Multiple Objective Optimization of Industrial Naphtha Cracking Process by Box-Behnken Response Surface Methodology

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ABSTRACT: *Naphtha in the presence of steam is cracked to produce ethylene, propylene, and 1,3-butadiene which are important feedstocks in the petrochemical industry. It is important to optimize industrial process conditions to maximize the yield of 16 desired products individually as well as a combination of those based on the market demand. The parameters influencing the naphtha cracking product yield are feed composition, Coil-Outlet Temperature (COT), coil-inlet pressure, residence time/feed flow rate, and Steam-to-Hydrocarbon Feed Ratio (SHFR). In this research, Box-Behnken response surface design has been used to evaluate the effects and interactions among three factors such as COT, SHFR, and feed flow rate on product yields by carrying out 15 experimental test runs. The SHFR, COT, and flow rates varied in the range from 0.38−0.5, 810−824 °C, and 14.8−17.2 tons per hour (tph), respectively. Models for three different naphtha feeds having different heavier hydrocarbon content (C_8+) have been developed. Another model has been developed considering 27 experimental test runs with C_8+ composition (3.74 wt.%, 6.81 wt.%, and 9.88 wt.%) as the fourth factor. These model results have been validated with Industrial process data on ethylene and propylene yields for ten case studies. The model-predicted yields match excellently well with that of industrial reactor yield. Response optimizer has been developed to optimize process conditions to maximize yields of ethylene, propylene separately, and also combined yield of ethylene+propylene+1,3-butadiene. It has been found that a higher COT has a favorable impact on Ethylene and 1,3-Butadiene yield. The Increased C_8+ content results in a lower yield of Ethylene, Propylene, and 1,3-butadiene. Increased SHFR and feed flow rate reduces the Ethylene yield. The optimized condition has been reported. The optimum was found at COT of 824°C, SHFR of 0.4919 kg-steam/kg-naphtha, the flow of 14.8 tph, and C_8+ content in a feed of 3.74 wt.%.*

KEYWORDS: *Naphtha; Thermal cracking; Kinetic model; Coil-outlet-temperature; Steam-to-hydrocarbon feed-ratio; Ethylene; Propylene; 1,3-butadiene.*

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INTRODUCTION

Thermal cracking of Ethane or naphtha in the presence of steam is used in most manufacturing process plants for the production of ethylene, propylene, and 1,3-butadiene. Thermal cracking of hydrocarbons is a major industrial process for the production of olefins like Ethylene and Propylene. These olefins are building blocks of the Petrochemical industries and hence the demand is tremendous for the same. The energy consumption is also high hence improvement of the thermal cracking process is very important to minimize the cost of production. Ethylene is used for the production of a variety of products like polyethylene used for food packaging and housewares, polyvinyl chloride used for piping and construction, polystyrene used for hard packing, insulation, appliances, etc. Global consumption of propylene for chemical applications is also increasing in comparison to Ethylene. Propylene is the monomer for the production of polypropylene used for films and packaging. Acrylonitrile is used for synthetic rubber and propylene oxide is used as an anti-freeze agent. Global consumption of propylene for chemical applications is also increasing in comparison to Ethylene. Most of the propylene used in the petrochemical industry is produced by naphtha cracking. It is required to optimize the process conditions with changes in product demand. Even if there is a small improvement in the naphtha steam cracking process, it would considerably increase the economic gain of the petrochemical industries.

The parameters that can affect the cracking process product yield are Coil Outlet Temperature (COT), Steam to Hydrocarbon Feed Ratio (SHFR), Feed flow rate [1], and coil Hydrocarbon partial pressure residence time [2]. Feed composition/Naphtha composition also plays a major role in controlling the main product yields. The feed/naphtha characterization is done in terms of the functional groups present in it, such as olefins, paraffins, naphthenes, and aromatics. The dominance of any of these functional groups affects the desired product quality on cracking. The naphtha feed contains mainly n-paraffins and i-prarffins. It contains naphthenes, aromatics, and a small quantity of olefins also. The quantity of ethylene, propylene, and 1,3-butadiene produced depends on naphtha feed quality. More ethylene yield for feed having higher n-paraffins and more propylene yield for feed having higher iso-paraffins. Feed rich in naphthenes when cracked gives more 1,3-butadiene yield. It is also possible to further segregate functional groups in terms of carbon number for more precise characterization *Parmar et al.* [3]. The feed composition of naphtha which goes for cracking is very dynamic as it is obtained/imported from several countries based on economics and procurement strategy. The role of modeling in the production of these fuels can fulfill one important aspect of achieving general engineering goals such as the prediction of product yields, linear programming, advanced process control, real-time optimization, offline process optimization, and so on.

Conventional experimentation for identifying important factors is carried out by varying one factor at a time while maintaining other factors constant. The statistical Design of Experiments (DoE) method is very useful to understand the interrelationship of factors and the response of the process. For biodiesel production, a study [4,5] indicated an increased yield of biodiesel using Response Surface Methodology (RSM). To determine the interaction between several parameters, the design of the experiments method can be used with favorable precision in the lower number of experiments. These empirical techniques have high computational speeds and can test many factors simultaneously to determine which factors and their interactions have a higher influence on the process performance. This can lead to the optimization of product yield, lower design and development period, lower operational costs, and reliable prediction of process responses. RSM is useful for the estimation of the interaction and quadratic effects of process variables on process performance and can provide an idea of the response curve. RSM can be used to optimize the process factors and provide conditions to get the best value of the process response. It can be used to troubleshoot process problems by decreasing process sensitivity to external uncontrollable influences. In the current study Box-Behnken design [6] was employed for the experimental design considering three and four factors. The models developed by this method are useful to predict response more accurately which is difficult with linear models.

Box-Behnken experimental design was used by Sedighi [7] for the optimization of naphtha cracking process parameters to maximize ethylene and propylene yield. The superiority of the DoE method over the conventional where at a time only one factor is changed is shown by 13 runs to optimize three factors including temperature, residence time, and dilution steam ratio. Full

Factorial Design with 27 experiments for the three factors temperature, residence time, and dilution steam ratio was used to maximize ethylene and propylene yields from steam cracking of naphtha [8]. Similarly, Central Composite Design (CCD) was used to optimize steam cracking of LPG in the presence of DMDS and H2S by 27 experiments over three factors including temperature, residence time, and sulfur content by Rahimi [9]. CCD was applied to optimize the heavy naphtha cracking process by 27 runs. A similar study was carried out for the cracking of atmospheric gas oil with three variables [10,11]. A composition-based model was developed by *Tian et al.* [12] using the Monte Carlo method for the prediction of ethylene, propylene, and 1,3-butadiene yield from steam cracking of naphtha. In a petrochemical plant, the production of polymer products varies as multiple-grade polymers are being produced. Also, production sequencing is important to minimize transitional off-spec production. Hence, the raw material availability from different suppliers is important to optimize the overall profitability. The mixed-integer linear programming model developed for large commercial plants was used for a multi-grade polypropylene plant by *Alfares* [13]. The importance and methodology of utilizing Response Surface Methodology (RSM) are well explained by *Bezerra* [14]. It can be used to optimize the process factors by providing the best-desired value of the process response. The optimal conditions for process parameters can be obtained by solving the regression equation and by analyzing the response surface contour plots [15]. For optimal production of shale gas, the uncertain factors are optimized by *Yu* [16] based on the design of experiment analysis and surface response methodology. A similar application of the Surface response model is for a reaction from rapeseed oil by *Zhang* and *Huang* [17]. The effects of five- to three factors (reaction temperature, methanol/oil molar ratio, and catalyst amount) were analyzed for interrelated interactions. The optimum conditions of these parameters can result in the highest conversion of about 99.3 %. It can also be used to troubleshoot process problems by decreasing process sensitivity to external uncontrollable influences. *Singh et al.* [18] have optimized the wear and friction characteristics of lubricants using response surface methodology.

The DoE approach used so far was limited to specific feed and hence the impact of feed quality on yields cannot be analyzed. Extensive analysis of commercial cracker feed composition and yield data indicated that feed C_8+ content varies significantly and it is necessary to capture the effect of feed C_8+ on product yields. In the present investigation, three sets of models were developed for three different quality naphtha. The fourth model was developed taking C_8+ as a factor so as to account for feed composition. The response values for some of the design runs were generated from an in-house developed kinetic model [19]. Models were developed to predict ethylene, propylene, and 1,3-butadiene yield. Models were coupled with an optimizer for individual products as well as multi-objective optimization.

Naphta thermal cracking industrial process description

Major process steps in the Naphtha Cracker Plant also called the Olefin unit where cracking of hydrocarbons (to produce olefins), compressing the effluent gas, and separating the cracked gas by low-temperature fractionation as shown in Fig. 1A. Naphtha is preheated-to 116 ^{o}C before entering into the top convection section of short residence time heater. The outlet of the top convection section goes to the mixed preheat section of the convection zone wherein steam is added at a specified ratio to reduce the partial pressure of naphtha before it starts fully vaporizing. The addition of steam reduces the coking tendency in the furnace coils. The mixed preheat outlet enters the radiant zone where the temperature is instantly raised to the required cracking temperature to facilitate thermal cracking. Furnaces being the first step in the production process, disturbances in the furnace operation affect the entire production process. The length and material used for the tubular reactor depend on the feed quality. Also, the operating parameters like coil outlet temperature, and steam to hydrocarbon ratio also depend on product yield and feed quality. The configuration of the coil in the radiant section varies depending on technology.

The cracked gases are instantaneously cooled to avoid undesired product and coke formation as well as to produce super high-pressure steam in the Transfer Line Exchangers (TLE). After TLE, the gases are cooled in the quenching section, followed by compression and low-temperature fractionalization. The yields of ethylene and propylene depend on the cracker feed composition and process severity. The cracking reactions are endothermic and require sufficient heat at high temperatures and low pressure. Hence for optimal operation, it is necessary

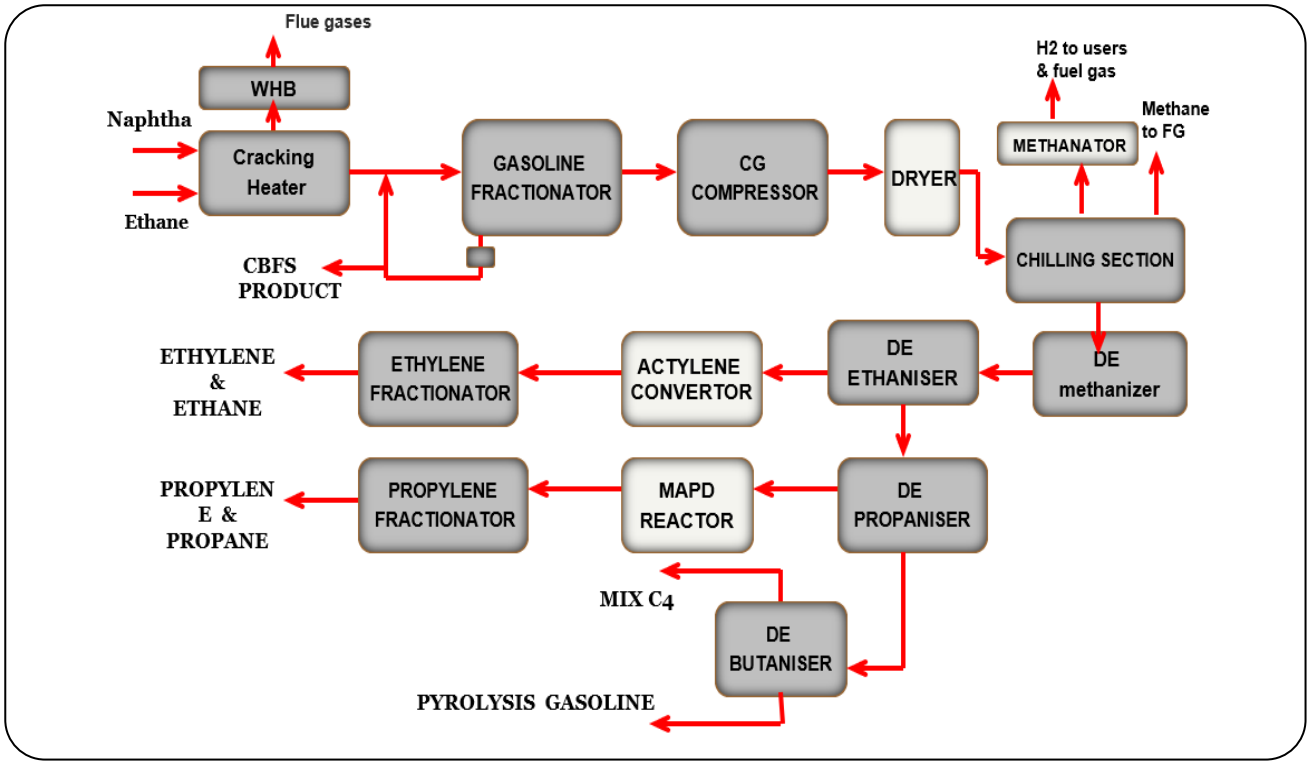

Fig. 1A: Process flow diagram of the main naphtha cracker plant (Olefin unit).

to understand the effect of various operating parameters using the rigorous model.

Kinetic model

A kinetic model has been developed based on material, energy, and momentum balance equations. The details of the model developments have been reported by *Parmar et al.*, [19, 20], hence only a few outlines are presented here. The model requires the primary reaction coefficients of all feed components considered in the model. The required primary reaction and secondary reaction coefficients of all feed components were established and tuned in the model to match the actual data. The eleven coefficients of each primary reaction of 20 naphtha feed components considered are determined from the corresponding primary reaction product distribution data obtained based on the mechanism. The principle of elemental balance of carbon and hydrogen needs to be followed during the estimation of the reaction coefficients for the primary reaction equation. This Model can predict the profile of temperature, concentration heat flux, etc. for the defined reactor system based on different operating conditions. The yields of ethylene and propylene products used in this research have been obtained from plant data as well as simulation experiments using the kinetic model at the design conditions. The product yields- ethylene and propylene used in this research have been simulated at various process conditions using this kinetic model.

EXPERIMENTAL SECTION

Materials and experimental run

Three different qualities of naphtha having varying quantities of C_8+ are used in the pilot plant as well as in the main running plant. A schematic diagram of the experimental setup for pilot plant naphtha cracking is shown in Fig. 1B [21]. The thermal cracking of all three cuts and heavy naphtha is carried out in the experimental cracker unit. Naphtha and water are stored in two SS (stainless steel) tanks. The naphtha is brought from the industrial plant and it is filtered. On the other hand, the water used is distilled water. The tanks are provided with two-level gauges with the help of which the flow rates of the feedstock can be checked at regular intervals of time. The tanks are placed on two separate electronic weighing balances.

Two metering pumps are also provided for pumping the feed to the next stage. Here, cold water is circulated through the pumps to control temperature. The naphtha

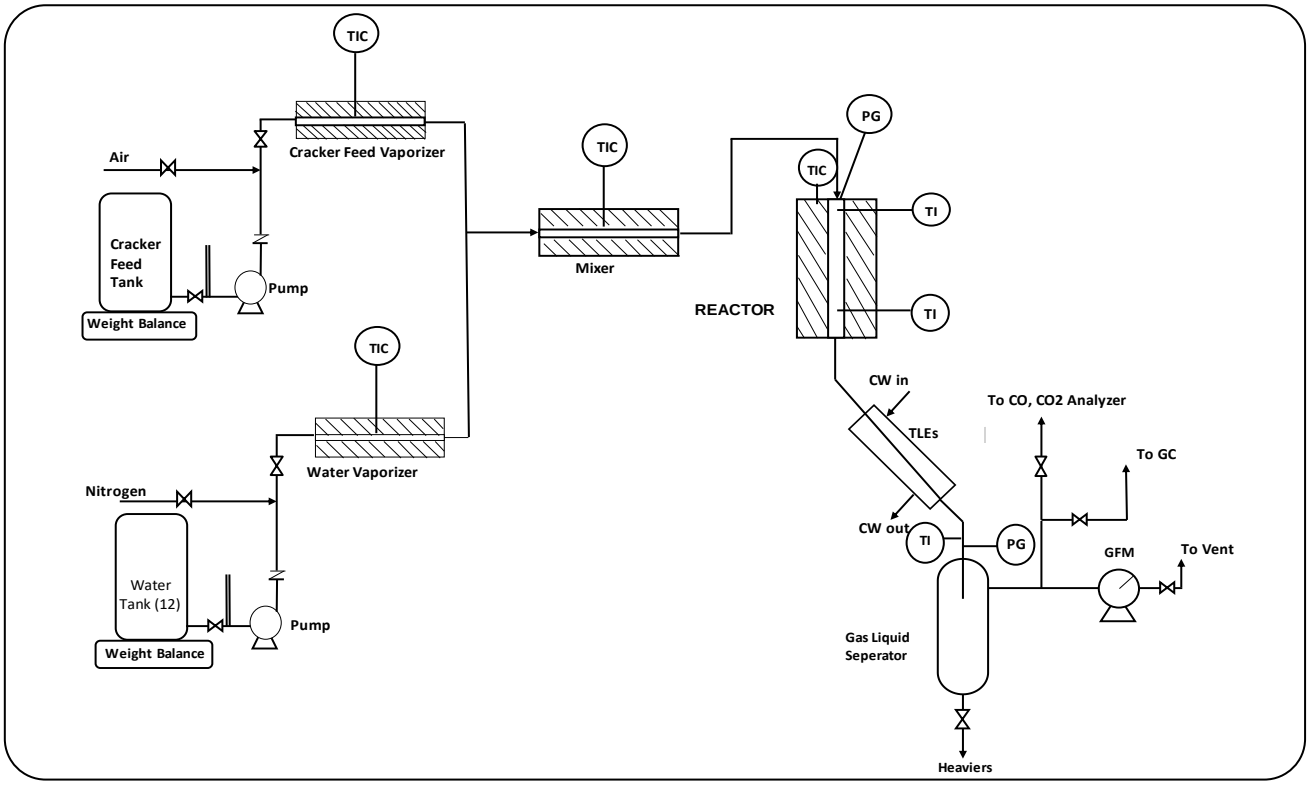

Fig. 1B: Experimental setup of pilot plant naphtha cracker unit: cracker feed tank, cracker feed vaporizer, water tank, water vaporizer, mixer, reactor, cooler, gas-liquid separator.

and water are passed through their respective vaporizers and are mixed in the mixer (also known as the convection section) before entering the furnace (radiation section). The process gas temperature is measured using a thermocouple. The pressure gauges located at two different points- one at the mixer inlet and the other at the top outlet of the gas-liquid separator keep track of the pressure drop within the system. It is heated electronically by means of radiant coils placed inside it.

Cracking runs have been carried out in a bench-scale cracker unit at coil outlet temperature of 810°C, steam dilution ratio of 0.5, and 0.4 sec residence time. Each run is carried out for 6 h. Initially, two runs have been carried out with heavy naphtha having a sulfur content of 8 ppmw. At the start of the run, the concentration of CO and CO_2 were higher and then reduced with time on the stream. Two runs have been carried out with naphtha having 150 ppm sulfur. Another two runs have been carried out at reduced temperatures of XOT and COT at 431 and 800°C, respectively. At identical conditions, it is found that good reproducibility of product yield is achieved. The second base run has been carried out at very low severity to compare ethylene and propylene yields from the cracking of two distillate cuts. The run has been carried out at XOT of 390°C and COT of 800°C.

In the running plant, for all three qualities of Naphtha, it is not advisable to operate the furnace in extreme conditions like high COT operation for feed having lower C_8+ content, Low throughput for a longer duration have a business impact. Similarly, maintain a very low SHFR ratio for a longer duration considering the reliability aspect. Such runs are carried out initially in the pilot plant. The results are validated using an in-house kinetic model. The experimental runs at various operating conditions for a specific time period based on pilot runs were taken. The product yields are estimated based on plant output data and used for further study.

DOE using RSM

Response surface design methodology enabled to refine models after determining important factors based on screening or factorial design. The quadratic in the response surface equation allows model curvature in the response, making them useful for:

- Plotting or understanding a region of the response surface
- Obtaining the levels of process variables that optimize the process response
- Choosing process conditions to meet product specifications

Box-Behnken design for four factors has been used for the experimental design. The DOE is carried out in the Minitab software version 16. The considered parameters that affect the cracking process are the COT, the feed flow rate (residence time), SHFR, and the feed composition. Four independent variables: SHFR (X1), COT (X2), feed flow rate (X3) and C_8+ content in feed (X4) are considered. The C_8+ content in the feed is used to classify the feed as lighter, medium, and heavier naphtha feedstocks. The ranges taken for each factor are within the usual plant operating range.

The procedure for modeling consists of estimating the coefficients of the response yields by fitting the kinetic model-generated data to the response functions, predicting the product responses using these coefficients, the goodness of fit of the designed model, and the comparison of the designed model yields to actual plant yields. Replicate experiments at the central point were performed to evaluate the error, maintain reproducibility, and minimize the effects of uncontrollable factors. A quadratic polynomial equation in the form of Eq. (1) is developed to determine the relationship between the independent variables and the responses including the interactions between all the variables.

$$Y = \beta_0 + \sum_{j=1}^{4} \beta_j X_j + \sum_{j=1}^{4} \beta_{jj} X_j^2 + \sum_{i<j} \beta_{ij} X_i X_j \qquad (1)$$

In Eq. (1), Y is the response (yield of main products) or dependent variable; X_i & X_j are the independent variables; β_0 is the intercept term; β_j are the linear terms; β_{ij} are the interaction terms among the five variables. The compositions of the three different naphtha feedstocks used for three designs are presented in Table 1. The composition analysis has been carried out in terms of wt.% of Paraffins, Iso paraffin, olefins, Napthenes, and Aromatics (PIONA Analysis). The detailed carbon number-wise PIONA analysis of the same feedstocks has been carried out in the laboratory based on ASTM D6730-01 method. The levels of the factors considered in the experimental design are given in Table 2. The design matrix and responses

Table 1: Feed composition of naphtha.

Feed (TPH)	Feed 1	Feed 2	Feed 3
n-Paraffin	37.33	35.39	33.03
i-Paraffin	34.06	32.03	33.40
Naphthenes	19.59	20.61	21.15
Aromatics	6.25	6.89	4.62
Olefins	2.61	4.62	4.43
C_8+	3.74	6.81	9.88

Table 2: Levels of factors used in the design.

Variables	-1	0	1
COT (X1)	810	817	824
Flow (X2)	14.8	16.0	17.2
Ratio (X3)	0.38	0.44	0.50
C_8+ (X4)	3.74	6.81	9.88

(ethylene, propylene, and,13-butadiene yields in wt.%) of all 15 design experiments for each feed are given in Tables 3, 4, 5, respectively.

The design for four factors including feed C_8+ as a factor using 27 runs is given in Table 6 with the respective product yields.

RESULTS AND DISCUSSION

Analysis of Experimental Designs

The model coefficients for yield of products ethylene and propylene were estimated using multiple regression techniques. These coefficients can be placed in Eq. (1) to obtain equations for each product yield respectively. The coefficients of the full quadratic model for the individual feeds are given in Table 7.

The analysis of variance, ANOVA, and P values for the final ethylene and propylene yield equations are given in Table-8.

P value for full quadratic model for ethylene prediction for some of the factors is higher than 0.05 which suggests the need for a simpler model. In the final model P-value for all factors is lower than 0.05. The square term is significant indicating a curvature in the response. P-values of full quadratic model for propylene indicate that some of the linear, square and interaction terms are significant. The models are modified such that only the statistically significant terms are considered. The final model coefficients for each individual feed are given in Table 9 and the p-values of ANOVA for each feed are given in Table 10.

Table 3: Design matrix and responses for feed condition 1.

COT (°C)	Flow rate (TPH)	STHR	Ethylene	Propylene	Butadiene
817	14.8	0.5	26.56	15.59	3.32
810	14.8	0.44	25.26	16.18	3.20
824	16.0	0.38	28.55	13.34	3.18
817	14.8	0.38	27.44	14.32	3.15
817	16.0	0.44	26.22	15.57	3.27
824	14.8	0.44	28.67	13.58	3.26
810	16.0	0.38	24.93	16.12	3.15
810	16.0	0.50	23.92	17.10	3.25
817	17.2	0.50	24.98	16.58	3.34
817	16.0	0.44	26.27	15.63	3.33
817	17.2	0.38	25.94	15.49	3.21
824	16.0	0.50	27.50	14.89	3.39
817	16.0	0.44	26.17	15.52	3.22
824	17.2	0.44	27.19	14.86	3.33
810	17.2	0.44	23.67	17.02	3.21

Table 4: Design matrix and responses for feed condition 2.

COT (°C)	Flow (TPH)	Ratio	Ethylene	Propylene	Butadiene
810	16	0.38	24.13	15.57	3.14
824	16	0.50	26.61	14.39	3.38
810	17.2	0.44	22.89	16.46	3.22
817	14.8	0.50	25.70	15.07	3.32
817	16.0	0.44	25.37	15.05	3.26
817	14.8	0.38	26.57	13.83	3.13
817	16.0	0.44	25.42	15.10	3.31
817	17.2	0.50	24.15	16.03	3.35
817	17.2	0.38	25.11	14.95	3.20
817	16.0	0.44	25.32	15.00	3.21
824	16.0	0.38	27.42	13.09	3.17
810	14.8	0.44	24.43	15.64	3.20
810	16.0	0.50	23.13	16.53	3.26
824	14.8	0.44	27.75	13.12	3.24
824	17.2	0.44	26.32	14.36	3.32

Table 5: Design matrix and responses for feed 3.

COT (°C)	Flow (TPH)	Ratio	Ethylene	Propylene	Butadiene
817	14.8	0.38	26.15	13.83	3.16
824	17.2	0.44	25.88	14.37	3.35
810	14.8	0.44	23.98	15.64	3.23
824	14.8	0.44	27.34	13.13	3.27
824	16.0	0.38	27.01	13.10	3.20
810	16.0	0.50	22.66	16.52	3.30
817	17.2	0.38	24.67	14.95	3.23
817	16.0	0.44	24.92	15.05	3.30
817	14.8	0.50	25.25	15.07	3.35
810	16.0	0.38	23.69	15.56	3.17
817	16.0	0.44	24.97	15.55	3.35
817	16.0	0.44	24.87	14.95	3.25
810	17.2	0.44	22.42	16.44	3.25
824	16.0	0.50	26.16	14.40	3.41
817	17.2	0.50	23.69	16.03	3.38

Table 6: Design matrix and responses for design with feed C8+ as a factor.

Sr.No.	Ratio	COT (°C)	Flow (TPH)	C_8+	Ethylene	Propylene	Butadiene
1	0.42	817	17.2	6.81	24.80	15.35	3.26
2	0.46	824	17.2	6.81	26.32	14.36	3.32
3	0.46	817	16.0	6.81	25.31	15.16	3.28
4	0.46	824	16.0	9.88	26.89	13.98	3.32
5	0.42	817	16.0	3.74	26.37	15.37	3.24
6	0.46	817	17.2	9.88	24.02	15.71	3.34
7	0.46	817	16.0	6.81	25.20	15.00	3.30
8	0.46	817	14.8	3.74	26.61	15.37	3.27
9	0.46	817	17.2	3.74	25.30	16.25	3.31
10	0.46	810	16.0	3.74	24.27	16.80	3.23
11	0.50	817	16.0	9.88	24.44	15.59	3.37
12	0.42	817	14.8	6.81	26.29	14.27	3.20
13	0.46	824	14.8	6.81	27.63	13.34	3.28
14	0.42	824	16.0	6.81	27.16	13.55	3.25
15	0.46	824	16.0	3.74	27.78	14.47	3.33
16	0.50	817	17.2	6.81	24.15	16.03	3.35
17	0.42	810	16.0	6.81	23.80	15.93	3.19
18	0.46	817	14.8	9.88	25.55	14.69	3.30
19	0.5.0	817	16.0	3.74	25.75	16.12	3.34
20	0.5.0	824	16.0	6.81	26.89	13.98	3.32
21	0.46	810	17.2	6.81	23.02	16.32	3.20
22	0.46	810	14.8	6.81	24.58	15.46	3.18
23	0.46	817	16.0	6.81	25.32	15.17	3.29
24	0.5.0	810	16.0	6.81	23.13	16.53	3.26
25	0.5.0	817	14.8	6.81	25.70	15.07	3.32
26	0.42	817	16.0	9.88	25.08	14.85	3.27
27	0.46	810	16.0	9.88	23.01	16.23	3.26

Table 7: Full quadratic model coefficients for product yields for Feed 1, Feed 2, Feed 3.

	Feed 1		Feed 2		Feed 3	
	Ethylene	Propylene	Ethylene	Propylene	Ethylene	Propylene
Term	Coef	Coef	Coef	Coef	Coef	Coef
Constant	-318.054	-1570.37	-660.124	-1190.59	-590.333	-2150.21
COT	0.657002	4.36373	1.57502	3.3503	1.39763	5.66463
Flow	-2.80597	-9.75216	-3.59326	-8.75014	-3.39854	-7.48055
Ratio	10.026	-242.027	-95.8683	-141.141	-96.2806	-125.319
COT× COT	-2.72E-04	-0.003	-8.79E-04	-0.00233	-7.66E-04	-0.00375
Flow× Flow	-0.00627	-0.0095	0.01493	-0.02772	0.016153	-0.07394
Ratio× Ratio	5.24205	-18.3125	-1.34315	-11.3303	-1.45974	-29.2978
COT × Flow	0.003051	0.013171	0.003215	0.012632	0.002904	0.012894
COT × Ratio	-0.02226	0.339965	0.115508	0.207832	0.115235	0.208171
Flow × Ratio	-0.28536	-0.58881	-0.30798	-0.57145	-0.27729	-0.58918
R-Sq	99.94	99.91	99.98	99.96	99.98	98.67
R-Sq (adj)	99.82	98.97	99.95	99.9	99.95	96.29
S	0.063	0.057	0.032	0.033	0.031	0.203

Table 8: P values for full quadratic models from ANOVA for Feed 1, Feed 2, Feed 3.

	Feed 1		Feed 2		Feed 3	
	Ethylene	Propylene	Ethylene	Propylene	Ethylene	Propylene
Source	P	P	P	P	P	P
Regression	0	0	0	0	0	0
Linear	0	0	0	0	0	0
COT	0	0	0	0	0	0
Flow	0	0	0	0	0	0.001
Ratio	0	0	0	0	0	0.001
Square	0.888	0.018	0.137	0.005	0.169	0.329
COT × COT	0.702	0.004	0.05	0.001	0.074	0.144
Flow × Flow	0.794	0.666	0.256	0.071	0.221	0.362
Ratio × Ratio	0.591	0.078	0.784	0.066	0.765	0.366
Interaction	0.766	0.007	0.067	0.002	0.073	0.601
COT × Flow	0.454	0.012	0.154	0.001	0.187	0.336
COT × Ratio	0.779	0.004	0.03	0.003	0.029	0.43
Flow × Ratio	0.544	0.199	0.227	0.058	0.267	0.694
Lack-of-Fit	0.352	0.499	0.994	0.964	0.998	1

Table 9: Coefficients for ethylene and propylene yield final models for all three feeds.

	Feed 1		Feed 2		Feed 3	
	Ethylene	Propylene	Ethylene	Propylene	Ethylene	Propylene
Term	Coef	Coef	Coef	Coef	-160.479	137.362
Constant	-166.043	-1482.84	-719.751	-1098.79	0.2435	-0.16334
COT	0.25222	4.17413	1.66616	3.15806	-0.63088	0.428364
Flow	-0.63958	-10.3152	-0.6242	-9.8887	-7.85485	9.54773
Ratio	-8.1121	-267.563	-101.978	-160.254	-	-
COT × COT		-0.00288	-9.03E-04	-0.00221	-	-
Flow × Flow	-	-	-	-	-	-
Ratio × Ratio	-	-	-	-	-	-
COT × Flow	-	0.013171	-	0.012632	-	-
COT × Ratio	-	0.339965	0.115508	0.207832	-	-
Flow × Ratio	-	-	-	-	-	-
R-Sq	99.91	99.77	99.96	99.85	99.91	96.97
R-Sq (adj)	99.89	99.6	99.94	99.74	99.89	96.14
S	0.049	0.07	0.036	0.054	0.0488	0.207

Table 10: P values from ANOVA for the process yield final model for all three feeds.

	Feed 1		Feed 2		Feed 3	
	Ethylene	Propylene	Ethylene	Propylene	Ethylene	Propylene
Source	P	P	P	P	P	P
Regression	0	0	0	0	0	0
Linear	0	0	0	0	0	0
COT	0	0	0	0	0	0
Flow	0	0	0	0	0	0
Ratio	0	0	0	0	0	0
Square	-	0.005	0.043	0.005	-	-
COT×COT	-	0.005	0.043	0.005	-	-
Flow × Flow	-	-	-	-	-	-
Ratio × Ratio	-	-	-	-	-	-
Interaction	-	0.003	0.026	0.003	-	-
COT × Flow	-	0.014	-	0.004	-	-
COT × Ratio	-	0.004	0.026	0.012	-	-
Flow × Ratio	-	-	-	-	-	-
Lack-of-Fit	0.602	0.39	0.852	0.511	0.615	0.924

Table 11: Full quadratic model coefficients for all product yields for design 4.

	Ethylene	Propylene	1,3-Butadiene
Term	Coef	Coef	Coef
Constant	968.87	-2157.42	-420.313
Ratio	-271.446	118.24	6.25375
COT	-2.23455	5.47451	1.02832
Flow	-6.2541	-3.04995	-0.27437
C_8+	-3.70588	-1.55905	0.439766
Ratio × Ratio	-30.3204	25.5688	-1.34786
COT × COT	0.001329	-0.00346	-6.30E-04
Flow × Flow	0.002089	-0.00741	-0.006840
C_8+ × C_8+	0.014860	0.04163	0.002379
Ratio × COT	0.363504	-0.15183	-0.00192
Ratio × Flow	-0.28742	-0.57222	-0.15460
Ratio × C_8+	-0.03159	-0.03171	0.022193
COT × Flow	0.007118	0.004763	0.000708
COT × C_8+	0.004370	0.000942	-5.93E-04
Flow × C_8+	-0.01531	0.009151	0.000349
R-sq	99.51	99.13	95.6
S	0.140	0.126	0.015

The coefficients of the full quadratic model for the design having four factors (design 4) are given in Table 11 and the ANOVA is given in Table 12.

The statistically significant terms are only considered for the final model for all the ethylene, propylene, and 1,3-butadiene product yields. The coefficients for the final model are given in Table-13 and the p values from ANOVA are given in Table-14. As can be observed as the C_8+ content increases in the feed, the statistically significant terms decrease in the propylene yield response.

The p-values of 0.192, 0.52, 0.427, 0.92, 0.092 0.417 for ethylene, propylene, 1,3-butadiene, hydrogen, methane, C_5+ respectively not less than 0.05. It indicates that there is no evidence that the models do not adequately explain the variation in the responses. Hence the models are considered adequate.

The model equations for ethylene, propylene, and 1,3-butadiene are given as:

$$\text{Ethylene} = -162.652 - 7.17204X1 + 0.24811X2 - 0.60827X3 - 0.38923X4 + 0.014443X4^2 \quad (2)$$

$$\text{Propylene} = -2271.04 + 8.34368X1 + 5.73935X2 + 0.403111X3 - 0.64686X4 - 0.00361X2^2 + 0.040828X4^2 \quad (3)$$

$$\text{1,3-Butadiene} = -399.577 + 1.14583X1 + 0.978571X2 + 0.015972X3 - 0.03353X4 - 0.0006X2^2 + 0.0027409X4^2 \quad (4)$$

Eqs (2), (3), and (4) are the final model equations in which statistically insignificant terms have not been considered.

Model validation

The correlations for the major products ethylene and propylene of the naphtha cracker plant were compared with actual plant yields for 10 typical cases. The comparison of the model predicted ethylene and propylene yields with that

Table 12: P values for full quadratic models from ANOVA for design 4.

	Ethylene	Propylene	1,3-Butadiene
Source	P	P	P
Regression	0	0	0
Linear	0	0	0
Ratio	0	0	0
COT	0	0	0
Flow	0	0	0
C_{8+}	0	0	0
Square	0.126	0	0.084
Ratio × Ratio	0.44	0.469	0.493
COT × COT	0.305	0.009	0.374
Flow × Flow	0.961	0.848	0.844
C_8+ × C_8+	0.04	0	0.019
Interaction	0.534	0.955	0.746
Ratio × COT	0.172	0.513	0.18
Ratio× Flow	0.847	0.671	0.997
Ratio × C_8+	0.957	0.952	0.971
COT × Flow	0.411	0.538	0.312
COT × C_8+	0.205	0.754	0.901
Flow × C_8+	0.437	0.603	0.614
Lack-of-Fit	0.172	0.386	0.071

Table 13: Coefficients for all product yields final models for design 4.

Ethylene		Propylene		1,3-Butadiene	
Term	Coefficient	Term	Coefficient	Term	Coefficient
Constant	-162.652	Constant	-2271.04	Constant	-381.587
Ratio	-7.17204	Ratio	8.34368	Ratio	1.12305
COT	0.24841	COT	5.73935	COT	0.934633
Flow	-0.60827	Flow	0.403111	Flow	0.016143
C_8+	-0.38923	C_{8+}	-0.64686	C_8+	-0.03291
C_8+ × C_8+	0.014443	COT×COT	-0.00361	COT*COT	-5.68E-04
		C_{8+} ×C_{8+}	0.040828	C_8+*C_8+	0.002697
R-sq	99.19	R-sq	98.97	R-sq	93.23

Table 14: P values from ANOVA for the process yields final model for design 4.

	Ethylene	Propylene	1,3-Butadiene
Source	P	P	P
Regression	0	0	0
Linear	0	0	0
Ratio	0	0	0
COT	0	0	0
Flow	0	0	0
C_8+	0	0	0.013
Square	0.018	0	0
C_8+ × C_8+	0.018	0	0
COT× COT		0	0
Lack-of-Fit	0.192	0.52	0.427

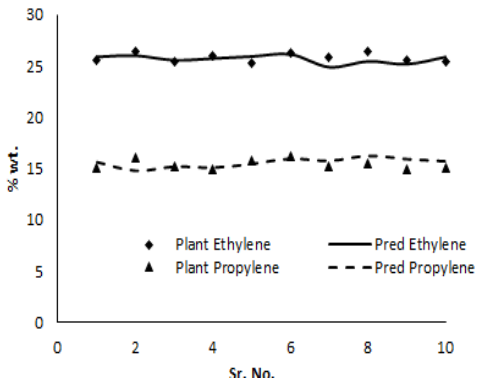

Fig. 2: Comparison of DoE model predicted yields with naphtha cracker plant (1A) yields.

of actual one is shown in Fig. 2. From Fig. 2, it is evident that the predicted yield values are in good agreement with the data obtained from the plant run.

Contour plots

The contour plots for the ethylene, propylene, and 1,3-butadiene yields were constructed by using their individual model equations and are presented in Figs. 3, 5, and 7, respectively. The product yields (wt.%) are plotted against SHFR, COT (°C), feed flow rate (tons per hour), and C_8+ content in the feed (wt.%). The contour plots allow a comparison of the impact of process parameters on product yields. Figs. 3, 5, and 7 provide a two-dimensional view indicating points having the same response are connected to form contour lines at constant responses. Surface plots are necessary as they provide a three-dimensional view which allows a clearer representation of the response surface. Figs. 4, 6, and 8 represent the surface plots for ethylene, propylene, and 1,3-butadiene yields. It is evident from Fig. 4 that the yield of ethylene increases with an increase in COT. The ethylene yield is higher at low values of feed flow rate and C_8+ content in the feed. As can be seen in Fig. 6, lower values of COT and C_8+ content and higher values of steam-to-hydrocarbon ratio and feed flow rate favor higher propylene yield.

Single response optimization

The objective function considered for the naphtha cracker performance optimization includes the maximization of ethylene, propylene, and 1,3-butadiene yields. The process parameters for this optimization are SHFR, COT, feed flow rate and, C_{8+} content in the feed. The starting values of the decision variables used for each product yield response are taken from their respective contour plots. The ranges for these decision variables are given as:

0.42 kg steam/kg hydrocarbon ≤ Steam to hydrocarbon feed Ratio ≤ 0.5 kg steam/kg hydrocarbon

810 °C ≤ COT ≤ 824 °C

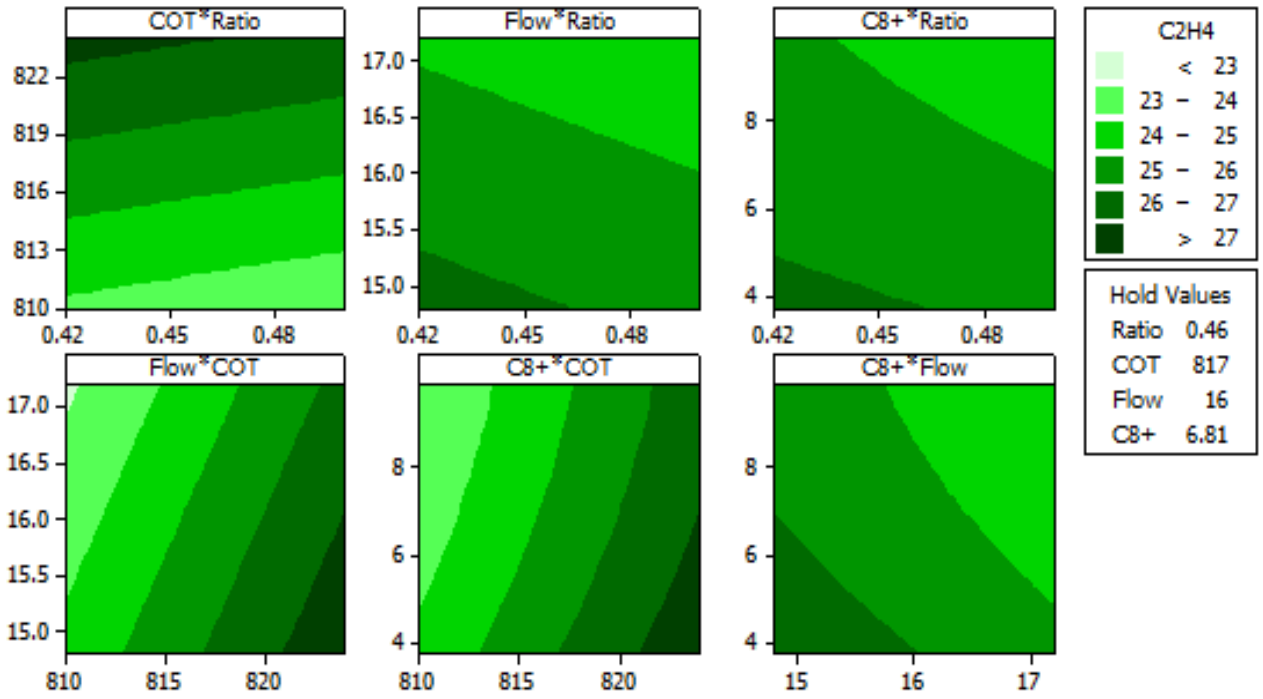

Fig. 3: Contour plot for Ethylene Yield.

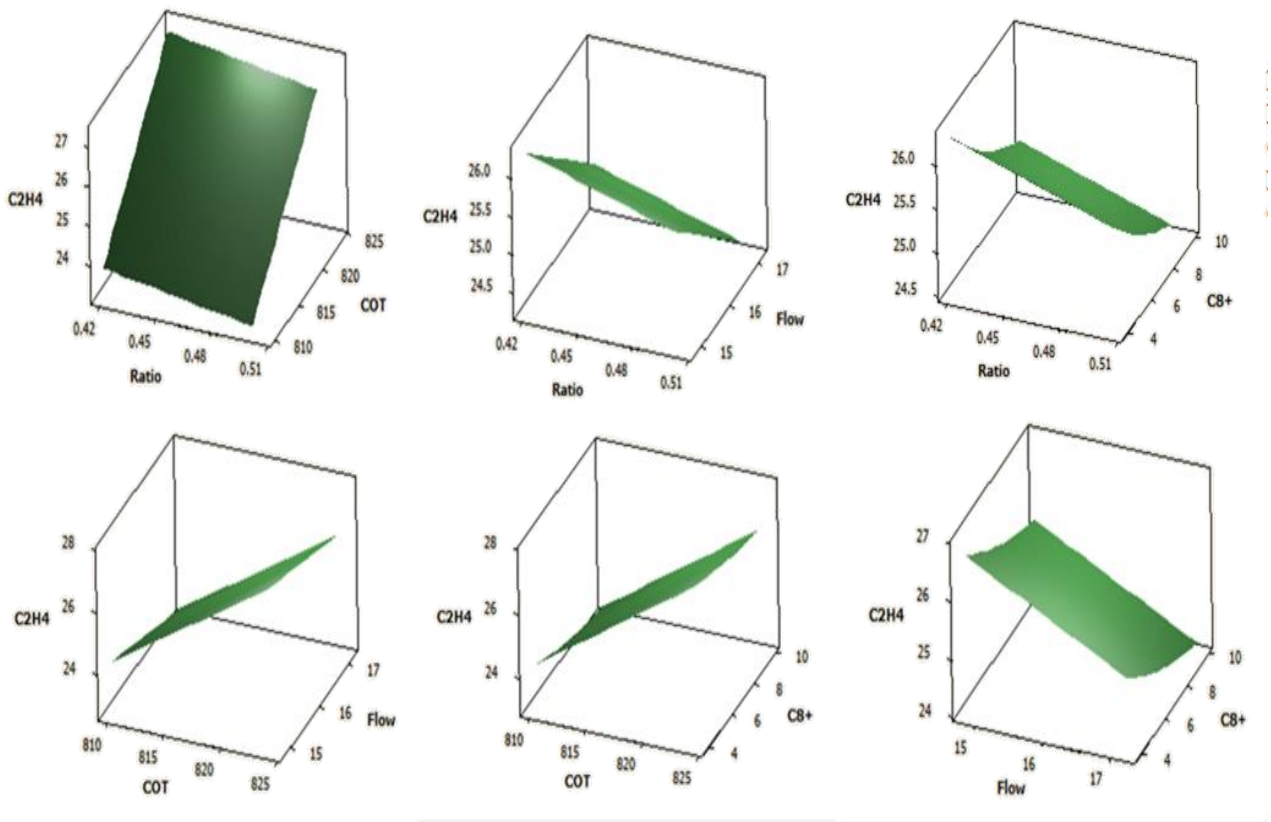

Fig. 4: Surface plot for ethylene yield.

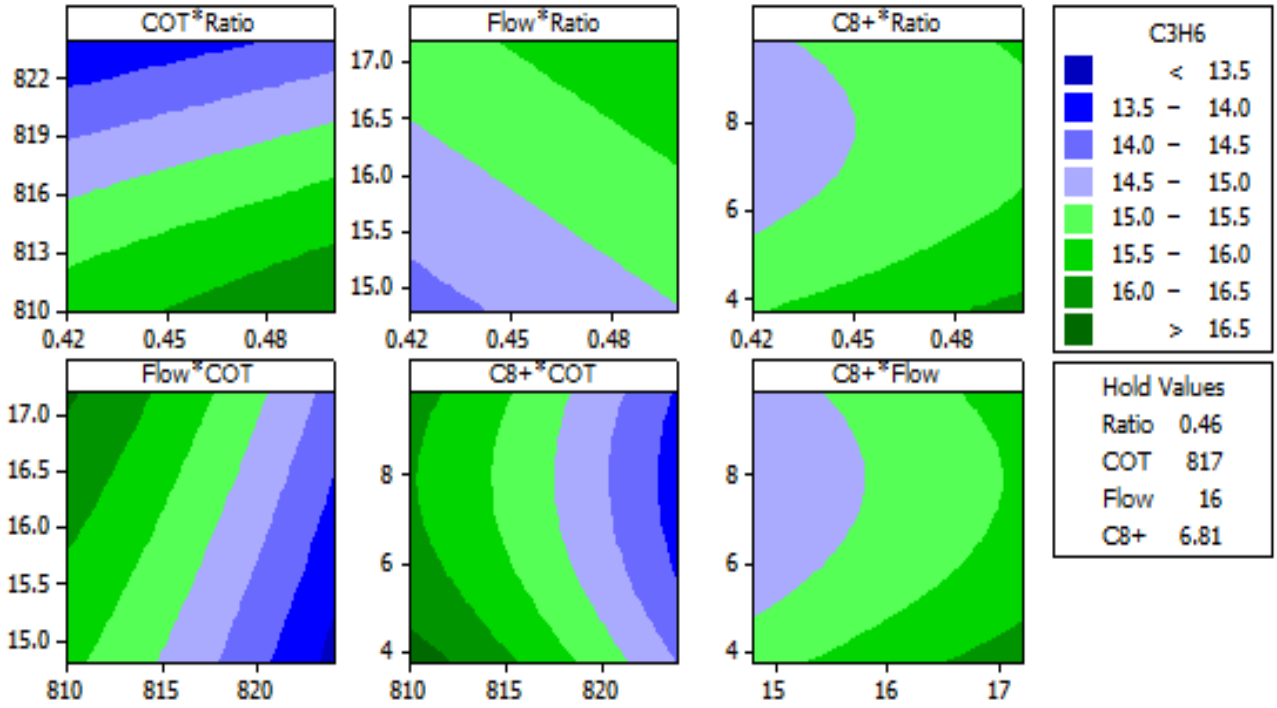

Fig. 5: Contour plot for propylene yield.

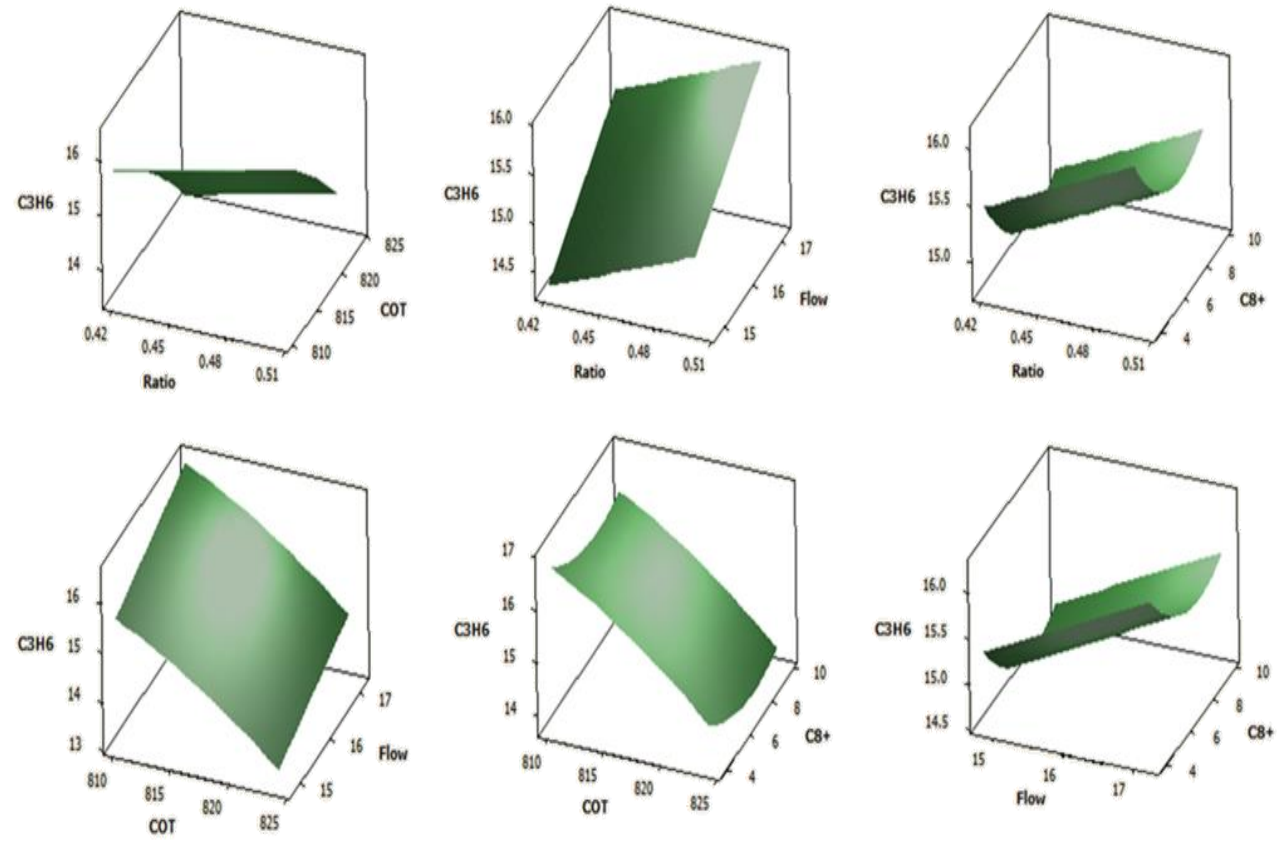

Fig. 6: Surface plot for propylene yield.

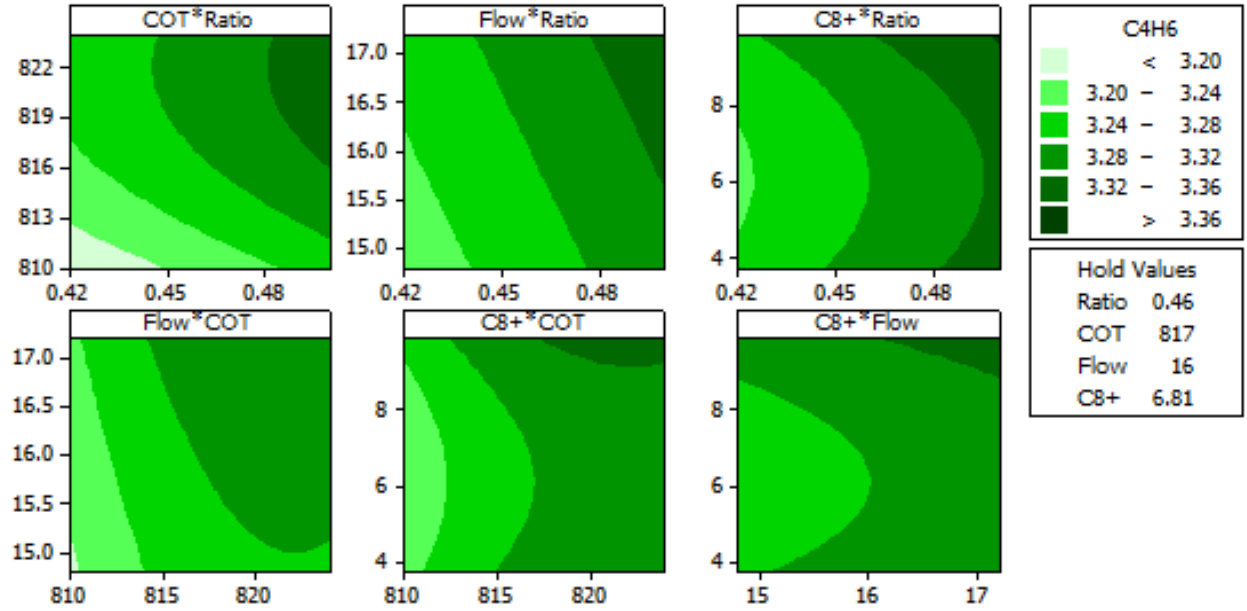

Fig. 7: Contour plot for 1,3-Butadiene yield.

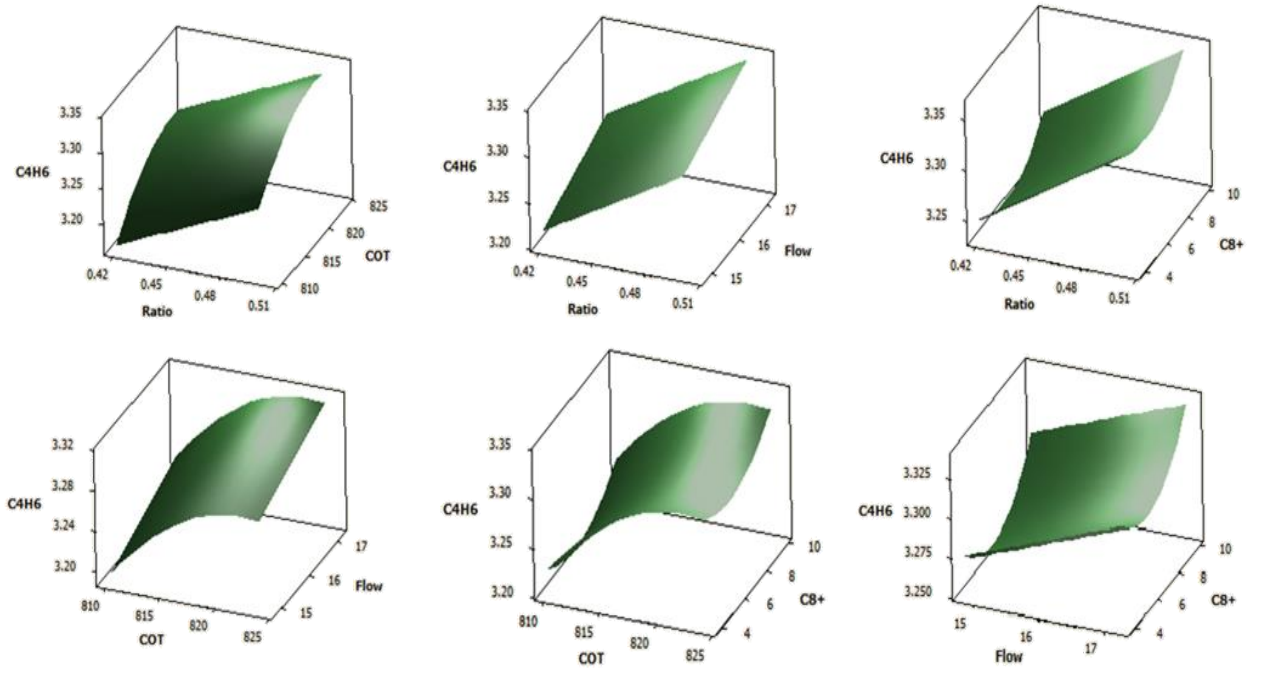

Fig. 8: Surface plot for 1,3-Butadiene yield.

14.8 tons per hour ≤ Naphtha feed flow rate ≤ 17.2 tons per hour

3.74 wt. % ≤ C_8+ content in Naphtha feed ≤ 9.88 wt. %

The yield of ethylene reaches the maximum value of 28.77 wt. % when SHFR, COT, flow rate, and C_8+ content in the feeds is kept at 0.42 kg steam/kg naphtha, 824 °C, 14.8 TPH, and 3.74 wt. % respectively. The yield of propylene is the maximum value of 17.51 wt. % when SHFR, COT, flow rate, and C_8+ content in the feeds is 0.5 kg steam/kg naphtha, 810 °C, 17.2 TPH, and 3.74 wt. % respectively.

Table 15: Optimized process parameters.

Factor	Ethylene	Propylene	1,3-Butadiene
Max. Yield	28.77	17.566	3.398
Ratio	0.42	0.5	0.5
COT	824	810	822.16
Flow	14.8	17.2	17.2
C_{8+}	3.74	3.74	9.88
D_{comp}	0.954	1	0.795

The yield of 1,3-butadiene reaches the maximum value of 3.398 wt. % when SHFR, COT, flow rate, and C_8+ content in the feeds is kept at 0.5 kg steam/kg naphtha, 821 °C,17.2 TPH, and 9.88 wt. % respectively. The optimized yields of all the responses are given in Table 15 with their respective optimized process conditions.

Thus, the maximum yield of ethylene and propylene occurs at considerably different process parameters. The cracking temperature i.e., COT has an opposing effect on the yields of ethylene and propylene; higher temperature favors ethylene production while low temperatures favor propylene production. The feed flow rate is indirectly linked to the residence times, higher residence times favor ethylene yields whereas lower residence times favor propylene yield. Therefore, multiple response optimization has to be carried out to optimize process parameters for optimum yield of both ethylene and propylene yield.

Multiple responses optimization

Optimizing the ethylene and propylene yields simultaneously is the goal of this multiple-response optimization. Steam to hydrocarbon ratio, coil outlet temperature, and flow rate have competitive natures in the yields of ethylene and propylene. Therefore, the best comprise has to be reached between the yields. For multiple-factor optimization, individual desirability functions can be combined into one composite desirability function. This is defined from zero to one of the goals. Numerical optimization techniques are used to find a point that will maximize the composite desirability function. The complete procedure for optimization using the composite desirability function can be obtained from the reference [22]. The composite desirability (D_{comp}) can be defined as the liner combination of individual d values.

$$D_{comp} \equiv (d_1 \times d_2 \times d_3 \times d_4 \times d_5)^{1/5} \quad (4)$$

where d_i are individual desirability functions. If the target 'T' for the response 'y' is a maximum value and 'L' is the lower limit of the response, then the individual desirability function is defined as in Eq. (5).

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

Where *L* denotes the lower limit of the response. When the weight

The desirability function is linear when the weight r =1. r > 1 indicates closer to the target value and r<1 away from the target value.

In this research, Minitab software has been used for analysis. For each predicted response, first, the individual desirability is calculated. After that, all the individual desirability for each response is combined into the composite desirability. The composite desirability combines all the individual desirability values into an overall value which indicates the relative importance of the responses. Minitab places equal importance on the responses which is by default at a value of one. The higher the desirability of a response, its value will be closer to one. The fitted model equations can be combined with the help of Equations (4) and (5) to be used with the composite desirability functions to optimize the process parameters.

The optimum was found at COT of 824 °C, SHFR 0.4919 kg steam/kg naphtha, the feed flow rate of 14.8 tons per hour, and C_8+ content in the feed of 3.74 wt.%. These conditions give the highest D_{comp} at 0.727 and the predicted ethylene yield of 28.25 wt.% and propylene yield of 14.26 wt. % with individual desirability of 0.751 and 0.529 respectively as can be seen in Fig. 9.

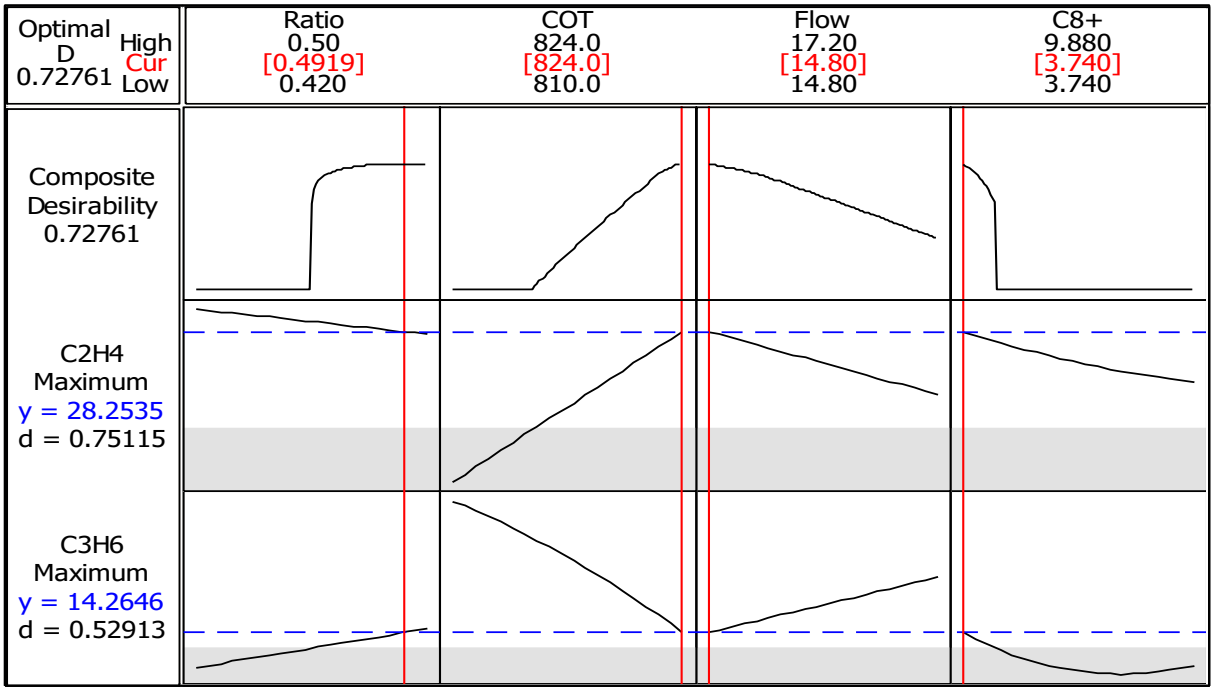

Fig. 9: Optimization plot for ethylene and propylene yields.

The values of ethylene and propylene yields were optimized by using the maximum target for both responses. The factors COT, feed flow rate, and SHFR have opposing effects on the responses i.e., ethylene and propylene yield. To maximize ethylene yield, the COT should be higher while the steam-to-hydrocarbon ratio and feed flow rate should be at lower values. Meanwhile, to maximize propylene yield, the steam-to-hydrocarbon ratio and the feed flow rate should be at the higher limits while COT should be kept at the lower limits.

Another optimization is to maximize the ethylene, propylene, and 1,3-butadiene yields respectively. The optimum was found as observed in Fig. 10, at a COT of 824°C, SHFR of 0.495 kg steam/kg naphtha, the flow rate at 14.8 tons per hour, and C_8+ content in the feed of 3.74 wt. %.

These conditions give the highest D_{comp} at 0.72 and the predicted ethylene yield of 28.23 wt %, and propylene yield of 14.29 wt. % and 1,3-butadiene yield of 3.328 wt. %. The individual composite desirability of ethylene, propylene, and 1,3-butadiene are 0.743, 0.583, and 0.655 respectively.

CONCLUSIONS

The industrial naphtha thermal cracking process was modeled by the use of the statistical design of experiments methodology. Model for product yields of ethylene and propylene for three feeds were obtained using 15 runs considering 3 factors including coil outlet temperature, feed flow rate, and steam to hydrocarbon dilution ratio. The SHFR, COT, and flow rates varied in the range from 0.38−0.5, 810−824 °C, 14.8−17.2 tons per hour (tph), respectively. An alternative approach considering C_8+ as the fourth factor with 27 runs using the Box Behnken DoE has been developed. The product yields corresponding to the experimental design were obtained from an in-house developed kinetic model. The effect of these four factors such as steam to hydrocarbon feed ratio, coil outlet temperature, feed flow rate, and C_8+ content in the feed and their interactions on the naphtha thermal cracking process yields were analyzed and it is found that the obtained models have statistically significant terms. It has been achieved that by increasing the coil-outlet temperature the yield of Ethylene and 1,3-Butadiene increases but it reduces the propylene yield. The Increased C_8+ content (3.74 %, 6.81 %, and 9.88 % by wt.) results in a lower yield of Ethylene, Propylene and 1,3-Butadiene. This shows that light naphtha cracking is beneficial for maximizing the yield of these products. SHFR and the feed flow rate have the opposite effect and it reduces the ethylene yield but increases propylene and 1,3-butadiene yield. The model correlations were validated with Naphtha Cracker plant data. The useful application of such model results is to be used as a soft sensor for day-to-day monitoring in the Industrial plant.

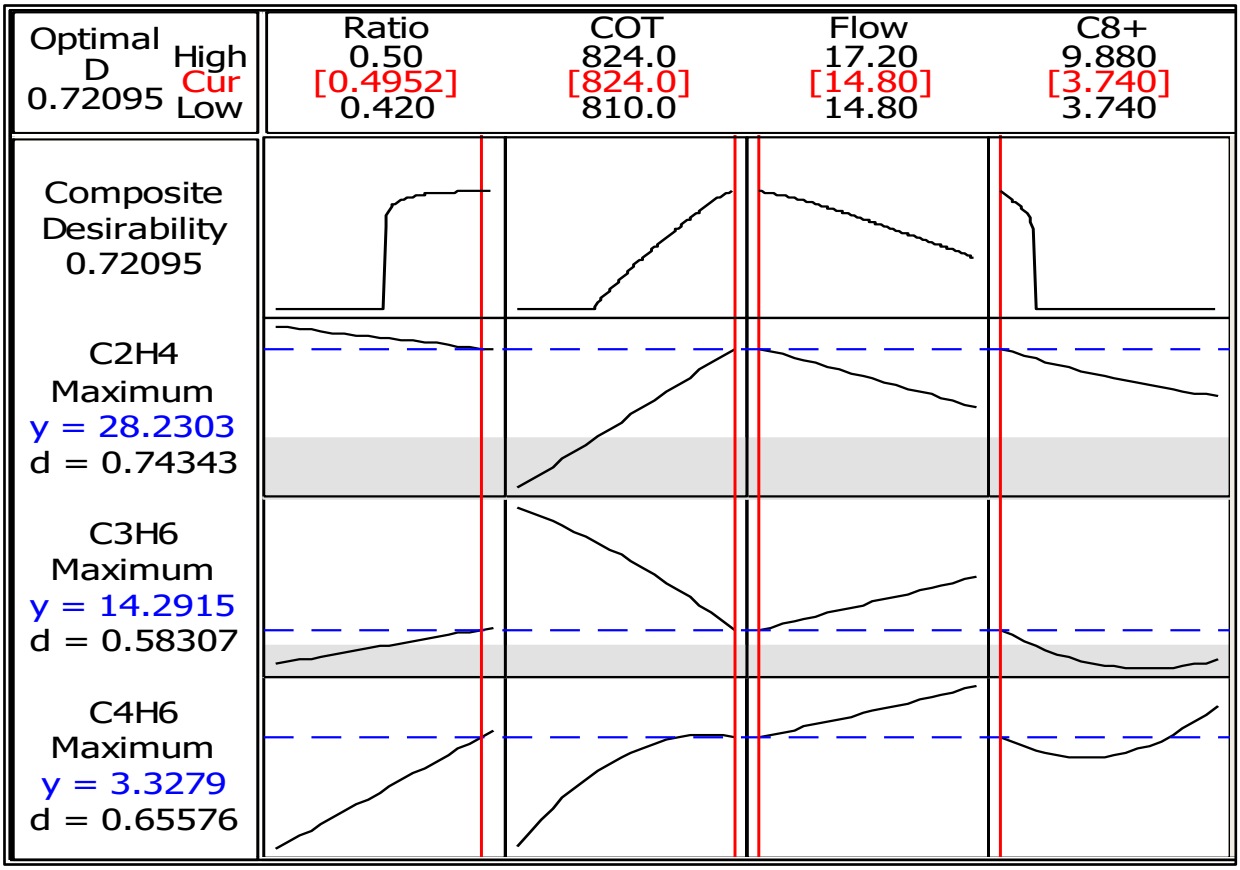

Fig. 10: Optimization plot for ethylene, propylene and 1,3-butadiene yields.

Nomenclatures

COT	Coil outlet Temperature, °C
C_8^+	Hydrocarbon with 8 Carbon and more in the chain
DoE	Design of experiments
GC	Gas Chromatography
FID	Flame Ionization Detector
PIONA	Paraffins, Iso paraffins, Olefins, Napthenes, Aromatics
SHFR	Steam to hydrocarbon feed ration, kg/kg
TCD	Thermal Conductivity Detector
TLE	Transfer Line Equipment
XOT	Cross over Temperature, °C
α	The distance of axial points from center
Y	Response (yield of main products) or dependent variable
X_i&X_j	Independent variables
β_0	Intercept term
β_j	Linear terms
β_{ij}	Interaction terms between the five variables
β_{jj}	Squared terms
ANOVA	Analysis of Variance
D_{comp}	Composite Desirability
di	Individual desirability functions
r	Weight for the parameter
T	Target
wt. %	Weight %
y	Maximum value of response
L	Lower limit of response
X1	Steam to Hydrocarbon Feed Ratio, kg/kg
X2	Coil Outlet Temperature, °C
X3	Feed Flow rate (Ton per h)
X4	C_8^+ content (composition, weight %) in feed

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