

## Evaluation of solvent dearomatization effect in heavy feedstock thermal cracking to light olefin: An optimization study

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**Abstract**—Response surface method was used to study the effect of aromatic extraction of heavy feedstock in thermal cracking. *N*-methylpyrrolidone as the solvent performing dearomatization of feedstock was at different temperature and molar solvent to oil ratios. Temperature, flow rate and steam-to-hydrocarbon ratio were in the range of 1,053-1,143 K, 1-2 g/g, and 0.75-1.2 g/min, respectively. From the CCD studies, the effects of flow rate and coil outlet temperature were the key factors influencing the yield of light olefins. Ethylene and propylene yields increased more than 10% by dearomatization.  $C_3^+$  decreased by 13% on average. Finally, we obtained the single maximum yield of ethylene, propylene, and simultaneous maximum yields for untreated and raffinate.

Key words: Thermal Cracking, Dearomatization, Response Surface, Olefin, Multi-response Optimization

### INTRODUCTION

Thermal cracking of hydrocarbons is the most important source for producing the main feedstock of the petrochemical industries. To reduce undesired side reactions, feed is mixed with dilution water. Then the mixture is preheated to primary cracking temperature (500-650 °C) [1]. Because of low accessibility and high price of naphtha, cracker units use heavier fractions as feeds. Heavy cut oils such as kerosene, gas oil and residues have received attention by some researchers [2-6]. These fractions are cheaper than naphtha. However, the direct using of heavy fractions as either main raw feedstock or an alternative feed (by its own or co-fed) is limited in the downstream equipment and recovery units. Heavier liquid feeds produce lower ethylene and propylene, though less desirable byproduct yield, such as fuel oil increase through cracking these feeds. High coking leaning with huge disturbing impurities, such as sulfur containing compounds, in these heavy fractions bring about short-term performance of the plant. High aromatic of heavy cut oils is the most important reason for these difficulties. Employing a pre-treatment process before the steam cracking is indispensable to improving heavy fractions quality [3,7]. Several treatments such as extracting aromatic [8], visbreaking [8], hydrotreating [9,10], hydrocracking [11], two-stage cracking [12] can upgrade heavy fractions.

Liu et al. [13] adopted the adsorption and solvent extraction process to separate group compositions in naphtha for improving the cracking feeds. They gathered the *n*-paraffins in naphtha through adsorption process using 5A molecular sieves. The ethylene yield improved by 13% using desorption of oil rich in *n*-paraffins as the cracking feed. Extraction of aromatics and cyclones from naphtha

improved the ethylene and the propylene yields to 3.0% and 1.5%.

Gaile et al. [14] studied the extractive refining of atmospheric gas oil with *N*-methylpyrrolidone in the presence of undecane to remove aromatics and sulfur-containing compounds and thus got a diesel oil ingredient. Further, El-Gayar et al. [15] studied aromatic extraction of vacuum gas oil using *N*-methyl-2-pyrrolidone as solvent. They reduced the aromatic concentration from 16.95% to 4.68% with extraction.

Response surface is a technique designed to find the best value of response and the influencing factors [16]. It was successfully applied in experimental work [17,18]. Keyvanloo et al. [19] studied the effect of temperature, residence time and steam ratio on the steam cracking of naphtha by experimental design coupled with response surface method. They also studied the quadratic and cubic interactions of key parameters affecting the products yield. Finding higher interaction is important; they considered them in their modeling. They also performed multiobjective optimization for simultaneous increase of ethylene and propylene.

Sedighi et al. [17,20] used central composite design to examine the effects of operating variables on the yield of light olefins in heavy hydrocarbon thermal cracking. From the CCD studies, the effects of COT and flow rate were the key factors influencing the yield of light olefins. They developed two empirical models, representing depending ethylene and propylene yields on operating condition. Empirical modeling using RSM is useful for optimizing the thermal cracking of feedstock. Abghari et al. [21] used central composite design to generate systematic experimental data and developed a semi-mechanistic model based on the results. Dicholkar et al. [22] studied modeling of dimethyl formamide steam cracking by using RSM coupled with Box-Behnken design. They developed eight empirical models to show the interaction effect of different parameters on conversion and yield of seven products [23].

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In our work, a heavy liquid hydrocarbon was subjected to solvent extraction under various conditions. Then, the raffinate phase with least aromatic content was exposed to steam cracking. We compared the product yields of the raffinate with those of the crude fraction under diverse working conditions. This paper develops a numerical approach for simultaneous multiresponses optimization for untreated and raffinate. Several experiments were performed to study the effects of different COT, flow rate and steam ratio on main products yields. To form systematic experimental data for covering a wide range of running conditions and to predict the maximum product yields, we used central composite design as a systematic experimental design method. This paper contains two empirical models for ethylene and propylene yields using central composite design and regression of analysis. Based on these models, we conducted two single-response optimization of ethylene and propylene separately and a multiresponse optimization of ethylene with propylene for before and after treatment feedstock.

## EXPERIMENTAL SET-UP

### 1. Steam Cracking Process

Fig. 1 shows a schematic diagram of the experimental set-up. Steam cracking of the crude gas oil and its raffinate fraction was performed in a tubular reactor of SS-316 with a 10 mm internal diameter and a 55 cm length suited in an electrical furnace. Separate proportional controllers controlled each zone temperature. Type K thermocouple measured axial temperature profile. Two syringe pumps cause continuous injection of feed and water. The effluent of the reactor was quenched in ice bath followed by water-cooled condensers in series. Then, the cracked gas flowed through a gas meter before collection in a gas sample bag for gas chromatography analysis. A CP-3800 GC model (Varian-Chrompack) was employed for analyzing the gaseous products.

### 2. Feed Characteristics

The selected feed was a heavy liquid hydrocarbon. This feed is a mixture of petrochemical industrial residue. It was a distilled fraction,  $180\text{ }^{\circ}\text{C} < \text{bp} < 345\text{ }^{\circ}\text{C}$ , with a specific gravity of 0.84. Physico-

**Table 1. Chemical composition and physicochemical characteristics of both crude feed and raffinate**

Property	Crude feed	Raffinate
Refractive index	1.46	1.45
Kinematic viscosity (Cp)	1.69	1.89
Density (16 °C) (g/ml)	0.84	0.81
Molecular weight	171	142
PNA analysis (wt%)		
Paraffin	52.6	53.7
Naphthene	16.3	27.7
Aromatic	31.1	18.6

chemical characteristics, composition, and mean molecular weight are presented in Table 1. As remarked, ca. 31% of hydrocarbon constituents fall into the aromatic group.

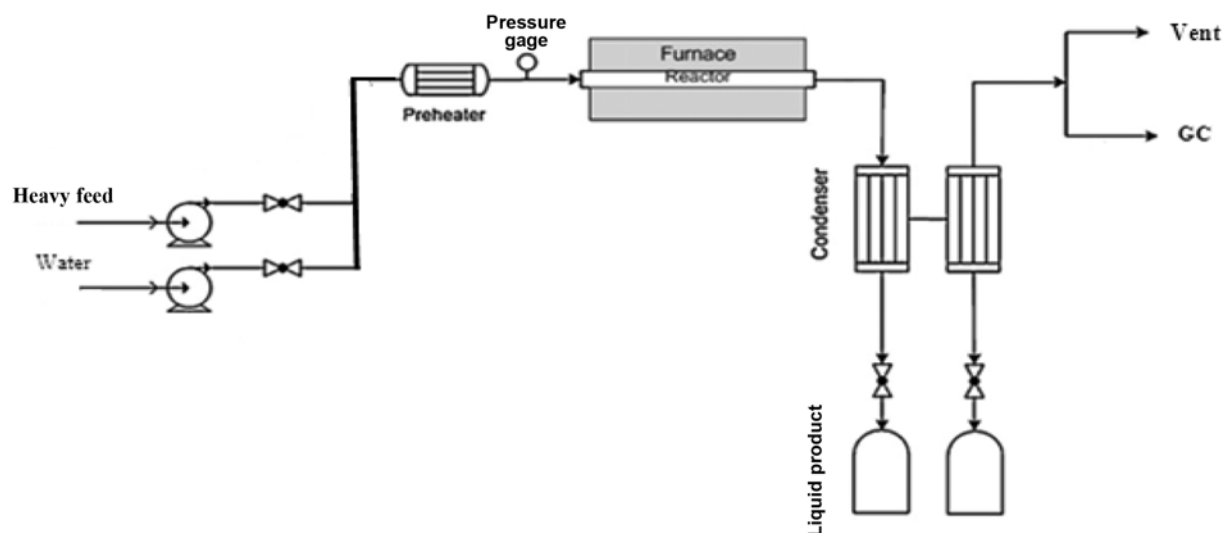
Extracting of aromatics was performed with *N*-methylpyrrolidone as the dearomatization solvent at different temperature and solvent-to-oil ratio. The raffinate of least aromatic percent, with the solvent to oil ratio of 1.0 at 25 °C, was chosen as the after-treatment feedstock for the steam cracking process. Table 1 points out the physicochemical characteristics of the raffinate.

## RESULTS AND DISCUSSION

### 1. Central Composite Design

A central composite rotatable design (CCRD) for three factors was employed for experimental design. We selected coil outlet temperature ( $x_1$ ), flow rate ( $x_2$ ), steam-to-hydrocarbon ratio ( $x_3$ ) as control variables. The design consists of two-level full factorial design ( $2^3=8$ ), six star points, and one center point. Furthermore, we carried out four reproduces at the central point to evaluate the pure error among each experiment.

The order of experiments was randomized to lower the uncontrolled effect of factors. A quadratic polynomial equation was developed to predict the responses as a role of independent variables involving their quadratic interactions and squared terms. We coded



**Fig. 1. Schematic of the experimental setup for steam cracking.**

the variables  $X_i$  as  $x_i$  according to Eq. (1):

$$x_i = \frac{X_i - X_0}{\Delta X_i}; \quad i=1, 2, 3, \dots, k \quad (1)$$

The basis of forming a polynomial equation is given in Eq. (2):

$$Y = \beta_0 + \sum_{j=1}^3 \beta_j X_j + \sum_{j=1}^3 \beta_{jj} X_j^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (2)$$

**Table 2. Factors and levels for CCD study**

Level	COT (°C), $X_1$	Flow rate (g/min), $X_2$	Steam ratio, $X_3$
$-\alpha$	780	1	0.75
-1	798	1.2	0.84
0	825	1.5	0.98
+1	852	1.8	1.11
$+\alpha$	870	2	1.2

We used multiple regression analysis techniques comprised in the RSM to estimate the models' coefficients. The low and high levels for the independent variables were based on industrial practice. Table 2 shows the design factors and levels for CCD studies for steam cracking of untreated feed and the raffinate; meanwhile, the list of design matrix with their corresponding results is in Table 3.

The resultant second-order models for the yields of ethylene and propylene are in Eqs. (3) and (4) for steam cracking of untreated feed:

$$C_2H_4 = +38.859 - 0.104X_1 - 9.876X_2 + 50.744X_3 + 2.67 \times 10^{-3}X_1X_2 - 0.0234X_1X_3 + 1.539X_2X_3 + 9.98 \times 10^{-5}X_1^2 + 0.988X_2^2 - 19.513X_3^2 \quad (3)$$

$$C_3H_6 = +491.65 - 1.0194X_1 - 25.563X_2 - 22.386X_3 + 0.0223X_1X_2 + 0.0328X_1X_3 + 1.529 \times 10^{-12}X_2X_3 + 5.23 \times 10^{-4}X_1^2 + 4.0178X_2^2 - 1.887X_3^2 \quad (4)$$

In addition, Eqs. (5) and (6) for steam cracking of raffinate:

**Table 3. Design matrix and experimental data of the main products for CCD study**

Run	Factors			Ave. residence time (sec)	Yield (wt%)					
	$X_1$	$X_2$	$X_3$		$C_2H_4$ untreated	$C_2H_4$ raffinate	$C_3H_6$ untreated	$C_3H_6$ raffinate	$C_5^+$ untreated	$C_5^+$ raffinate
1	798	1.8	1.11	0.32	22.58	24.81	11.93	13.53	43.94	37.15
2	798	1.8	0.84	0.41	23.35	26.44	12.05	12.96	40.61	35.11
3	798	1.2	1.11	0.48	24.11	26.65	10.1	10.82	40.83	37.93
4	798	1.2	0.84	0.61	24.5	26.75	9.91	10.68	40.15	36.90
5	852	1.8	1.11	0.3	24.87	26.21	7.54	9.26	44.16	38.89
6	852	1.8	0.84	0.39	25.43	29.05	6.95	7.19	41.98	36.83
7	852	1.2	1.11	0.45	25.92	28.86	4.95	7.08	45.96	39.02
8	852	1.2	0.84	0.58	27.21	31.17	4.45	7.16	42.62	34.80
9	780	1.5	0.98	0.43	24.2	25.64	12.25	13.18	40.98	35.73
10	870	1.5	0.98	0.4	27.83	31.75	4.62	3.45	44.43	41.15
11	825	1	0.98	0.63	28.14	31.32	5.18	7.16	41.64	33.89
12	825	2.0	0.98	0.31	23.75	26.24	11.48	11.95	42.68	37.90
13	825	1.5	0.75	0.53	26.05	29.12	7.03	8.27	39.79	34.95
14	825	1.5	1.2	0.35	23.21	26.26	7.48	9.16	46.15	39.04
15	825	1.5	0.98	0.42	25.33	27.73	7.69	9.23	42.95	36.46
16	825	1.5	0.98	0.42	25.37	27.73	7.73	9.25	42.97	36.45
17	825	1.5	0.98	0.42	25.37	27.77	7.72	9.26	42.97	36.45
18	825	1.5	0.98	0.42	25.35	27.76	7.72	9.25	43.02	36.49
19	825	1.5	0.98	0.42	25.38	27.75	7.75	9.22	42.89	36.44

**Table 4. ANOVA for the ethylene and propylene yields model for untreated feed**

Ethylene						
Source	Sum of squares	Degree of freedom	Mean square	$F_{Value}$	p-Value	$R^2$
S.S. regression	35.65	9	3.96	11.98	0.0005	0.93
S.S. error	2.98	9	0.33			
S.S. total	38.63	18				
Propylene						
Source	Sum of squares	Degree of freedom	Mean square	$F_{Value}$	p-Value	$R^2$
S.S. regression	113.46	9	12.61	33.19	<0.0001	0.97
S.S. error	3.42	9	0.38			
S.S. total	116.88	18				

**Table 5. ANOVA for the ethylene and propylene yields model for raffinate feed**

Ethylene						
Source	Sum of squares	Degree of freedom	Mean square	F <sub>Value</sub>	p-Value	R <sup>2</sup>
S.S. regression	64.75	9	7.19	13.4	0.0003	0.93
S.S. error	4.83	9	0.54			
S.S. total	69.58	18				
Propylene						
Source	Sum of squares	Degree of freedom	Mean square	F <sub>Value</sub>	p-Value	R <sup>2</sup>
S.S. regression	103.95	9	11.55	15.23	0.0002	0.94
S.S. error	6.82	9	0.76			
S.S. total	110.77	18				

$$C_2H_4 = -30.884 - 0.0512X_1 + 34.19X_2 + 74.16X_3 - 0.051X_1X_2 - 0.062X_1X_3 - 3.2X_2X_3 + 1.498 \times 10^{-4}X_1^2 + 2.513X_2^2 - 12.77X_3^2 \quad (5)$$

$$C_3H_6 = -57.618 + 0.278X_1 + 21.494X_2 - 61.84X_3 - 0.0451X_1X_2 + 0.0443X_1X_3 + 9.02X_2X_3 - 2.0919 \times 10^{-4}X_1^2 + 3.565X_2^2 + 7.04X_3^2 \quad (6)$$

Table 4 shows the analysis of variance (ANOVA) for Eqs. (3) and (4). Fischer's 'F' value with a low probability 'P' represents a high significance of the regression model [22]. Calculations of mean square of the model and error are:

$$MS_{model} = \frac{SS_{model}}{df_{model}} \quad (7)$$

$$MS_{error} = \frac{SS_{error}}{df_{error}} \quad (8)$$

where MS, SS, and df are the mean squares, sum of squares and degree of freedom, respectively. The F value can be calculated by the following expression:

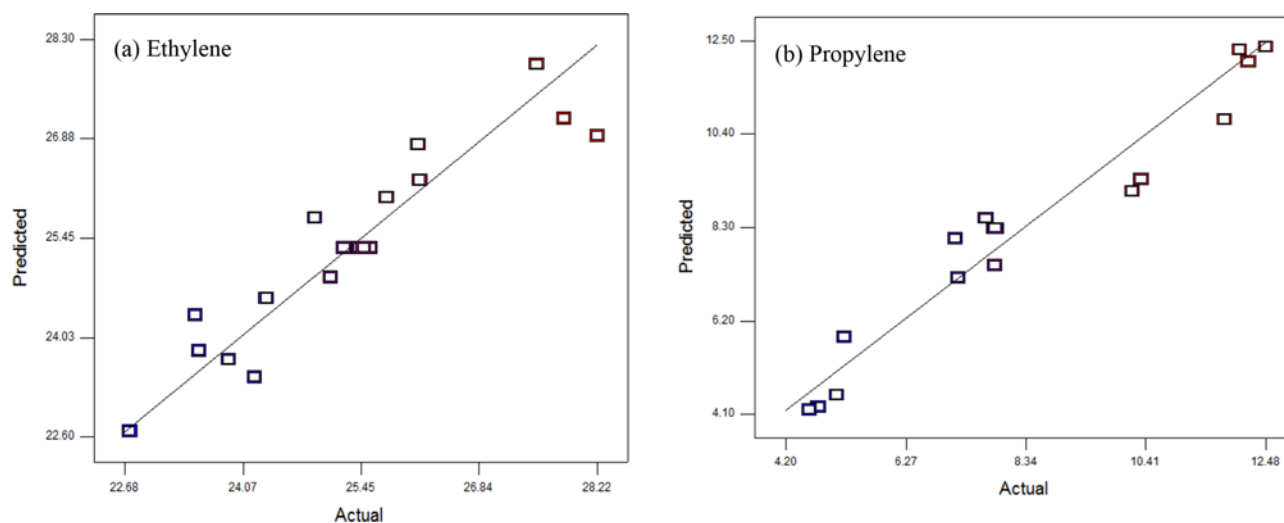
$$F = \frac{MS_{model}}{MS_{error}} \quad (9)$$

Table 5 shows the analysis of variance (ANOVA) for Eqs. (5) and (6). The ANOVA suggests that all three variables and their interactions are significant and play important roles in the main product yields. The F values of the model support that the models are highly significant. P-values are associated with F values as they are useful to display whether F values are large enough to show the statistical significance. In the models above, linear and quadratic parameters were significant with  $P < 0.05$ . The P-value fewer than 0.05 shows the model is significant at the 95% confidence limit. High values of  $R^2$  for Eqs. (3) to (6) mean a good fitting for the experimental data and predicted values.

Figs. 2 and 3 explain the observed relative to predicted values. From the figures, most of the points of experimental values lie close to the straight line, which are the predicted values.

## 2. Response Surface Plots and Contour Plots

Eqs. (3) to (6) were used to set up the response surface and contour plots for the yields (wt%) of ethylene, propylene,  $C_5^+$  against temperature and flow rate at best value of steam ratio. These plots facilitate a clear comparison of the dependent yield on the key process variables. Figs. 4 and 5 show response surface plots of the ethylene yield (wt%) as a design variables for untreated and raffinate, respectively. Besides main effects, the interaction effects among the factors are explained. These figures are based on holding the third



**Fig. 2. Actual versus predicted values for ethylene and propylene for untreated feed.**

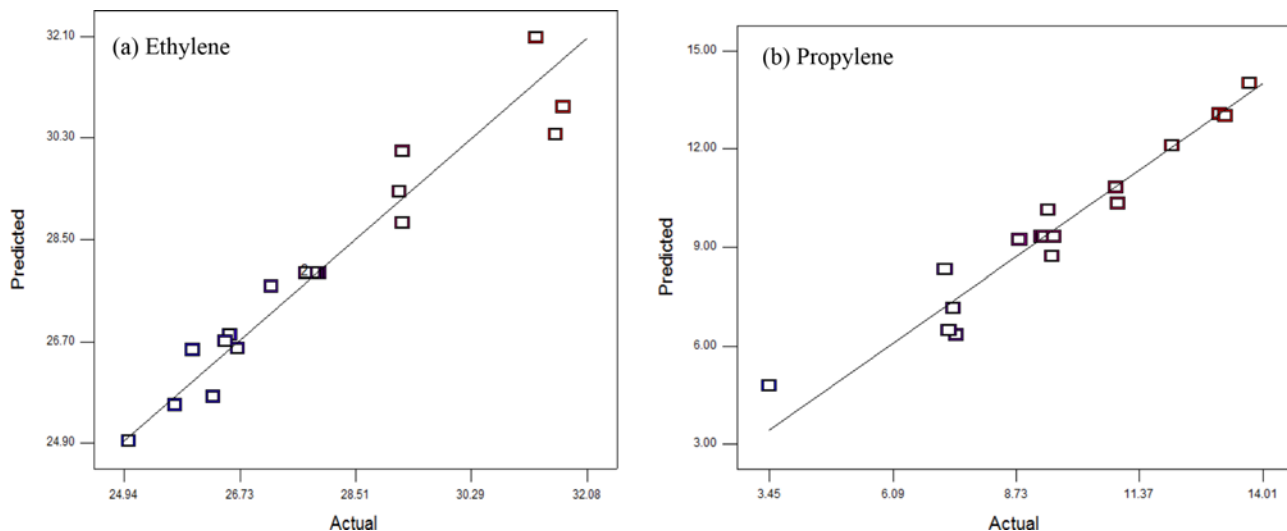


Fig. 3. Actual versus predicted values for ethylene and propylene for raffinate.

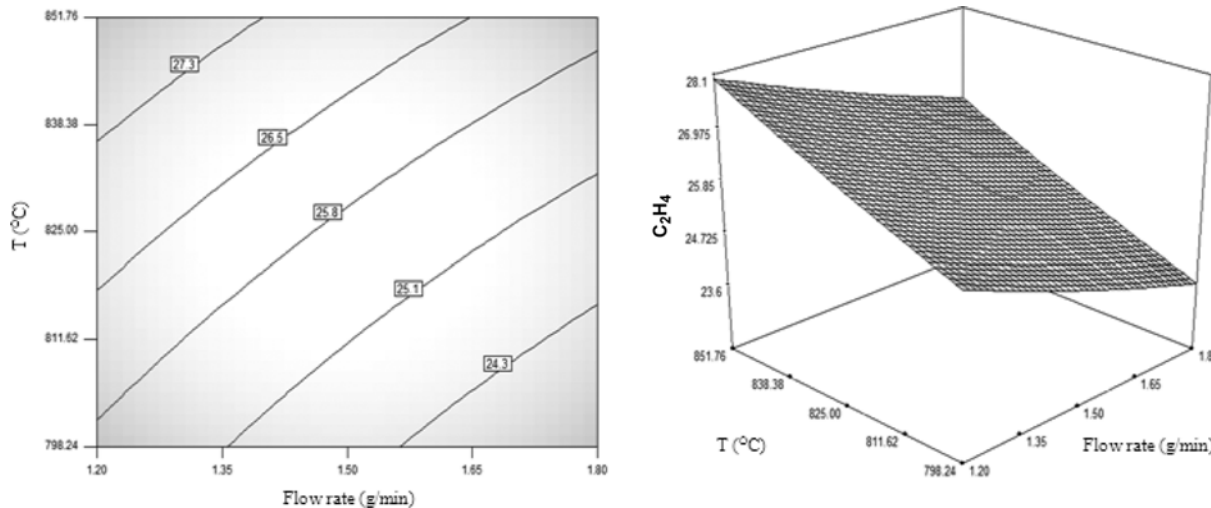


Fig. 4. Ethylene (untreated)-response surface plot and contour-lines map depending on T (°C) and flow rate (g/min), holding the third variable at fixed level, SR=0.84.

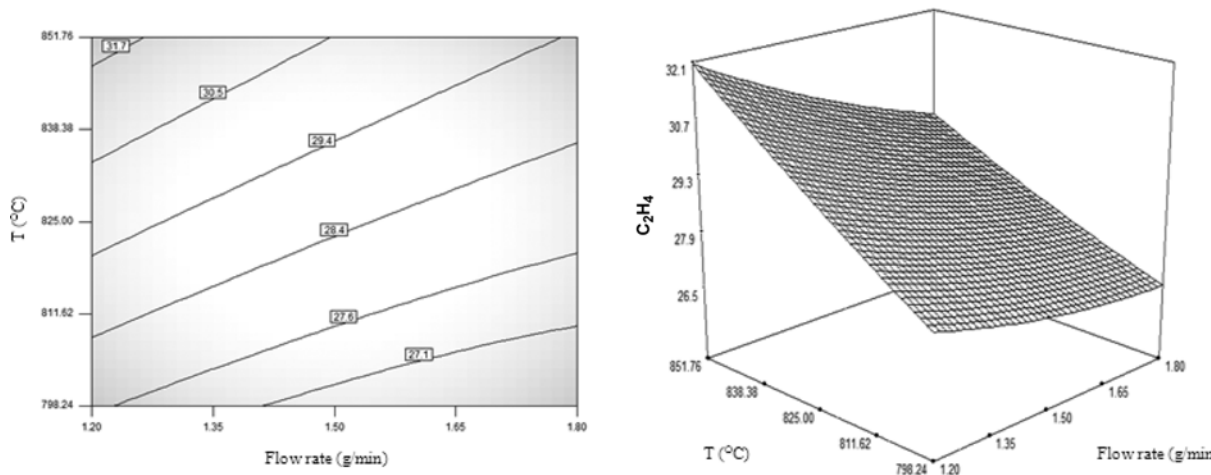


Fig. 5. Ethylene (raffinate)-response surface plot and contour-lines map depending on T (°C) and flow rate (g/min), holding the third variable at fixed level, SR=0.85.

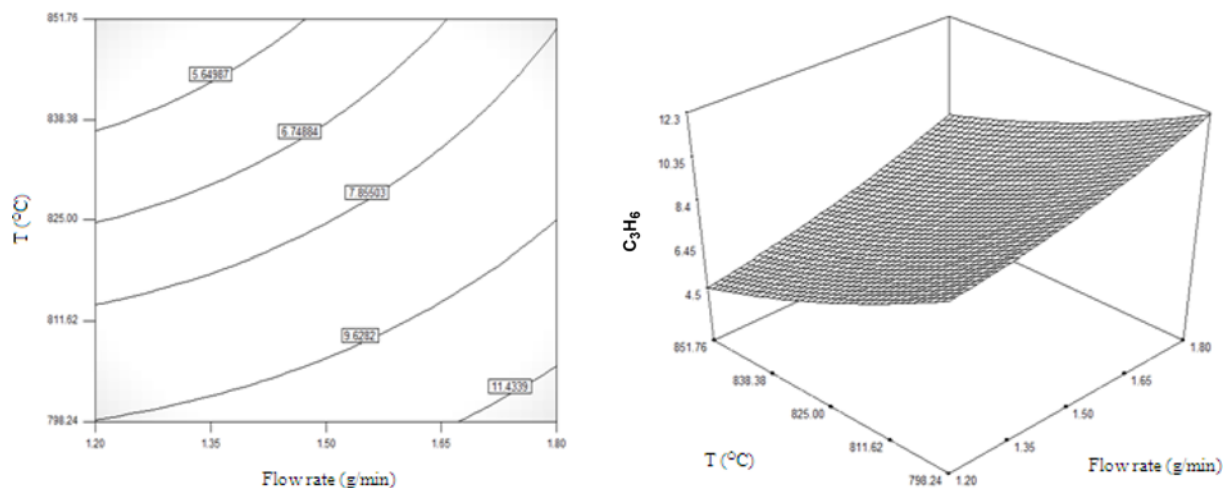


Fig. 6. Propylene (untreated)-response surface plot and contour-lines map depending on T (°C) and flow rate (g/min), holding the third variable at fixed level, SR=1.01.

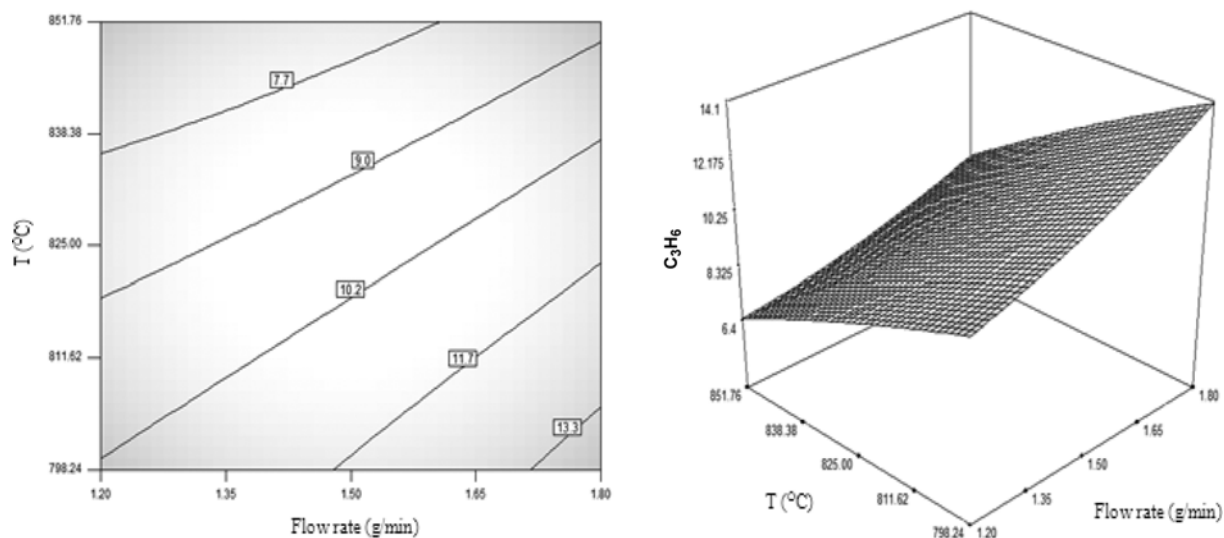


Fig. 7. Propylene (raffinate)-response surface plot and contour-lines map depending on T (°C) and flow rate (g/min), holding the third variable at fixed level, SR=1.11.

variable at the best values. The best steam ratios for the untreated and raffinate are 0.84 and 0.85, respectively. Therefore, the yield of ethylene significantly increased with raising the temperature and decreased with the raising the flow rate.

We see a large amount in producing ethylene with raising temperature from 780 to 870 °C, which is expected. This value is higher for the raffinate. We assigned this to the high aromatics, which is resistance to the cracking reactions in untreated feedstock. These cyclic hydrocarbons bring about secondary reactions and promote the consumption reactions of ethylene. In other words, lower selectivity of untreated than raffinate occurs.

We changed the hydrocarbon flow rate as a direct measure of the residence time on the product yields obtained for raffinate and feed. In principle, raising the flow rate decreases the residence time, thereby resulting in lower conversion. Thus, ethylene yields are reduced. The same effect occurs for temperature compared with the steam ratio. With rising steam ratio, the ethylene yield decreases

(not shown here). From the figure, we find the yields of ethylene increase by more than 4% by dearomatizing.

Lower ethylene production of untreated feed is assigned to spreading carbon type, especially the aromatics in the feed. In addition, major part of undesirable species, such as sulfur, is in the structure of aromatics. Aromatics do not produce ample light olefins and lead to form heavy liquid products. In addition, aromatics are the main precursors for coke formation.

Figs. 6 and 7 show the response surface plots and counter-lines maps of propylene product for untreated and raffinate, respectively. The yield of propylene increases with lowering temperature and raising flow rate. Increasing steam ratio causes the propylene yield improvement. The results mean that yields of propylene increase by more than 3% by dearomatizing. The best steam ratios for the untreated and raffinate are 0.84 and 0.85, respectively.

From the result, we remark that desired propylene increased with the extracting aromatic of the first feedstock. During dearomatiza-

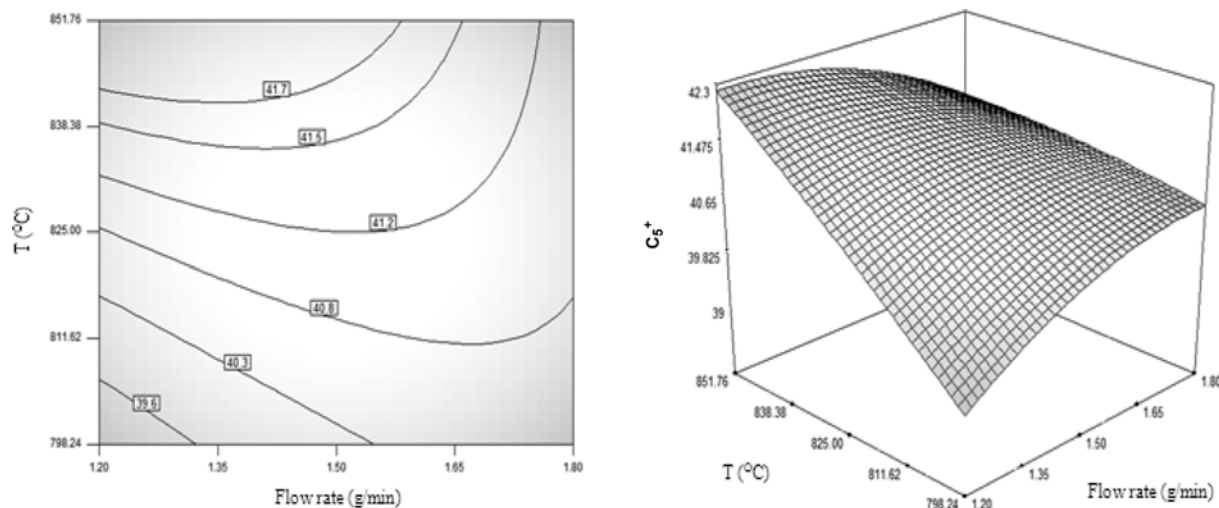


Fig. 8.  $C_5^+$  (untreated)-response surface plot and contour-lines map depending on  $T$  ( $^{\circ}\text{C}$ ) and flow rate (g/min), holding the third variable at fixed level,  $\text{SR}=0.84$ .

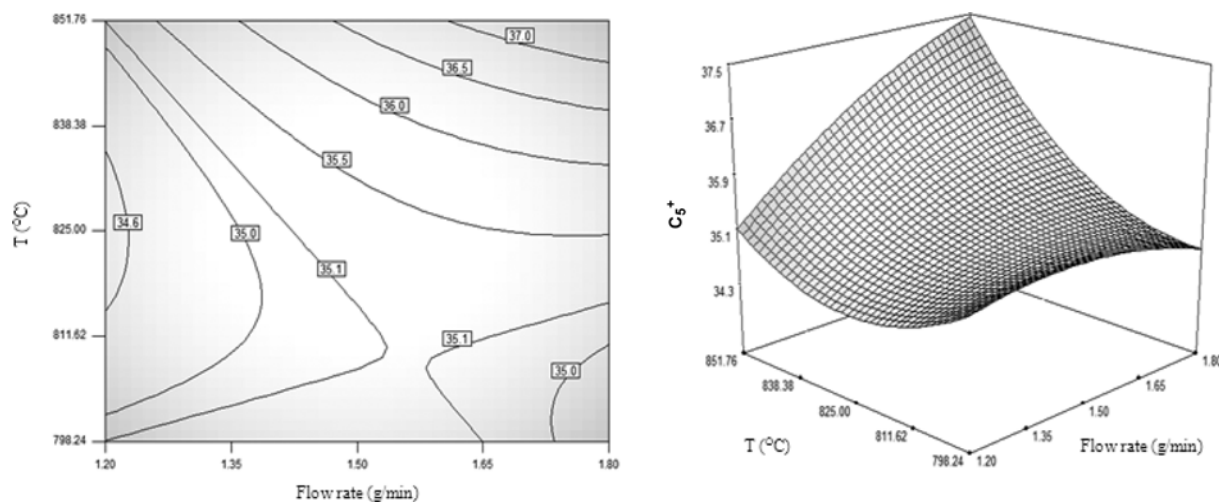


Fig. 9.  $C_5^+$  (raffinate)-response surface plot and contour-lines map depending on  $T$  ( $^{\circ}\text{C}$ ) and flow rate (g/min), holding the third variable at fixed level,  $\text{SR}=0.84$ .

tion feed is mixed with *N*-methylpyrrolidone and solubilized in the solvent. The insoluble pitch will precipitate out of the mixed feedstock as aromatics. This brings about different chemical composition and physicochemical characteristics. Especially, the weight percent of naphthene goes up by dearomatization. Higher naphthenic compounds in the raffinate and the higher concentration of aromatics in the original feed explain the difference in the behaviors of the two fractions. Naphthenes and paraffins are easier to crack to produce light olefin, while aromatic molecules are more stable.

Decreasing propylene from cracking raffinate is more intense at higher temperatures. However, temperature's effect is similar to untreated and raffinate. Increasing the temperature causes reducing propylene yield. This is ascribed to the higher consumption rate than production rate of propylene at high temperatures. As mentioned above, flow rate is a direct measure of the residence time. Thus, by lowering the residence time, a lower time exists for propylene consumption in secondary reactions, thereby raising propylene yield.

Response surface and contour curves in Figs. 8 and 9 highlight the effect of design variables on  $C_5^+$  yields for untreated and raffinate, respectively. For untreated, decreasing temperature and flow rate result in lowering  $C_5^+$  yield. On the contrary, increasing steam ratio heightens  $C_5^+$  yield.

Fig. 9 shows that at the lower values of the flow rate, the best value of temperature is in the range of 820–830  $^{\circ}\text{C}$ , leading to the minimum yield of  $C_5^+$ . For higher flow rate levels raising the temperature leads to the slight increase of  $C_5^+$ . This result is the same as steam ratio. Therefore, lowering flow rate and steam ratio is favorable. The results suggest the yield of  $C_5^+$  decreases by more than 5% on dearomatization.

Behavioral discrepancies of the untreated and raffinate can be explained by the higher naphthenic compounds in the raffinate and the higher concentration of aromatics in the original feed. Naphthenes are easier to crack and may be favorable with paraffins, while aromatic molecules are more stable and considered refractory to

cracking conditions. Aromatics are also the main precursors for coke formation. Liquid product of raffinate is much less than untreated feedstock. The rudimentary factor of  $C_5^+$  production in thermal cracking reactions is aromatics. Thus, lowering available aromatics in the raffinate brings about reducing the liquid yield. Raising temperature results in increasing conversion, yield of liquid product and produced coke.

Decreasing the residence time increases the liquid hydrocarbon yield. This happens by lowering the conversion. In other words, high part of liquid product in high flow rate condition does not react and it remains uncracked.

Above results and discussion show that the statistical experimental method can identify the key variables affecting the yield of light olefins. The ethylene and propylene yields can be controlled by the simultaneous change in the temperature, flow rate and steam ratio.

## OPTIMIZATION

### 1. Single-response Optimization

The Nelder-Mead Simplex method was used to look for the best conditions in which each response variable reaches a maximum value. We selected the cracking reactor's performance as the decision variables. The ranges of decision variables are as follows:

$$\begin{aligned} 798.24 \leq T \leq 852 \text{ } ^\circ\text{C} \\ 1.2 \text{ g/min} \leq \text{flow rate} \leq 1.8 \text{ g/min} \\ 0.84 \leq \text{steam ratio} \leq 1.11 \end{aligned}$$

For untreated, the yield of ethylene reaches to its maximum at 28.1 wt% when COT, flow rate and steam ratio is 851.76 °C, 1.2 g/min and 0.84, respectively. Thus, an optimum happens at high COT but low steam ratio and flow rate. The optimum point for propylene is 12.22 wt% when COT, flow rate and steam ratio is 798.24 °C, 1.8 g/min, and 1.01. This optimum value is at low COT, high flow rate, and intermediate steam ratio. Thus, the maximum yield of propylene occurs at significantly different working conditions. For raffinate, the yield of ethylene reaches its maximum at 32.1 wt% when COT, flow rate and steam ratio is 851.76 °C, 1.2 g/min and 0.85,

respectively. Therefore, it has an optimum at high COT but low steam ratio and flow rate. The optimum point for the propylene product is 14 wt% when COT, flow rate and steam ratio is 798.24 °C, 1.8 g/min and 1.11. This optimum value is at low COT, high flow rate and steam ratio.

### 2. Multi-responses Optimization

For the optimization study of the steam cracker, the objectives are to maximize the ethylene and the propylene yield simultaneously. Desirability function helps to carry out optimization by two or more responses. According to this methodology, each response  $y$  must be converted into the individual desirability function  $d_i$ , that ranges from 0 (undesirable) to 1 (desirable). Such transformation may be presented as follows [24]:

$$d_i(\hat{y}_i(x)) = \exp[-\exp(- (a_{i1} + a_{i2}\hat{y}_i(x)))] \quad (10)$$

The coefficients  $a_{i1}$  and  $a_{i2}$  were calculated by assigning for two values of  $y_i$  the corresponding two values of  $d_i$ , preferably in the range  $0.2 < d_i < 0.8$  [24]. Afterward, the overall desirability function,  $D$ , contains the individual desirability values as [25,26]:

$$D(x) = [d_1(\hat{y}_1(x)) \times d_2(\hat{y}_2(x)) \times \dots \times d_s(\hat{y}_s(x))]^{1/s} \quad (11)$$

where  $s$  is the responses involved (in our specific case  $s=2$ ). In this case, expressing multiresponse optimization problem is to maximize desirability function and may be written as:

$$\begin{aligned} \text{Max } D(x) \\ x \in \Omega \\ = \max \{ [d_1(\hat{Y}(x)) \times d_2(\hat{U}(x))]^{1/2} \} \end{aligned} \quad (12)$$

In the thermal cracking process discussed in the present paper, the overall desirability function approach combines two responses, ethylene ( $\hat{Y}(x)$ ) and propylene ( $\hat{U}(x)$ ). The detailed description of optimization procedure is explained by Montgomery [27].

The fitted model from Eqs. (3) to (6) is used to map empirically the response function over the experimental region. They combined with each other with Eqs. (10) to (12). Contour plot helps in assessing the effect of any two variables in combination with the desired product. Fig. 10 shows the response surface and contour plots for

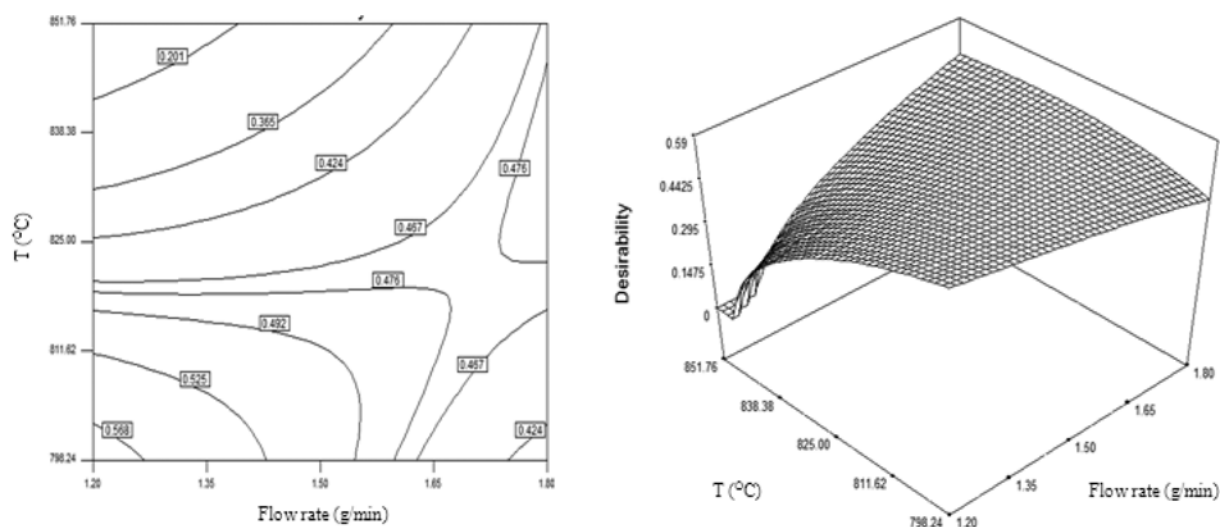
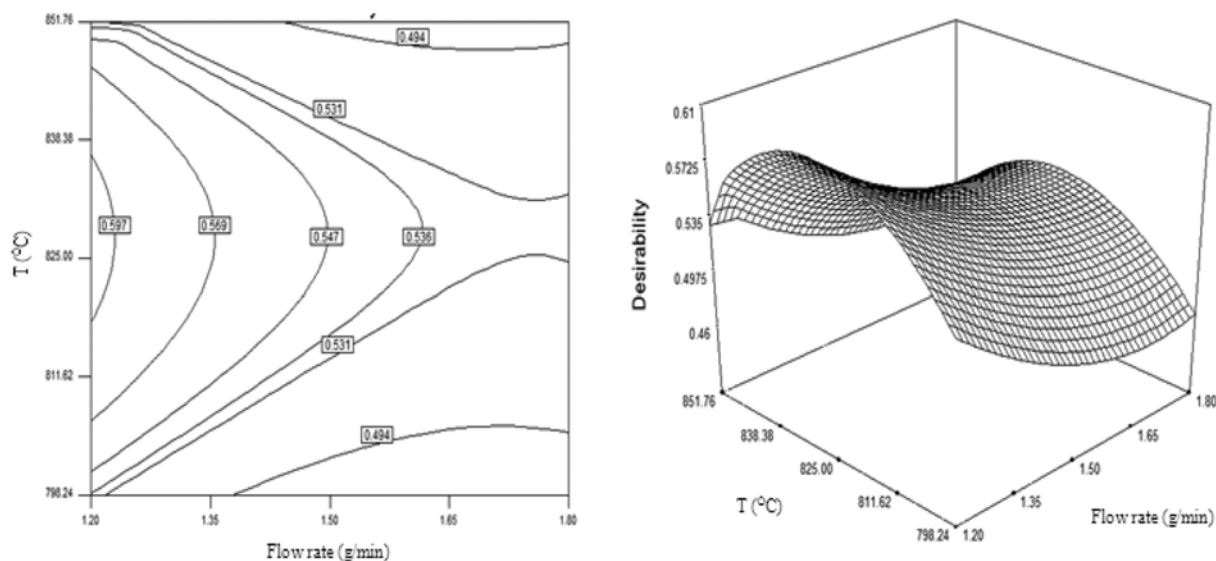


Fig. 10. Maximum olefin (untreated) - Response surface and contour plots describing composite desirability depending on  $T$  ( $^{\circ}\text{C}$ ) and flow rate (g/min), holding the third variable at optimum fixed level,  $\text{SR}=0.88$ .





**Fig. 11. Maximum olefin (raffinate) - Response surface plot and contour plots describing composite desirability depending on T (°C) and flow rate (g/min), holding the third variable at optimum fixed level, SR=0.84.**

the composite desirability function against temperature, and flow rate for untreated feedstock. From the figure, the yield of light olefins (ethylene and propylene) increases at low COT and flow rate. The best value of steam ratio was 0.88. However, the figure shows that temperature is more significant than flow rate in reaching optimum olefins.

Fig. 11 shows the response surface and contour plots for the composite desirability function against the temperature, and flow rate for raffinate. From Fig. 10, the yield of light olefins (ethylene and propylene) increases up to a roughly intermediate COT and low flow rate. The best value of steam ratio was 0.84. Increase in the steam ratio results in decreasing olefin yields. Desirability function scores in optimum values are above 0.5 for untreated and raffinate, indicating that all these points are of interest.

To corroborate multiobjective optimization of the olefins yields, we carried out two more runs and compared the final best points with those from experimental data at similar conditions. Table 6 shows the average relative error for the ethylene and propylene yields for untreated is 2.2% and 3.64%, respectively. Similarly, the average relative error for the ethylene and propylene yields for raffinate is 1.91 and 3.96, respectively.

## CONCLUSION

The response surface methodology involving central composite design and regression of analysis helps to carry out steam cracking of untreated heavy feedstock and raffinate phase with least aromatic content. Quadratic models were successfully developed and provided satisfactory predictions. ANOVA results confirmed that significant agreement occurred between the models and the experimental data.

The COT influenced the light olefins' yields, because the reaction is endothermic. Besides, high temperature favors ethylene yield, but it has an opposite effect on the yield of propylene.

Varying values of decision parameters at the optimum conditions show that multiobjective optimization results are reliable. For untreated, light olefins yield increased up at low COT, flow rate and intermediate steam ratio. For raffinate, light olefins yield increased up at intermediate COT, low flow rate and steam ratio. Yields of ethylene and propylene increased by more than 10%, while the liquid products with five or more carbon atoms decreased by 13% on average on dearomatization. This is assigned to higher content of naphthene in raffinate, which is easier to crack to produce light olefin.

**Table 6. Result validations of the final optimal point in the multi-responses optimization**

C <sub>2</sub> H <sub>4</sub> yield (wt%)			C <sub>3</sub> H <sub>6</sub> yield (wt%)		
Untreated					
Y <sub>multiobjective</sub>	Y <sub>experimental</sub>	% Relative error	Y <sub>multiobjective</sub>	Y <sub>experimental</sub>	%Relative error
27.45	28.21	2.69	11.87	12.29	3.41
27.45	27.93	1.71	11.87	12.35	3.88
%Average relative error		2.2	%Average relative error		3.64
Raffinate					
31.39	31.83	1.38	13.4	13.95	3.94
31.39	32.18	2.45	13.4	13.87	3.38
%Average relative error		1.91	%Average relative error		3.66

Further content of aromatics in the untreated feed leads to forming heavy liquid products and higher coke formation.

### NOMENCLATURE

D	: composite desirability function
d	: individual desirability value
m <sup>o</sup>	: mass flow rate
x	: coded independent variable
X	: uncoded independent variable
X <sub>0</sub>	: uncoded independent variable at center point
ΔX	: step change
Y	: predicted response

### Indices

0	: intercept
i	: independent variables
j	: independent variables
g	: gas
HC	: hydrocarbon
n	: number of responses

### Greek Symbols

$\beta$	: coefficients of quadratic model
$\beta_i$	: linear term
$\beta_{ij}^2$	: squared term
$\beta_{ij}$	: interaction term

### Abbreviations

CCD	: central composite design
CCRD	: central composite rotatable design
COT	: coil outlet temperature [°C]
RSM	: response surface methodology

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