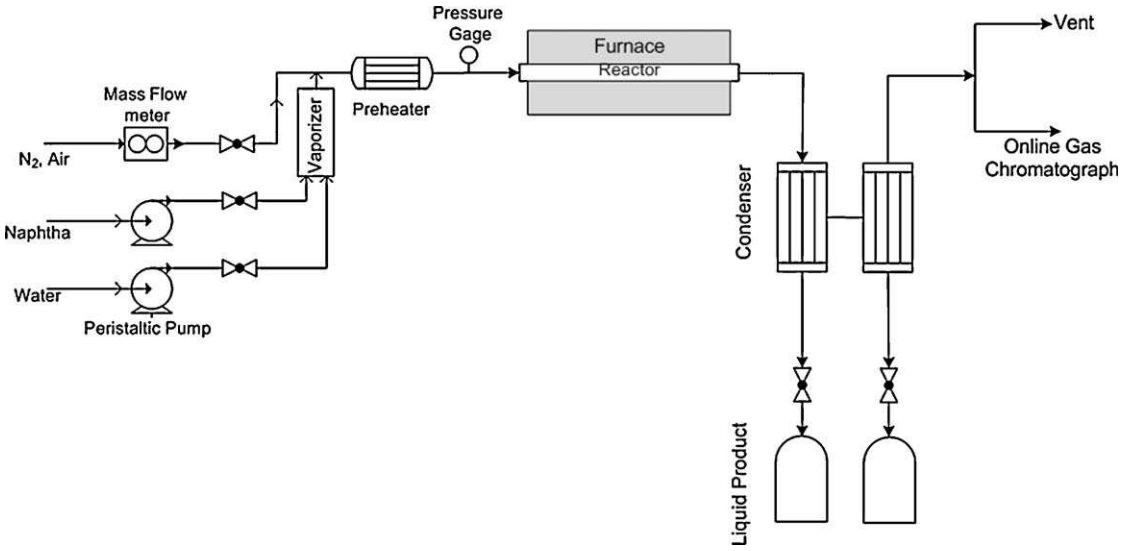

Fig. 1. Schematic diagram of the thermal cracking setup.

follows:

$$\text{Ethylene} = 433.18 - 1.18X_A - 3280.07X_B + 13.69X_C + 8.23X_AX_B + 8.05 \times 10^{-4}X_A^2 - 5.07 \times 10^{-3}X_A^2X_B \quad (2)$$

$$\text{Propylene} = -669.52 + 1.47X_A + 656.82X_B + 10.15X_C - 0.68X_AX_B + 3.24X_BX_C - 7.96 \times 10^{-4}X_A^2 - 135.87X_B^2 - 0.04X_AX_BX_C \quad (3)$$

where X_i denotes the actual variables for factor (i.e., A, B, and C). Note in Eqs. (2) and (3) that the terms without statistical significance was deleted from the full-effect model based on the analysis of variance. These effects were considered as errors in the experiments and their variances were accordingly pooled into the sum of squares of errors (i.e., SSE). Therefore, the multiple correlation coefficient squared, $R^2 = 1 - (\text{SSE}/\text{SST})$ equal to 0.971 for Eq. (2), indicates a very good fitting for the experimental data of ethylene on factors A, B and C. The R^2 value of Eq. (3) is 0.951, also indicating that this regression model is a good representation for dependence of propylene yield on factors A, B and C. The main effects (i.e., A, B, and C) and two-factor interactions effects (i.e., $A \times B$ and $A \times C$) for ethylene and propylene are shown in Figs. 2(a) and (b), 3(a) and (b), respectively.

From Fig. 2(a), the yield of ethylene was increased by increasing the reaction temperature (A), residence time (B) and steam ratio (C). Note in Fig. 2(b) that the effect of factor B was negligible when factor A was set at the high level. On the other hand, a sharp increase in yield, from ≈18 to 32 wt% was found for factor B as factor A was kept at the low level. This phenomenon is referred to as an interaction between factors A and B (denoted as $A \times B$). The same discussion can be given for Fig. 3. From Fig. 3(a), the yield of propylene was decreased slightly by increasing the reaction temperature (A) and residence time (B), but no significant change was observed by increasing the steam ratio. In Fig. 3(b), the effect of factor B was negligible when factor A was set at low level. On the other hand, a sharp decrease in yield, from ≈19 to 6 wt% was found for factor B as factor A was kept at high level. Similarly, these synergistic effects on the yields of ethylene and propylene can be found for the other interactions A^2, A^2B and $A \times B$, $B \times C$, A^2, B^2, $A \times B \times C$, respectively.

Table 2
Factors and levels for the 3-level full factorial design.

	Factor	Level		
		–	0	+
A	Temperature (°C)	780	830	880
B	Residence time (s)	0.15	0.275	0.4
C	Steam-to-naphtha ratio (g/g)	0.5	0.7	0.9

3.3. Contour plots

Eqs. (2) and (3) were used to construct the contour plots for the yields (in wt%) of ethylene and propylene against temperature, residence time and steam-to-naphtha ratio as shown in Fig. 4. These contour plots facilitate a straightforward comparison of the dependence of the yield on the key process variables. From Fig. 4(a) and (b), the yield of ethylene is significantly increased with the

Table 3
The design matrix and experimental data of the ethylene and propylene yield from the experimental design.

Run	Factors			Yield (wt.%)	
	A	B	C	Ethylene	Propylene
1	780	0.15	0.5	13.96	11.27
2	830	0.15	0.5	21.73	16.76
3	880	0.15	0.5	25.75	17.05
4	780	0.275	0.5	18.25	15.37
5	830	0.275	0.5	28.38	19.5
6	880	0.275	0.5	33.08	14.28
7	780	0.4	0.5	29.43	21.82
8	830	0.4	0.5	36.24	15.76
9	880	0.4	0.5	38.03	6.16
10	780	0.15	0.7	19.15	14.33
11	830	0.15	0.7	23.27	17.18
12	880	0.15	0.7	32.39	17.82
13	780	0.275	0.7	25.07	18.17
14	830	0.275	0.7	32.09	19.66
15	880	0.275	0.7	34.24	14.82
16	780	0.4	0.7	31.87	21.31
17	830	0.4	0.7	38.2	15.01
18	880	0.4	0.7	39.27	6.20
19	780	0.15	0.9	21.49	15.72
20	830	0.15	0.9	25.74	17.47
21	880	0.15	0.9	33.3	17.21
22	780	0.275	0.9	27.66	20.45
23	830	0.275	0.9	34.7	17.18
24	880	0.275	0.9	35.41	14.82
25	780	0.4	0.9	34.57	18.17
26	830	0.4	0.9	40.01	14.94
27	880	0.4	0.9	41.27	6.12

Table 4
Analysis of variance for the yield of ethylene from the experimental design.

Factor	df	SS	MS	F
A	1	462.99	462.99	299.60
B	1	318.46	318.46	206.07
C	1	135.04	135.04	87.38
AB	1	16.66	16.66	10.78
AC	1	6.69	6.69	4.33
BC	1	4.01	4.01	2.60
A^2	1	13.04	13.04	8.44
B^2	1	1.16	1.16	0.75
C^2	1	2.71	2.71	1.75
A^2B	1	10.05	10.05	6.51
Error	16	24.73	1.55	
Total	26	1375.36		

Table 5
Analysis of variance for the yield of propylene from the experimental design.

Factor	df	SS	MS	*F*
A	1	98.61	98.61	77.36
B	1	20.74	20.74	16.27
C	1	0.94	0.94	0.74
AB	1	239.23	239.23	187.69
AC	1	2.27	2.27	1.78
BC	1	8.05	8.05	6.32
A^2	1	23.80	23.80	18.67
B^2	1	27.05	27.05	21.22
C^2	1	1.49	1.49	1.17
ABC	1	7.80	7.80	6.12
Error	16	20.39	1.27	
Total	26	450.37		

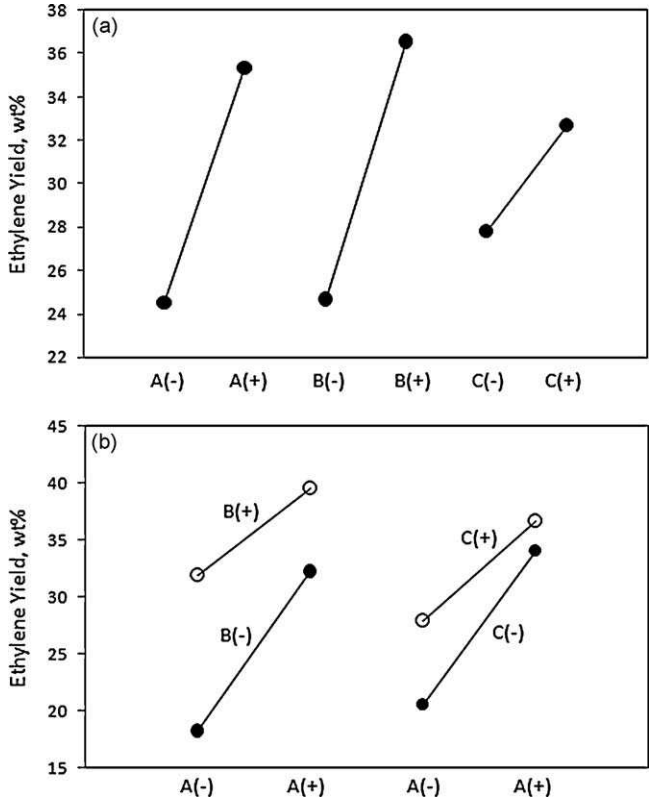

Fig. 2. (a) Main effects of (*A*) reaction temperature (*B*) residence time, (*C*) steam-to-naphtha ratio on the yield of ethylene. (b) Interaction effects of $A \times B$, $A \times C$ on the yield of ethylene: where (+) and (−) indicate the high and low levels of these factors, respectively.

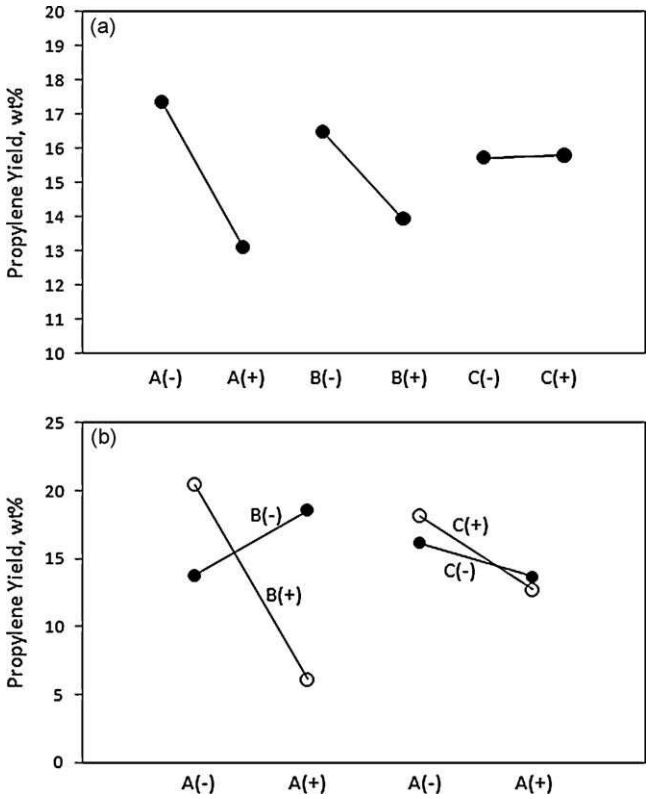

Fig. 3. (a) Main effects of (*A*) reaction temperature (*B*) residence time (*C*) steam-to-naphtha ratio on the yield of propylene. (b) Interaction effects of $A \times B$, $A \times C$ on the yield of propylene: where (+) and (−) indicate the high and low levels of these factors, respectively.

simultaneous increase of temperature, residence time and steam ratio. They show a curvature at the upper right corner. Therefore there are the significant interactions as a comparison to Fig. 4(c), although we only consider that the interaction $A \times B$ is highly significant according the value of *F* test.

From the contour plot in Fig. 4(d), notice that the yield of propylene increases from the upper right corner to a maximum at approximately residence time of 0.19 s, temperature of 860 °C and steam ratio of 0.5 g/g and then decreases as we approach the lower left corner. Similar trend can be seen in Fig. 4(f) at approximately residence time of 0.32 s, temperature of 810 °C and steam ratio of 0.57 g/g.

Interactions plots can also provide useful insights. Fig. 5 presents an interaction effect plot for the saddle-shaped surface in Fig. 4(d). Notice that at high residence time (*B*) the mean response is decreasing in temperature (*A*), whereas at low *B* the mean response is increasing in *A*. Thus, the presence of interaction effects is clearly indicated by the plot. Absence of interaction effects would be indicated, as usual, by parallel curves.

From the above results and discussion, the key variables affecting the yield of light olefins can be easily identified by means of the statistically experimental methodology. The yield of ethylene and propylene can be simply controlled by the simultaneous change in the temperature, residence time and steam ratio.

3.4. Multiobjective optimization

In most optimization studies on thermal cracking and other processes, the common objective is profit or costs. Hence, this study considers different kinds of objectives that increase the scope of making profit rather than maximizing the profit itself.

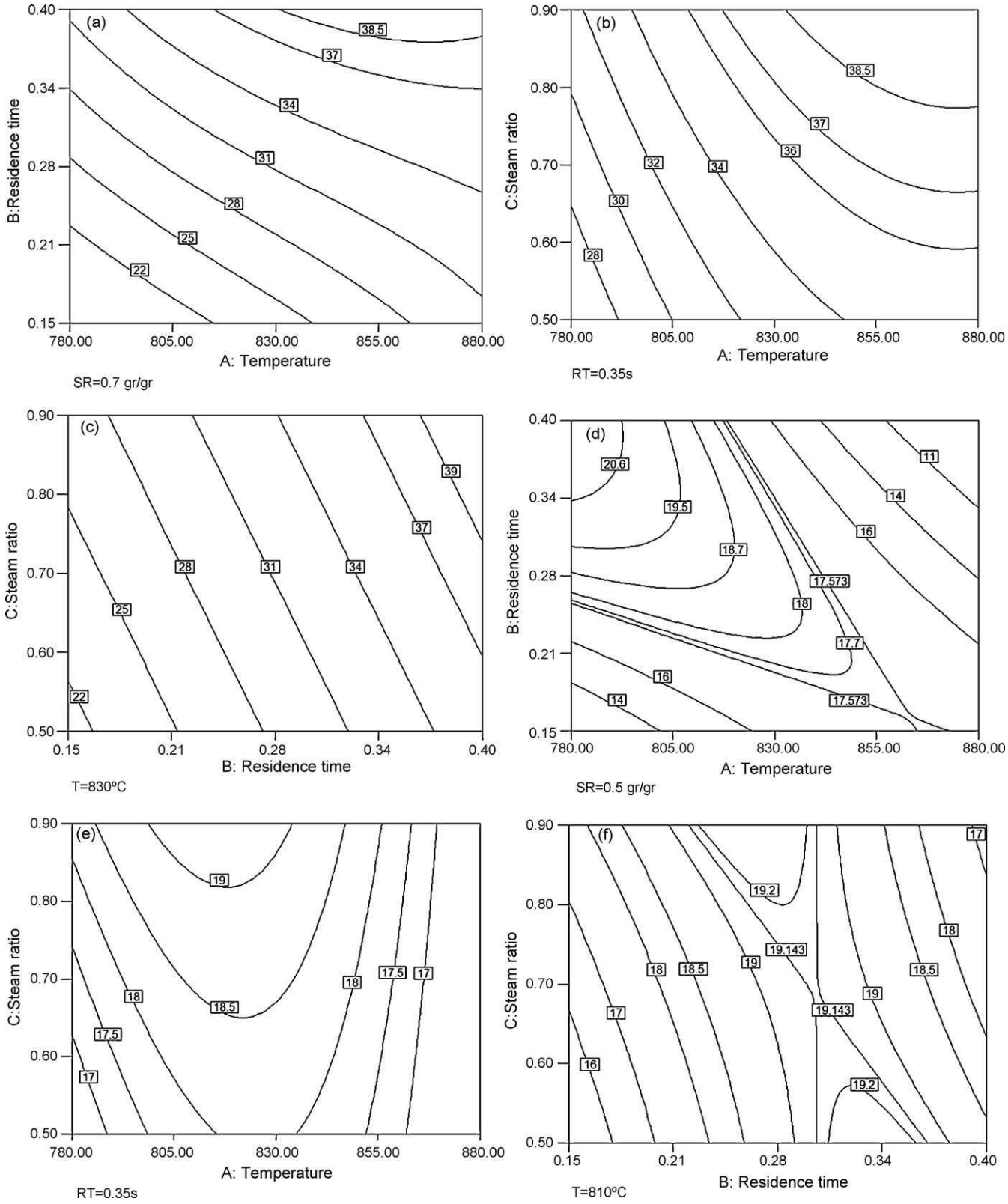

Fig. 4. Contour plots describing the response surface for ethylene as a function of (a) temperature vs. residence time, (b) temperature vs. steam ratio, and (c) residence time vs. steam ratio and for propylene as a function of (d) temperature vs. residence time, (e) temperature vs. steam ratio, and (f) residence time vs. steam ratio.

They are also fundamental in characterizing the cracker performance.

The objectives considered for naphtha cracker optimization are maximization of ethylene and propylene yield and selectivity index, and minimization of severity index. Ethylene and propylene production are obviously important in many industries. In this paper, we present and discuss results for two cases, each with two objectives.

The variables that affect the cracking reactor performance and were discussed in our experimental design were chosen as the

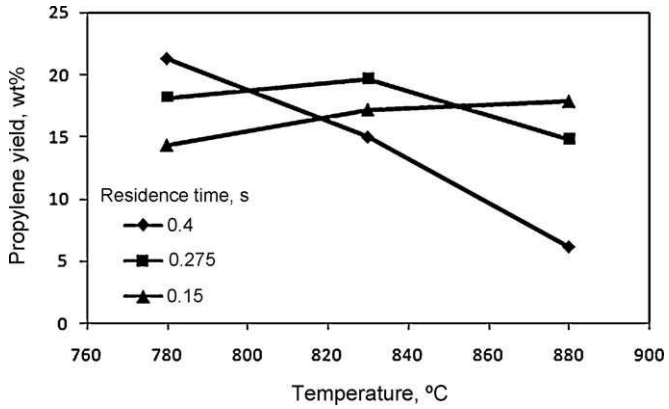

Fig. 5. Interaction effect plots for saddle-shape surface of Fig. 4(d) (at steam ratio = 0.5 g/g).

decision variables. The ranges of decision variables used are as follows:

$800\,^{\circ}\mathrm{C} \leq T \leq 850\,^{\circ}\mathrm{C}$

$0.15\ \mathrm{s} \leq \text{residence time} \leq 0.25\ \mathrm{s}$

$0.5 \leq \text{steam ratio} \leq 0.65$

Bounds on the decision variables are selected according to industrial practice. The results of multiobjective optimization can be used to recommend the operating conditions for further experimental works in naphtha steam cracking especially in the kinetic studies.

3.4.1. Maximization of ethylene and propylene yield

For the optimization study of the naphtha steam cracker the objectives are to maximize the ethylene production and maximize the propylene production simultaneously. The two optimization objectives are competitive. Therefore we must achieve the best compromise between ethylene and propylene yield.

A parameter set which is able to maximize either ethylene and propylene yield could be obtained analytically from Eqs. (2) or (3). However, our goal is to optimize the light olefins (ethylene and propylene) and this requires the simultaneous maximization of both responses. The scaled value was denoted as the "desirability" of a certain parameter set with respect to the studied response, and the composite desirability (D_{comp}) of a parameter set was defined as the linear combination of the individual d values. This is a general approach to cut the dimensionality of a simultaneous optimization problem to just one: finding the parameter set which maximizes D_{comp}, as shown in Eq. (4):

$$D_{\mathrm{comp}} = \left(\prod_{i=1}^{n} d_i\right)^{1/n} \tag{4}$$

where d_i are desirable ranges for each response and n is the number of responses in the measure. The desirable ranges are from zero to one (least to most desirable, respectively).

If the objective or target T for the response y is a maximum value, then the individual desirability function is defined as follow in Eq. (5):

$$d = \begin{cases} 0 & y < L \\ \left(\dfrac{y-L}{T-L}\right)^{r} & L \leq y \leq T \\ 1, & y > T \end{cases} \tag{5}$$

where L denotes the lower limit of the response. When the weight $r = 1$, the desirability function is linear. Choosing $r > 1$ places more emphasis on being close to the target value, and choosing $0 < r < 1$ makes this less important. In this work we choose $r = 1$. The detailed description of optimization procedure is explained by Montgomery [21]. Eqs. (2) and (3) are combined with each other with the help of Eqs. (4) and (5).

In our case the optimum was found at temperature = 848.53 °C, residence time = 0.25 s, steam ratio = 0.643 g/g. This set gave the highest D_{comp} at 0.675 and predicted ethylene yield = 30.936 wt% and propylene yield = 17.629 wt% for optimized responses.

The values optimized for these decision variables were toward its upper limit to boost higher yield of ethylene and propylene. Temperature has an opposing effect on yield of ethylene and propylene; high temperature maximizes ethylene production while low temperature maximizes propylene production. But the total yield of ethylene and propylene is increased in the defined range for temperature. Based on our experimental results, a large steam-to-naphtha ratio increases the yield of ethylene by decreasing hydrocarbon partial pressure, instead increases energy consumption. On the other hand, a small steam-to-naphtha ratio increases the rate of coking. A lower steam-to-naphtha ratio value is more desirable due to reduction of material handling. Residence time is a function of flow rate. This optimal value for residence is also tend to its upper bound, because maximization of both ethylene and propylene yield are goals. The optimal conditions and the yield of ethylene and propylene are consistent with the work of Li et al. [16] that studied the optimization of the naphtha cracking unit.

3.4.2. Maximization of ethylene selectivity and minimization of severity

The ethylene selectivity index is the ratio of ethylene weight fraction to ethane weight fraction, and the severity index is the ratio of some lighter fraction (such as propane, propylene, propadiene, ethane, ethylene, acetylene, methane, and hydrogen) to the propylene fraction. Van Geem et al. [22] concluded that, for naphtha and similar feed stocks, these two indices can be used to relate experimental data obtained for different coil configuration for the steam cracking process. Hence, the objectives-selectivity and severity indices are not dependent on reactor sizes and geometries, and the optimization results are applicable to cracking of similar naphtha feed stocks in different coil configurations.

In our case the optimum was found at temperature = 837.91 °C, residence time = 0.25 s, steam ratio = 0.56 g/g. This set gave the highest D_{comp} at 0.729 and predicted ethylene yield = 28.55 wt% and propylene yield = 18.17 wt% for optimized responses.

Temperature increases steadily in order to increase the selectivity index but it does not reach to its upper bound, because the methane yield increases sharply beyond a conversion of 85% that have seen in our results (not included) and the other researchers [2,23]. Methane yield has a significant effect on the severity index along with ethylene and propylene. On the other hand the optimizer decrease the feed flow rate, therefore increase the residence time in order to increase the selectivity.

4. Conclusion

The successful application of the statistical design of experiments approach for the optimization of naphtha steam cracking has been reported. Based on our previous experience with steam cracking, three factors affecting performance have been identified, which were then optimized using full factorial design. Thus, we were able to achieve the best performance on our local experimental bench by performing 27 experimental runs. The appropriate experimental design applied which is a full factorial with three level (rather than central composite designs, Box-Behnken designs, etc.) to investigate quadratic and cubic interactions along with main effects. The factors of temperature and

residence time have the highest effect on the production yield of ethylene. Along with these key factors, some quadratic (AB, A^2) and cubic (A^2B) interactions proved to be significant and should be considered in experimental modeling of ethylene. On the other hand the higher interactions play an important role in propylene yield. The interaction of temperature and residence time (AB) proved to be much more significant compare with the other interactions even with key factors and cannot be ignored. In addition, some square terms (A^2 and B^2) and the cubic interaction, ABC, are important in the production yield of propylene.

The variation of values of decision parameters at the optimum conditions can be explained qualitatively, which shows that MOO results are reliable. Temperature is the most important decision variable and has an opposing effect on the yield of ethylene and propylene, so at intermediate temperature we can achieve the highest yield of ethylene and propylene. The influence of other decision variables such as residence time and steam ratio, also considered.

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