

Experimental study and optimization of heavy liquid hydrocarbon thermal cracking to light olefins by response surface methodology

Mehdi Sedighi, Kamyar Keyvanloo[†], and Jafar Towfighi

Chemical Engineering Department, Tarbiat Modares University, P. O. Box 14115-143, Tehran, Iran
(Received 20 November 2009 • accepted 7 January 2010)

Abstract—Response surface methodology coupled with central composite design (CCD) was used to investigate the effects of operating variables, namely, coil outlet temperature (COT), flow rate and steam ratio, on the yield of light olefins (ethylene and propylene) in thermal cracking of heavy liquid hydrocarbon. From the CCD studies the effects of COT and flow rate were concluded to be the key factors influencing the yield of light olefins. Based on this experimental design, two empirical models, representing the dependence of ethylene and propylene yields on operating conditions, were developed. The single maximum response of ethylene and propylene yields and simultaneous maximization of both responses have also been obtained at the corresponding optimal independent variables. The results of the multi-response optimization could be used to find the suitable operating conditions.

Key words: Thermal Cracking, Response Surface Methodology, Heavy Liquid Hydrocarbon

INTRODUCTION

Light olefins, ethylene and propylene, are produced commercially through steam cracking of various hydrocarbons. These low molecular weight olefins are basic feedstocks for the petrochemical industry [1]. The worldwide demand and production of olefins are relatively higher than for any other chemicals. The mixed hydrocarbon stream and steam are heated to incipient cracking temperature (500–650 °C). Then, it is cracked in fired tubular reactors where the reactions take place at higher temperatures. Upon leaving the reactor, the gases are cooled in a transfer line exchanger (TLE) to prevent secondary reactions and then the gases are separated. Feedstock selection is an important factor in product yields. For example, propylene is produced in amounts depending upon conditions and the alkyl branching in the feed and the feeds containing aromatic nuclei will yield a wide range of aromatic products [2]. The higher prices for lighter hydrocarbons have caused a tendency to the higher boiling petroleum fractions such as gasoil and residue as feedstocks for olefin production. Kaiser et al. [3] reported the yield distribution of thermal cracking of several feedstocks such as ethane, propane, butanes, full range naphtha cuts and atmospheric gasoil. They reported that the yield of ethylene production for ethane feed is 80 percent and for gasoil is 25 percent. The influence of feed composition, total pressure and inlet partial pressure on the product distribution of the kerosene thermal cracking was investigated by Van Camp et al. [4]. They also investigated the kinetics of cracking of individual components and developed an empirical model. It was found that maximum obtained yields for ethylene and propylene were about 29% and 15% in mass, respectively. Zahedi et al. [5] studied the thermal cracking of atmospheric gas oil. The obtained maximum yield of ethylene was equal to 30.9 wt% as well as the maximum yield of propylene was 12.2 wt%. Depeyre et al. [6] stud-

ied the effects of temperature, steam to gas oil ratio and residence time on major products in gas oil thermal cracking, which was performed in a laboratory-scale tubular quartz or inconel reactor. The best yield of ethylene, 27% in mass, was obtained in the quartz reactor at 770 °C, residence time of 0.6 s, and mass ratio of steam to gas oil equal to 1. Thermal cracking of kerosene for producing ethylene and propylene has been studied in an experimental setup by Ghassabzadeh et al. [7]. Box-Behnken design was used to generate the experimental data. A semi-mechanistic kinetic model was also developed to predict yield distribution of products. Pyrolysis of LPG and its mechanistic reaction model was developed by Towfighi et al. [8]. Recently, Keyvanloo et al. [9] investigated the effect of temperature, residence time and steam ration on the steam cracking of naphtha by design of experiments coupled with response surface methodology. They have also studied the quadratic and cubic interactions of key parameters affecting the yield of products. They have found that the higher interactions are important and should be considered in their modeling. A multi-objective optimization was also carried out for maximization of ethylene and propylene simultaneously. Other authors [10–12] have also studied the thermal cracking of high boiling point petroleum fractions.

In all the above cases the thermal cracking of higher boiling point petroleum fractions is conducted and kinetic models are developed; however, empirical modeling using RSM combined with multi-responses optimization is useful for optimizing the thermal cracking of heavy liquid hydrocarbon in certain ranges of independent variables before kinetic studies are implemented. RSM is a set of techniques designed to find the optimum value of response and the influencing factors. It has been successfully applied in the field of experimental work [13–15].

The main objective of this paper is to develop a numerical approach for simultaneous multi-responses optimization in thermal cracking of heavy liquid hydrocarbon. Several experiments were carried out to study the effects of different variables: COT, flow rate and steam ratio, on the yield distribution of major products. To gen-

[†]To whom correspondence should be addressed.
E-mail: Kamyar.keyvanloo@yahoo.com

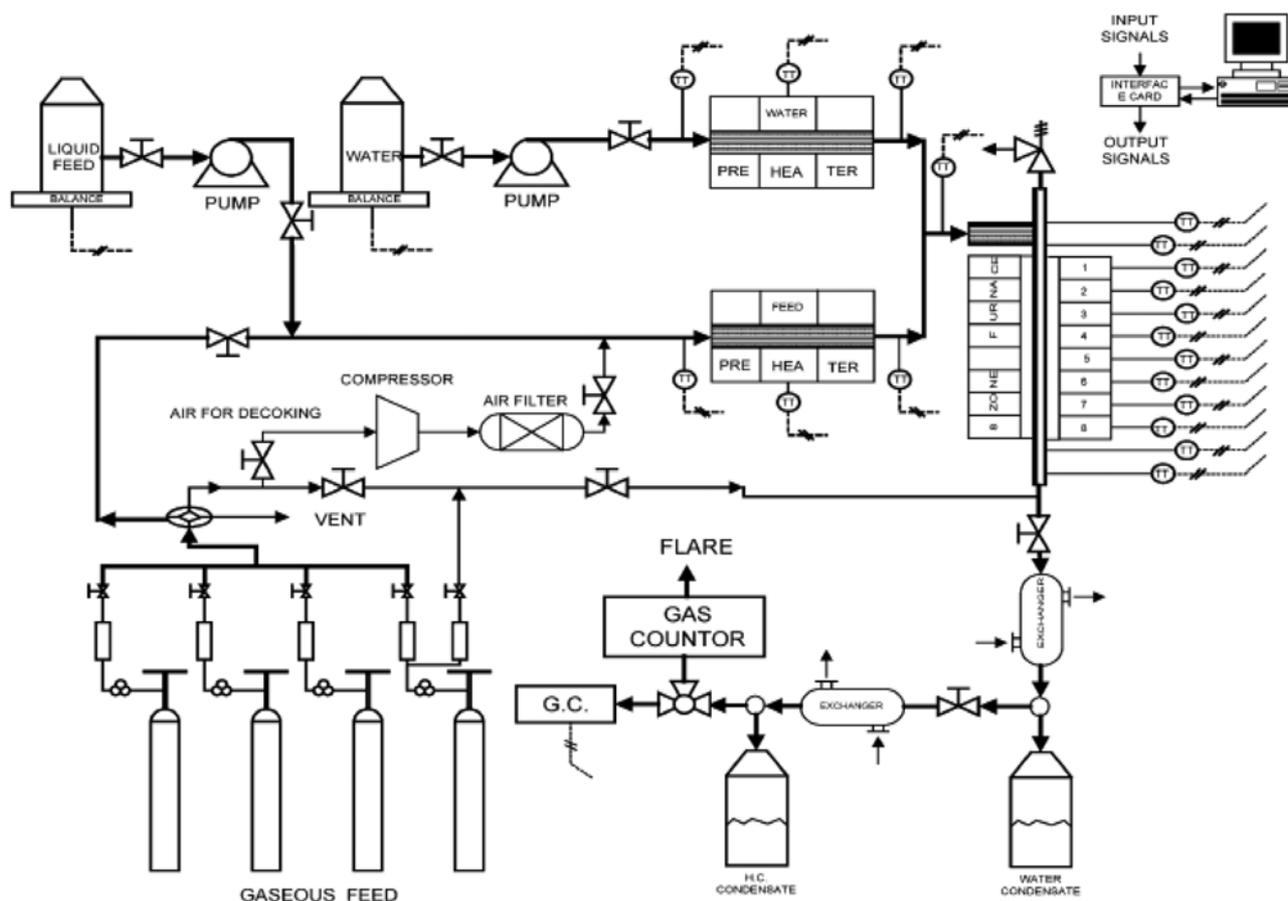


Fig. 1. Schematic diagram of the thermal cracking setup.

erate systematic experimental data for covering a wide range of operating conditions and to predict the maximum product yields, response surface design (central composite design) was used as a systematic experimental design method. Then, RSM involving central composite design and regression of analysis was used to develop two empirical models for ethylene and propylene yields. Based on these models, two single-responses optimization (ethylene and propylene maximization, separately) and a multi-responses optimization (maximization of ethylene and propylene, simultaneously) were carried out.

EXPERIMENTAL SET-UP

The experimental setup was designed and assembled for thermal cracking of the hydrocarbon feedstocks in the range from ethane

Table 1. Physicochemical characteristics and composition of heavy liquid hydrocarbon

| Physical properties | | | | | | |
|----------------------------|------------|-----------|-----------|---------|-----------------------------|--|
| Specific gravity, gr/cc | 0.769 | | | | | |
| Initial boiling point, °C | 32 | | | | | |
| Final boiling point, °C | 324 | | | | | |
| Chemical composition (wt%) | | | | | | |
| n-paraffin | I-paraffin | Naphthene | Aromatics | Olefins | C ₅ ⁺ | |
| 26.25 | 28.29 | 17.84 | 19.3 | 0.17 | 7.75 | |

to heavy hydrocarbons. The setup is a computer-controlled pilot plant unit as shown in Fig. 1. The feed was injected into the reactor at the required flow rate by using a dosing pump. The reactor (1 cm i.d.×1.27 cm o.d.×120 cm long) was made of stainless steel 316 and heated in a three-zone furnace. Physicochemical properties and composition of the feed are demonstrated in Table 1. The temperature of each zone was controlled by separate proportional controllers. Wall temperature profile was measured in five points through the wall, using a type K thermocouple. The hydrocarbon and dilution water were heated to the cracking temperature (550 °C) by two separated furnaces as a preheater.

The reactor effluent was quenched by passing through a double pipe heat exchanger. The condensed liquid hydrocarbon products and any unconverted reactant were collected in separating flash drum attached to exchanger; then the gas phase passed through a series of condensers and was entered in a filter in the final stage. During the course of a run, the condensed liquid as well as the composition of the liquid and gaseous products was measured at regular intervals. After each run, a fraction of product gas was withdrawn for analysis by a Varian Chrompack CP3800 gas chromatograph.

RESULTS AND DISCUSSION

1. Central Composite Design

A central composite rotatable design (CCRD) for three factors was employed for experimental design. Three independent variables,

namely coil outlet temperature (COT) (x_1), flow rate (x_2), steam-to-hydrocarbon ratio (x_3), were selected as control variables. The design consists of two-level full factorial design ($2^3=8$), six star points and one center point. Note that for CCD study, five replicates at the central point were performed to evaluate the pure error between each experiment.

The sequence of experiments was randomized to minimize the effects of uncontrolled factors. A quadratic polynomial equation was developed to represent the responses as a function of independent variables involving their quadratic interactions and squared terms.

The variables X_i were coded as x_i , according to Eq. (1).

$$x_i = \frac{X_i - X_{0i}}{\Delta X_i}, \quad i=1, 2, 3, \dots, k \quad (1)$$

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

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

Multiple regression analysis techniques included in the RSM were used to estimate the coefficients of the models.

The low and high levels for the independent variables were based

Table 2. Factors and levels for CCD study

| Level | COT (°C), X_1 | Flow rate (gr/min), X_2 | Steam ratio, X_3 |
|------------|-----------------|---------------------------|--------------------|
| - α | 750 | 3 | 0.5 |
| -1 | 780.4 | 3.8 | 0.68 |
| 0 | 825 | 5 | 0.95 |
| +1 | 869.6 | 6.2 | 1.22 |
| + α | 900 | 7 | 1.4 |

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

| Run | Factors | | | Yield (wt%) | | | | | |
|-----|---------|-------|-------|-------------|----------|--------|----------|----------|----------|
| | X_1 | X_2 | X_3 | C_2H_4 | C_3H_6 | CH_4 | C_2H_6 | C_3H_8 | C_4H_8 |
| 1 | 780.4 | 3.8 | 0.68 | 20.74 | 13.31 | 9.35 | 3.41 | 1.18 | 3.44 |
| 2 | 780.4 | 6.2 | 0.68 | 18.53 | 14.03 | 8.34 | 2.5 | 1.49 | 3.51 |
| 3 | 780.4 | 3.8 | 1.22 | 21.73 | 13.38 | 9.67 | 3.45 | 1.14 | 3.4 |
| 4 | 780.4 | 6.2 | 1.22 | 19.1 | 14.17 | 8.6 | 2.51 | 1.4 | 3.52 |
| 5 | 869.6 | 3.8 | 0.68 | 30.09 | 10.4 | 15.77 | 2.2 | 0.84 | 1.74 |
| 6 | 869.6 | 6.2 | 0.68 | 27.8 | 11.85 | 14.93 | 2 | 0.94 | 2.07 |
| 7 | 869.6 | 3.8 | 1.22 | 30.11 | 10.54 | 15.78 | 2.16 | 0.89 | 0.82 |
| 8 | 869.6 | 6.2 | 1.22 | 28.34 | 12.05 | 15 | 1.93 | 0.93 | 1.95 |
| 9 | 750 | 5 | 0.95 | 19.75 | 13.21 | 8.72 | 3.72 | 1.75 | 3.71 |
| 10 | 900 | 5 | 0.95 | 29.9 | 9.45 | 16.35 | 1.82 | 0.67 | 1.47 |
| 11 | 825 | 3 | 0.95 | 28.4 | 13.49 | 15.32 | 2.69 | 0.84 | 2.15 |
| 12 | 825 | 7 | 0.95 | 23.45 | 15.37 | 10.7 | 1.97 | 1.63 | 2.93 |
| 13 | 825 | 5 | 0.5 | 24.74 | 13.71 | 12.76 | 2.61 | 1.42 | 2.49 |
| 14 | 825 | 5 | 1.4 | 26.12 | 15.12 | 14.8 | 2.17 | 1.2 | 2.1 |
| 15 | 825 | 5 | 0.95 | 25.8 | 14.31 | 13.25 | 2.27 | 1.22 | 2.26 |
| 16 | 825 | 5 | 0.95 | 25.3 | 14.41 | 13.27 | 2.23 | 1.25 | 2.26 |
| 17 | 825 | 5 | 0.95 | 25.07 | 14.55 | 13.28 | 2.19 | 1.26 | 2.24 |
| 18 | 825 | 5 | 0.95 | 25.52 | 14.37 | 12.97 | 2.31 | 1.26 | 2.18 |
| 19 | 825 | 5 | 0.95 | 25.12 | 14.08 | 13.36 | 2.19 | 1.14 | 2.20 |

Table 4. ANOVA for the ethylene yield model

| Source | Sum of squares | Degree of freedom | Mean square | F_{Value} | R^2 |
|-----------------|----------------|-------------------|-------------|-------------|-------|
| S.S. regression | 236.28 | 9 | 26.25 | 21.86 | 0.96 |
| S.S. error | 10.45 | 7 | 1.20 | | |
| S.S. total | 247.09 | 16 | | | |

Table 5. ANOVA for the propylene yield model

| Source | Sum of squares | Degree of freedom | Mean square | F_{Value} | R^2 |
|-----------------|----------------|-------------------|-------------|-------------|-------|
| S.S. regression | 45.81 | 9 | 5.09 | 15.76 | 0.94 |
| S.S. error | 2.91 | 7 | 0.32 | | |
| S.S. total | 48.72 | 16 | | | |

on industrial practice. The design factors and levels for both CCD studies are shown in Table 2; meanwhile, the design matrix with their corresponding results is listed in Table 3.

The resultant second-order models for the yields of ethylene and propylene are generated as shown in Eqs. (3) and (4):

$$C_2H_4 = -169.64 + 0.38X_1 - 2.21X_2 + 11.92X_3 + 1.22 \times 10^{-3} X_1 X_2 - 7.75 \times 10^{-3} X_1 X_3 - 0.06 X_2 X_3 - 1.82 \times 10^{-4} X_1^2 + 0.02 \times 10^{-3} X_2^2 - 2.06 X_3^2 \quad (3)$$

$$C_3H_6 = -383.48 + 0.99X_1 - 1.13X_2 + 3.09X_3 + 3.22 \times 10^{-3} X_1 X_2 + 2.19 \times 10^{-3} X_1 X_3 - 0.02 X_2 X_3 - 6.27 \times 10^{-4} X_1^2 - 0.10 X_2^2 - 2.20 X_3^2 \quad (4)$$

The analysis of variance (ANOVA) for Eqs. (3) and (4) is shown in Tables 4 and 5. The F value is a ratio of the mean square due to regression to the mean square due to error. If the calculated value of F is greater than the value in the F table at a specified probability level (e.g., $F_{0.01}(9,7)=5.62$), a statistically significant factor or interaction is obtained. From ANOVA table, the value of F for yield of ethylene and propylene are 21.86 and 15.76, respectively. These F values are much higher than the F table, which is 5.67.

The value of R^2 is a measure of total variation of observed values about the mean explained by the fitted model. Therefore, R^2 equal to 0.96 for Eq. (3) indicates a very good fitting for the experimental data and predicted values. The R^2 value of Eq. (4) is 0.94, also indicating that this regression model is a good representation for dependence of propylene yield on factors X_1 , X_2 and X_3 .

The observed versus predicted values are illustrated in Figs. 2(a) and (b). From both figures, it can be seen that most of the points of experimental values lie close to the straight line, which is the predicted values.

2. Effect of Operating Conditions on the Yield of Main Products

To investigate the effect of residence time on the main products, we need to convert the total flow rate to residence time with following equations:

$$\tau = \frac{V_r}{Q_g} \quad (5)$$

$$Q_g = \left[\frac{\dot{m}_{HC}}{MW_{HC}} + \frac{\dot{m}_{Water}}{MW_{Water}} \right] \frac{RT}{P} \quad (6)$$

As shown in these equations, the residence time is a function of naphtha and water flow rate, temperature and pressure, and changing

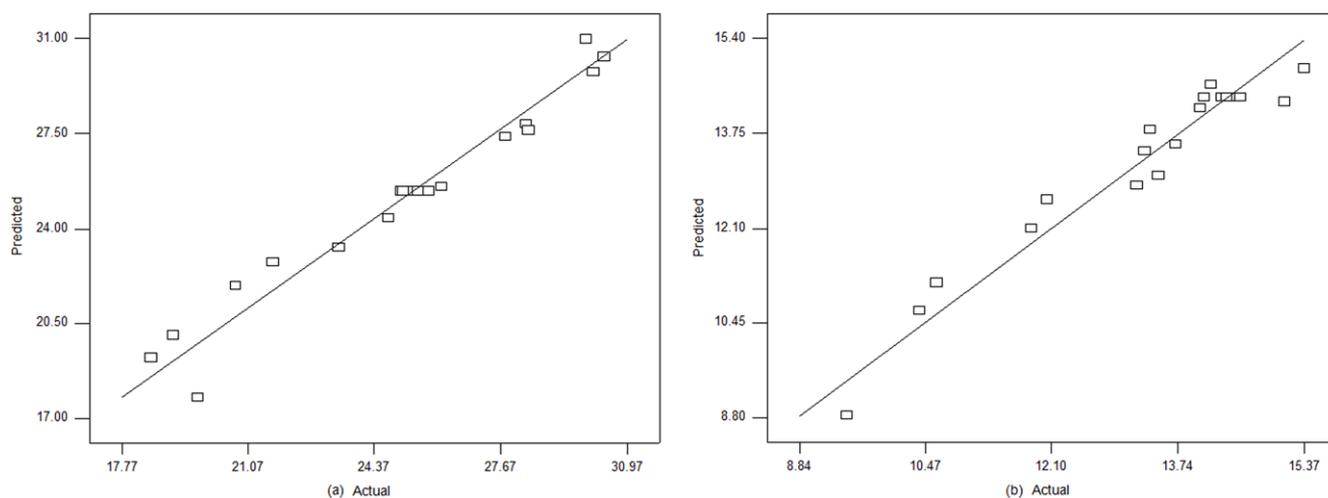


Fig. 2. Actual versus predicted values for (a) ethylene and (b) propylene.

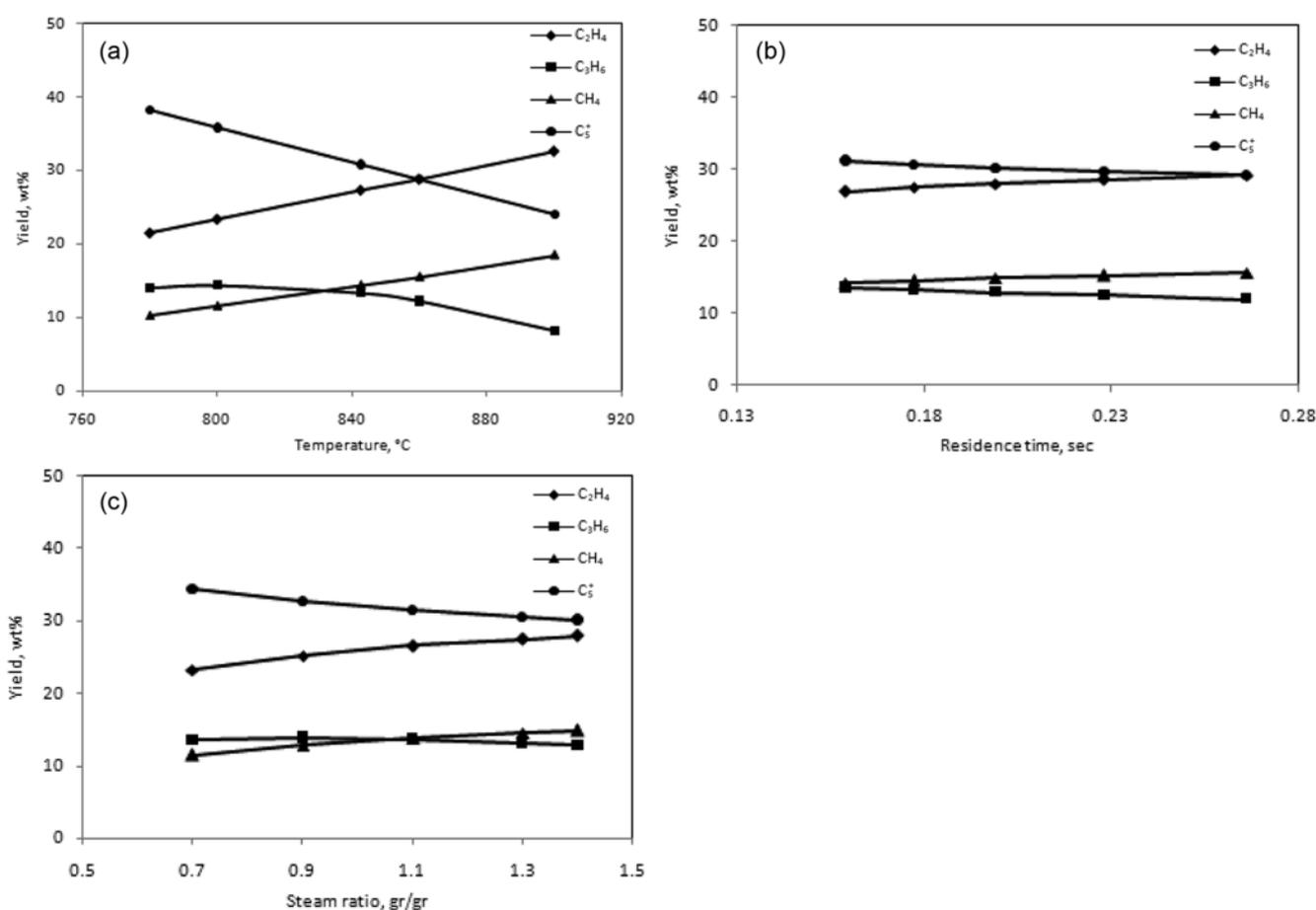


Fig. 3. Effect of (a) COT (b) residence time (c) steam ratio on methane, ethylene, propylene and C_5^+ yields.

the naphtha flow rate (\dot{m}_{HC}) and steam ratio ($\dot{m}_{Water}/\dot{m}_{HC}$) leads to changing of residence time. Due to experimental set up limitation and also lower effects of pressure on the product yields compared to the three other variables, the reactor pressure is maintained at 1 atm.

The variation of main products of heavy liquid hydrocarbon py-

rolysis with temperature, residence time and steam ratio is shown in Fig. 3. The influence of COT on the yields of CH_4 , C_2H_4 , C_2H_6 and C_5^+ is shown in Fig. 3(a). For these sets of runs, the residence time and steam ratio were kept fixed at 0.17 s and 1.24 gr/gr, respectively. The yields of methane and ethylene increased with temperature, whereas the yield of propylene passed through maxima

with increasing temperature; on the other hand, C_5^+ showed a decrease. The effect of residence time was studied in the range of 0.16–0.27 s, as shown in Fig. 3(b), keeping the COT and steam ratio fixed at 842.6 °C and 1.24 gr/gr, respectively. The yields of various products have different manner with increasing the residence time. It depends on the stability of hydrocarbon products and relative reactions. Thus, methane yield increased monotonically with residence time, whereas propylene slightly decreased with increasing the residence time. Ethylene yield also gradually increased in this range. Yield of C_5^+ decreased by increasing the residence time but tended to level off at higher residence time. Fig. 3(c) demonstrates the effect of steam ratio on the distribution of major products. The steam ratio was varied from 0.7 to 1.4 gr/gr at a temperature of 842.6 °C. The flow rates of water and hydrocarbon were adjusted such that the residence time was maintained at 0.17 s. Apparently, the decrease in the partial pressure of the reacting components does not have an appreciable effect on the yield of propylene. However, the yields of ethylene and methane slightly increased with increasing the steam ratio and C_5^+ tended to level off at higher steam ratio.

3. Single-response Optimization

The Nelder-Mead Simplex method was used to look for the optimal conditions in which each response variable achieved a maximum value. The variables that affect the cracking reactor performance and were discussed in our experimental design were chosen as the decision variables. The ranges of decision variables used are as follows:

$$\begin{aligned} 780.4\text{ }^\circ\text{C} \leq T \leq 869.6\text{ }^\circ\text{C} \\ 3.89\text{ gr/min} \leq \text{flow rate} \leq 6.2\text{ gr/min} \\ 0.68 \leq \text{steam ratio} \leq 1.22 \end{aligned}$$

The yield of ethylene reaches to its maximum at 30.32 wt% when COT, flow rate and steam ratio are 869.6 °C, 3.81 gr/min and 1.20, respectively. So it has an optimum at high COT and steam ratio but low flow rate. The optimum point for propylene yield is 15.11 wt% when COT, flow rate and steam ratio are 807.04 °C, 6.19 gr/min and 1.13. This optimum value is at intermediate COT, high flow rate and steam ratio. Therefore, the maximum yield of propylene

occurs at significantly different operating conditions.

4. Multi-responses Optimization

For the optimization study of the heavy liquid hydrocarbon steam cracker the objectives are to maximize the ethylene production and maximize the propylene production simultaneously. As we have shown, the COT and flow rate have a significant effect on the yield of light olefins. The two optimization goals are competitive. Therefore, we can achieve the best compromise between ethylene and propylene.

We define the composite desirability function (D) that ranges from zero outside of the limits to one at the goal. The numerical optimization finds a point that maximizes the desirability function. For multiobjective, the goals get combined into one desirability function.

$$D_{comp} = (d_1 \times d_2 \times \dots \times d_n)^{\frac{1}{n}} \quad (7)$$

where d_i are individual desirability functions for each response and n is the number of responses in the measure.

If the objective or target T for the response y is a maximum value, then the individual desirability function is defined as follows in Eq. (8):

$$d = \begin{cases} 0 & y < L \\ \left(\frac{y-L}{T-L}\right)^r & L \leq y \leq T \\ 1 & y > T \end{cases} \quad (8)$$

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 D.C. Montgomery [15].

The fitted model from Eqs. (3) and (4) can be used to map empirically the response function over the experimental region. They combined with each other with the help of Eqs. (7) and (8). A contour plot helps in assessing the effect of any two variables in combination on the desired product.

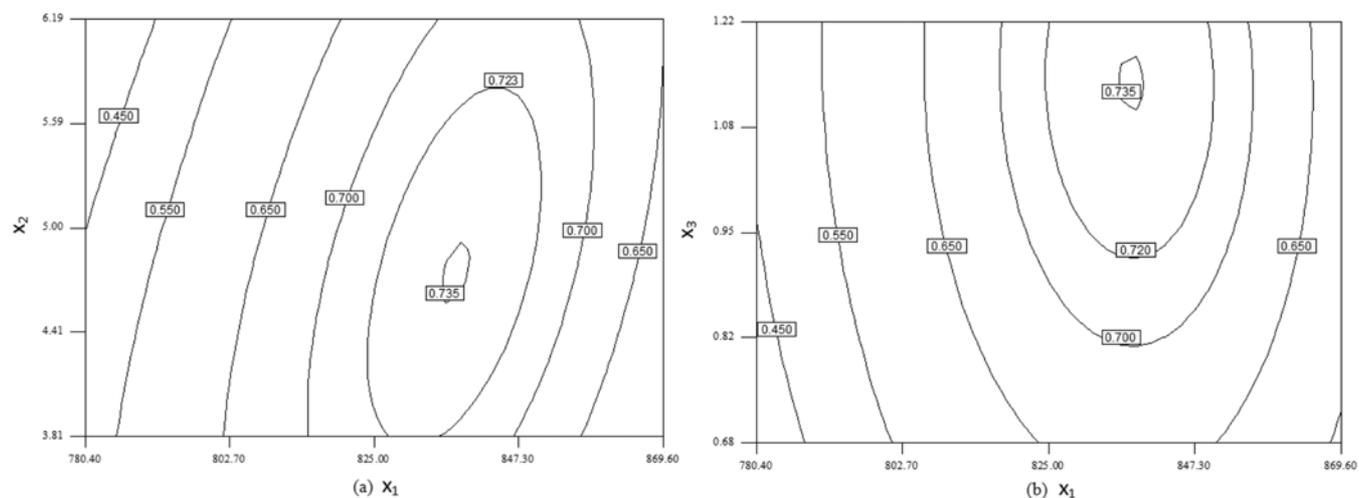


Fig. 4. Contour plots describing the response surface of composite desirability as a function of (a) temperature and flow rate, and (b) temperature and steam ratio.

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

| C ₂ H ₄ yield (wt%) | | | C ₃ H ₆ yield (wt%) | | |
|---|---------------------------|-----------------|---|---------------------------|-----------------|
| Y _{multiobjective} | Y _{experimental} | %Relative error | Y _{multiobjective} | Y _{experimental} | %Relative error |
| 26.93 | 27.63 | 2.53 | 13.87 | 14.33 | 3.21 |
| 26.93 | 27.51 | 2.10 | 13.87 | 14.56 | 4.73 |
| %Average relative error | | 2.31 | %Average relative error | | 3.97 |

The contour plots for the composite desirability function against the temperature (X_1), flow rate (X_2) and steam ratio (X_3) are shown in Fig. 4. From Fig. 4(a), the yield of light olefins (ethylene and propylene) is increased up to an approximately intermediate COT and flow rate. It is in consistent with the fact that ethylene reaches to its maximum at higher COT and lower naphtha flow rate. From Fig. 4(b), the yield of light olefins gradually increased with an increase in steam ratio up to approximately 1.1 gr/gr.

In this case the optimum was found at COT=837.41 °C, flow rate=4.71 gr/min, steam ratio=1.17 gr/gr. This set gave the highest D at 0.728 and predicted ethylene yield=26.93 wt% and propylene yield=13.87 wt% for optimized responses.

To verify the multiobjective optimization of ethylene and propylene yields, two more runs were performed and the final optimal points were compared with those from experimental data at similar conditions. As shown in Table 6 the average relative error for ethylene and propylene yields is 2.31% and 3.97%, respectively.

CONCLUSION

The response surface methodology involving central composite design and regression of analysis is used in finding the optimum point of the operating variables, namely, COT, flow rate and steam ratio, and in assessing their effects on the two responses considered. The second order polynomial equation model whose validity is agreed upon is estimated using ANOVA statistical testing and yields 99% degree of confidence of response behaviors to variables. The COT had a significant effect on the yields of light olefins, probably because the reaction is endothermic. Furthermore, the high temperature favors the yield of ethylene, but it has an opposite effect on the yield of propylene. In other words, the propylene yield reaches its maximum at intermediate temperature.

The operating conditions from multi-response optimization of ethylene and propylene yields were obtained as a recommendation for the heavy liquid hydrocarbon thermal cracking. The maximum values of 26.93 and 13.87 wt% for ethylene and propylene yield, respectively, were achieved with respect to the optimal operating variables: COT=837.41 °C, flow rate=4.71 gr/min and steam ratio=1.17 gr/gr.

NOMENCLATURE

| | |
|-----------|-----------------------------------|
| D | : composite desirability function |
| d | : individual desirability value |
| Q | : volume flow rate |
| \dot{m} | : mass flow rate |
| MW | : molecular weight |
| x | : coded independent variable |

| | |
|------------|--|
| X | : uncoded independent variable |
| X_0 | : 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

| | |
|--------------|-----------------------------------|
| β | : coefficients of quadratic model |
| β_i | : linear term |
| β_{ij} | : squared term |
| β_{ij} | : interaction term |
| τ | : residence time |

Abbreviations

| | |
|------|--------------------------------------|
| CCD | : central composite design |
| CCRD | : central composite rotatable design |
| COT | : coil outlet temperature (°C) |
| RSM | : response surface methodology |
| TLE | : transfer line exchanger |

REFERENCES

1. B. Belohlav, P. Zamostn and T. Herink, *Chem. Eng. Process.*, **42**, 461 (2003).
2. J. E. Gwyn, *Fuel Process. Technol.*, **70**, 1 (2007).
3. V. Kaiser, D. Gilbourne and C. A. Pocini, *Hydrocarbon Processing*, April (1977).
4. C. E. Van Camp, P. S. Van Damme and G. F. Froment, *Ind. Eng. Chem. Process Des. Dev.*, **23**, 155 (1984).
5. S. Zahedi, J. Towfighi, R. Karimzadeh and M. Omidkhan, *Korean J. Chem. Eng.*, **24**, 681 (2008).
6. D. Depeyre, C. Flicoteaux, F. Arbabzadeh and A. Zabaniotou, *Ind. Eng. Chem. Res.*, **28**, 967 (1989).
7. H. Ghassabzadeh, J. Towfighi and P. Zaheri, *J. Anal. Appl. Pyrolysis*, **86**, 221 (2009).
8. J. Towfighi, A. Niaei, R. Karimzadeh and G. Saedi, *Korean J. Chem. Eng.*, **23**, 8 (2006).
9. K. Keyvanloo, J. Towfighi, S. M. Sadrameli and A. Mohamadlizada, *J. Anal. Appl. Pyrolysis*, **87**, 224 (2010).
10. S. B. Zdonik, G. L. Hayward and S. H. Fishtine, *Hydrocarbon Processing*, December (1975).

11. M. Hirato, S. Yoshioka and Matanuska, *Hitachi Rev.*, **20**, 326 (1971).
12. M. Hirato and S. Yoshioka, *Intern. Chem. Eng.*, **13**, 347 (1973).
13. A. Kukovecz, D. Mehn, E. Nemes-Nagy, R. Szabo and I. Kiricsi, *Carbon*, **43**, 2842 (2005).
14. Istadi, A. S. Amin, *Chem. Eng. J.*, **106**, 213 (2005).
15. L. M. Kasanakala, Y. Xue, Y. Weilong, S. D. Hong and Q. He, *Biore-sour. Technol.*, **98**, 3338 (2007).
16. D. C. Montgomery, *Design and analysis of experiments*, John Wiley & Sons, New York, 451 (2001).