

Effect of process variables on product yield distribution in thermal catalytic cracking of naphtha to light olefins over Fe/HZSM-5

Mina Alyani, Jafar Towfighi[†], and Seyed Mojtaba Sadrameli

Faculty of Chemical Engineering, Tarbiat Modares University, P. O. Box 14115-114, Tehran, Iran

(Received 25 October 2010 • accepted 11 December 2010)

Abstract—The effect of temperature, WHSV and Fe loading over HZSM-5 catalyst in thermal-catalytic cracking (TCC) of naphtha for the production of light olefins has been studied. The response surface defined by three most significant parameters is obtained from Box-Behnken design method and the optimal parameter set is found. The results show that ethylene increases with temperature, while propylene shows an optimum at 650 °C. Moderate WHSV is favorable for maximum production of light olefins. Addition of Fe to HZSM-5 has a favorable effect on the production of light olefins up to 6% of loading. Excess amount of loading decreases the conversion of naphtha, which leads to a drop in light olefin yields. The yield of light olefins (ethylene and propylene) at 670 °C, 44 hr⁻¹ and 6 wt% Fe has been increased to 5.43 wt% compared to the unmodified HZSM-5 and reaches to 42.47 wt%.

Key words: Thermal-catalytic Cracking, Naphtha, Fe-HZSM-5, Light Olefins, Response Surface

INTRODUCTION

Thermal cracking of heavy hydrocarbons for production of low molecular weight olefins such as ethylene and propylene is one of the most important processes in petrochemical industry. The conventional cracking processes have some problems such as high reaction temperature, high energy cost and high green house gasses emissions. Furthermore, the demand for ethylene and propylene has been increased recently, which highlights the importance of developing new routes for production of light olefins such as thermal-catalytic cracking (TCC). TCC consists of thermal cracking and catalytic cracking, which produces higher combined yields of light olefins in lower temperature.

There have been some studies on catalytic cracking of hydrocarbons, such as cracking of n-heptane over acidic zeolite ZSM-5 [1] and conversion of naphtha over ZSM-5 catalysts [2]. Recently Keyvanloo et al. [3] studied the performance of mixed molybdenum with cerium and lanthanide oxides supported on HZSM-5 in the thermal catalytic cracking of naphtha. They used central composite design for generating the experimental data. Two empirical models were proposed by response surface methodology. A simultaneous maximization of ethylene and propylene was also carried out by NSGA-II. They have found that the optimum catalyst was obtained at moderate La or Ce loading. Liu et al. [4] investigated catalytic cracking of naphtha at 650 °C over modified ZSM-5. Modified catalysts with transition metals increased the yield of light olefins and cracking stability. The obtained yield of ethylene and propylene is higher than 50 wt% kept for more than 30 h. Catalytic pyrolysis of naphtha has been carried out with KVO₃ impregnated α -Al₂O₃ [5]. The yields of ethylene and propylene during naphtha pyrolysis at 880 °C showed 34.5% and 16.6% over KVO₃-B₂O₃/ α -Al₂O₃ catalysts, which are 9.8 and 3.4% higher compared to ther-

mal pyrolysis at the same operation condition. Steam pyrolysis of n-heptane over different calcium aluminates and potassium impregnated calcium aluminate in a fixed bed reactor has been studied by Pant et al. [6]. The yields of ethylene and propylene over different catalyst were investigated. Compared to thermal cracking, the conversion and yields of products are increased in the presence of these catalysts. Yoshimura et al. [7] developed La₂O₃/P/ZSM-5 catalysts to produce light olefins. They showed high catalytic cracking activity and high selectivity to light olefin. The yield of ethylene and propylene was achieved 60% at 650 °C, which is 10% higher than steam cracking operated at 820 °C. Zhen et al. [8] investigated the effects of rare earth on the catalytic performance of HZSM-5. The catalytic cracking of butane to light olefins over RE/HZSM-5 was carried out in a fixed bed microreactor at 600 °C. Light rare earth metals on HZSM-5 catalysts increase the selectivity of light olefins, especially propylene. Moreover, Ce/HZSM-5 showed the highest yield of light olefins and Nd/HZSM-5 gave the highest yield for propylene. Catalytic pyrolysis of C₄ hydrocarbons over modified ZSM-5 was investigated by Li et al. [9]. With increasing the temperature, the yield of ethylene increases monotonically and propylene yield has a maximum amount at 580 °C. Furthermore, increasing dilution ratio up to 2 has a positive effect on the yields of ethylene and propylene. Catalytic cracking of isobutane over Cr/HZSM-5 with different amounts of Cr was studied by Zhao et al. [10]. At Cr loading of 0.004 mmol/g, the selectivity of ethylene and propylene was increased greatly in comparison with unmodified HZSM-5. At 625 °C and 0.004 mmol/g of Cr, the yield of light olefins (ethylene and propylene) achieved 56.1%. To increase the yield of ethylene and propylene in catalytic pyrolysis of heavy feedstock, Xianfeng et al. [11] recently developed ZSM-5 modified with Fe₂O₃ and TiO₂. The results showed that the dispersion of Fe species on the surface of ZSM-5 was improved by Ti species and Fe₂O₃ promoted the TiO₂ reduction. Catalytic cracking performance of Fe-Ti/ZSM-5 for n-decane was better than catalysts Ti/ZSM-5, Fe/ZSM-5 and ZSM-5. The yield of light olefins over Fe-Ti/ZSM-5 at 650 °C was 3.2 or 1.8%

[†]To whom correspondence should be addressed.

E-mail: towfighi@modares.ac.ir

more than that over Fe/ZSM-5 or ZSM-5, respectively.

The effect of alkaline earth modification on HZSM-5 for catalytic cracking of n-butane was investigated by Wakui et al. [12]. The yields of ethylene and propylene over alkaline earth modified HZSM-5 catalysts were high compared with the non-modified HZSM-5. With Ba-ZSM-5, the highest yield of ethylene and propylene was obtained. The yields of aromatic products were lower than non-modified HZSM-5. Cracking of C₄ alkanes to produce light olefins over HZSM-5 zeolites modified by different amounts of phosphorus (P/HZSM-5) was studied by Zhao et al. [13]. Phosphorus (P) modification was favorable for enhancing the selectivity to light olefins especially to propylene. With increasing P loading, aromatics yield decreased due to the reduction of strong acid and the formation of new basic site.

Unlike the other researchers who focused on the catalytic cracking of light hydrocarbons and giving the general features of the effect of loading and temperature, in this work, naphtha was used as a feedstock to investigate its thermal catalytic cracking over HZSM-5 catalysts for the production of light olefins. Furthermore, we are attempting to provide some basic insights into the effect of three key factors, namely, temperature, WHSV, and Fe loading, with the help of statistical design of experiments. Therefore, the factors and interactions with high significance are selected and considered in our developed empirical models. These models are used to carry out the single and multi-objective optimizations, and finally an optimum catalyst and process conditions are proposed.

EXPERIMENTAL

1. Experimental Set-up

The experiments were conducted in a tubular reactor with 1.35 cm ID and 45 cm length. The pressure drop in the length of the reactor was insignificant and the pressure in whole reactor was considered 1 atm. Steam, which was used as an inert, was generated in a vaporizer and mixed with the naphtha before the preheater. Steam is used to increase the olefin selectivity and to reduce the coke formation by decreasing the hydrocarbon partial pressure. Mixtures of naphtha and steam were pumped into the preheater and its temper-

Table 1. Properties and composition of naphtha

Physical properties				
Specific gravity (g/cm ³)				0.655
Initial boiling point (°C)				60.7
Final boiling point (°C)				120.3
Chemical composition (wt%)				
Carbon no.	n-Paraffin	i-Paraffin	Naphthene	Aromatics
C ₄	2.16	0.12	0	0
C ₅	27.34	21.38	3.58	0
C ₆	10.19	12.29	3.84	1.58
C ₇	3.29	3.82	4.34	1.57
C ₈	1.04	1.2	0.92	0.55
C ₉	0.26	0.5	0	0.03
Sum	44.28	39.31	12.68	3.73

ature increased to 550 °C, then it entered the reactor. Properties and compositions of naphtha are shown in Table 1. The catalysts with various amounts of Fe were loaded into the reactor. The experiments were done with 2.0 g Fe/HZSM-5 in different temperature, WHSV, and Fe loading.

The effluent from the reactor was quenched in ice bath followed by two water-cooled condensers placed in series. After separating the liquid products and water, the gas mixture was analyzed online by Hewlett-Packard 5890B gas chromatograph. The experimental setup is shown in Fig. 1.

2. Catalyst Preparation

HZSM-5 (SiO₂/Al₂O₃=28) with a surface area of 313 m²/g and a pore volume of 0.16 cm³/g was used as a support which was obtained from Research Institute of Petrochemical Industry (RIPI) in Iran. HZSM-5 catalyst was impregnated by certain concentration of Fe(NO₃)₃·9H₂O solution. The Fe loadings were 2, 6, 10 wt%, respectively. The impregnation period lasted for 20 minutes at ambient temperature and then dried at 120 °C for about 4 h and finally calcined at 700 °C in air for 4 h. For instance, 6%wt Fe/HZSM-5 catalyst was prepared by impregnation of the HZSM-5(2 g) with 0.87

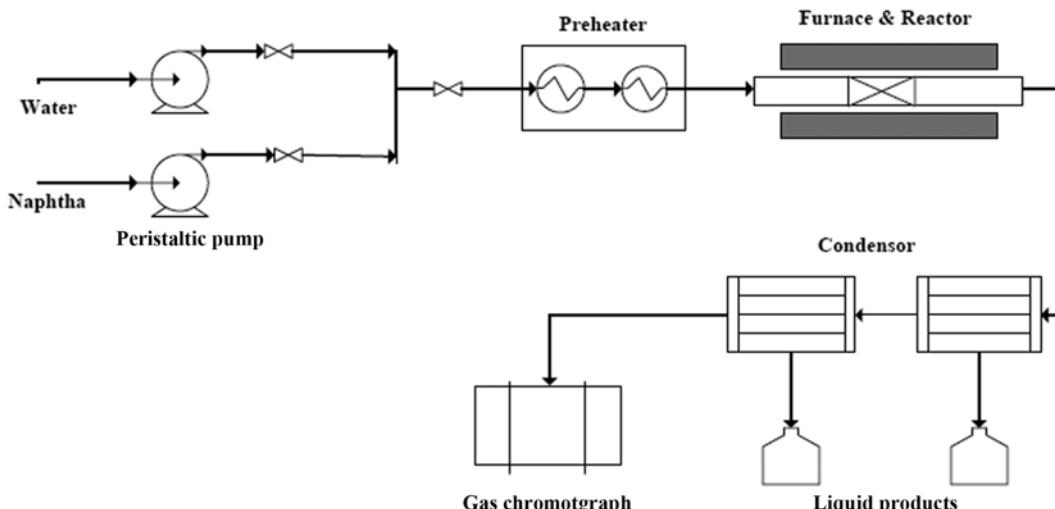


Fig. 1. Schematic diagram of the experimental setup.

g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) dissolved in 12 ml of deionized water. Material was stirred until a paste was formed and dried at 120 °C for about 4 h and then calcined at 700 °C for 4 h in an air stream, and then the catalysts were meshed to 1-2 mm particles.

3. Catalyst Characterization

The catalysts were characterized by BET and XRD analysis. The BET, specific surface area of the samples, was measured by a single

point N_2 adsorption method at liquid- N_2 temperature (-196°C). XRD analysis was performed using an Xpert MPD X-ray diffractometer with Co radiation, with step size of $0.02^\circ 2\theta$ and scan range of 5° - $80^\circ 2\theta$ at 40 kV and 30 mA. The BET surface areas and total pore volumes of the parent and modified HZSM-5 catalysts were reported in Table 2. Because HZSM-5 pores have been filled up with iron oxides, the BET surface area and total pore volume have decreased in the modified zeolite catalyst.

Patterns of the bulk and modified HZSM-5 are compared in Fig. 2. Both catalysts show similar XRD patterns between 2θ values of 5° and 80° . The peaks which show iron oxide are indicated in this Figure. XRD pattern for Fe/HZSM-5 catalyst indicates that iron oxide was dispersed on the surface of HM zeolite.

RESULTS AND DISCUSSION

1. Response Surface Exploration

To investigate the effect of operating conditions and catalyst preparation and to find an optimum catalyst, enough data should be collected. Therefore, the response surfaces were defined by the three chosen variables (temperature, WHSV, and Fe loading). Among the various kinds of experimental designs, the least resource-demanding design for three factors is the three-level Box-Behnken design which can be used for identification of nonlinearities between three factors. Our composition required 13 runs (denoted as run #1-#15) as detailed in Table 3. This design includes three replicates at the center point. Three more runs on parent HZSM-5 in different temperatures were also conducted in order to better study the effect of Fe on the yield of light olefins. Steam to naphtha ratio and catalyst mass were held in these experiments at 0.5 and 2 g, respectively.

Data of ethylene and propylene yields shown in Table 3 were subjected to regression analysis to estimate the effect of process variables. The ANOVA calculation on the yields of ethylene and

Table 2. Specific surface area of the fresh supports and iron catalysts

Catalysts	Metal content (%)	BET surface area (m^2/g)	Total pore volume (cm^3/g)
Fresh HZSM-5	-	313	0.16
Fe/HZSM-5	6	297.37	0.13

Metal content was determined by ICP analysis

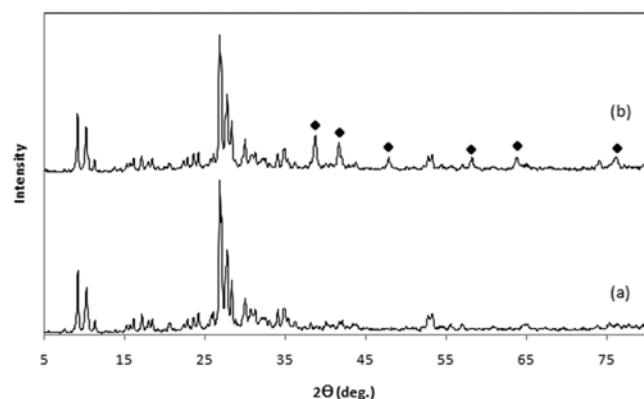


Fig. 2. XRD patterns of (a) fresh HZSM-5, (b) 6% wt Fe/HZSM-5.

Table 3. The catalytic performance of Fe/HZSM-5 catalysts in different temperature, loading and WHSV

Run	Loading (gr Fe/100 gr HZSM-5)	Temperatures (°C)	WHSV hr^{-1}	Yield (wt%)				
				Methane	Ethane	Ethylene	Propane	Propylene
1	10	680	44.85	4.94	8.58	17.91	12.15	20.96
2	10	650	50.1	4.11	5.44	13.13	4.09	18.69
3	10	650	39.6	3.95	7.26	14.67	10.04	20.39
4	10	620	44.85	3.22	7.55	14.37	14.99	20.72
5	6	680	39.6	8.02	6.03	18.52	2.53	22.35
6	6	650	44.85	4.42	7.54	16.33	8.43	23
7	6	620	50.1	2.77	6.49	13.19	12.64	13.99
8	6	680	50.1	7.16	5.74	17.28	2.79	22.56
9	6	650	44.85	4.49	6.89	16.21	7.57	24
10	6	620	39.6	3.59	6.71	14.86	9.5	23.21
11	6	650	44.85	5.54	7.55	17.1	4.99	23.5
12	2	650	39.6	4.31	7.7	13.5	4.89	21.34
13	2	680	44.85	4.75	7.76	17.14	9.1	21.22
14	2	650	50.1	3.1	6.3	11.21	9.67	13.46
15	2	620	44.85	2.39	4.59	10.93	5.39	17.35
16	0	620	44.85	2.1	4.28	9.13	2.11	15.44
17	0	650	44.85	4.82	8.22	12.19	11.05	18.9
18	0	680	44.85	3.46	7.24	16.89	8.24	20.15

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

Factor	df	SS	MS	F
A	1	38.28	38.28	189.25
B	1	5.68	5.68	28.07
C	1	6.66	6.66	32.93
AC	1	1.78	1.78	8.81
A ²	1	1.75	1.75	8.64
B ²	1	5.97	5.97	29.54
C ²	1	17.02	17.02	84.15
Error	7	1.42	0.2	
Total	14	78.64		

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

Factor	df	SS	MS	F
A	1	4.22	4.22	23.73
B	1	43.2	43.2	242.78
C	1	6.83	6.83	38.37
AB	1	22.23	22.23	124.94
AC	1	3.29	3.29	18.51
BC	1	9.55	9.55	53.66
A ²	1	1.74	1.74	9.88
B ²	1	19.24	19.24	108.11
C ²	1	27.87	27.87	156.65
AB ²	1	1.62	1.62	9.10
Error	4	0.71	0.11	
Total	14	149.11		

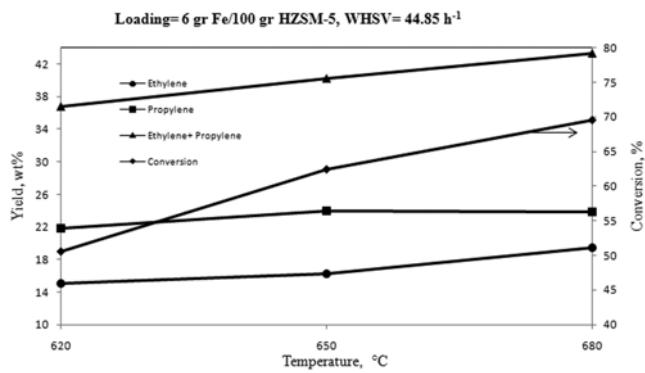
propylene in wt% is summarized in Tables 4 and 5, respectively. If the calculated value of F is greater than the value in the F table at a specified probability level (e.g., F_{0.05}(1,8)=5.32), a statistically significant factor or interaction is obtained. The F is defined as F=MSF/MSE, where MSF and MSE are the mean squares of factors or interactions, and errors, respectively.

After carrying out the ANOVA test, the factors A, B, C and interactions AC, A², B², C² are proved to be statistically significant effect on the yield of ethylene and factors A, B, C and interactions AB, AC, BC, A², B², C², AB² exhibit statistically significant effect on the yield of propylene. The F value is an indication of the level of significance. The higher the F is the more significant effect the factor has on the response. As the ANOVA calculation for ethylene shows, some squared terms such as B², C² are proved to be more significant than factors B and C alone. This can be also inferred for the propylene from its ANOVA calculation. The squared term, C², is much more significant compared with the other square terms, even with the key factor, C.

From a combination of estimates for the variables and the ANOVA results, a polynomial model with statistical significance can be generated. This model is presented as follows:

$$\text{Ethylene} = 178.56 - 0.89X_A + 3.98X_B + 5.45X_C - 5.56 \times 10^{-3}X_AX_B + 7.64 \times 10^{-4}X_A^2 - 0.05X_B^2 - 0.13X_C^2 \quad (1)$$

$$\text{Propylene} = -1473.42 + 2.59X_A + 60.28X_B + 3.91X_C$$

**Fig. 3. The yield of ethylene, propylene and conversion of naphtha as a function of temperature.**

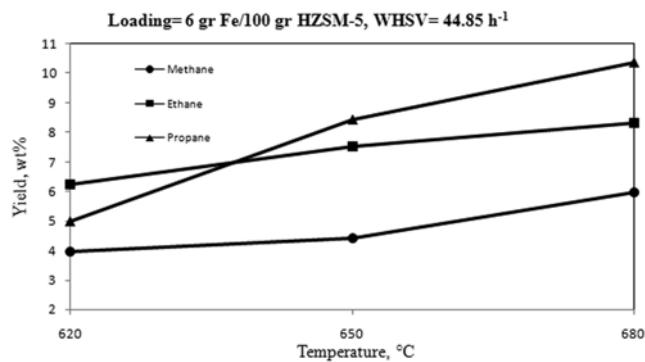
$$\begin{aligned} & -0.08X_AX_B - 7.56 \times 10^{-3}X_AX_C + 0.07X_BX_C \\ & - 7.67 \times 10^{-4}X_A^2 - 0.79X_B^2 - 0.17X_C^2 + 1.09 \times 10^{-3}X_AX_B^2 \end{aligned} \quad (2)$$

X_i denotes the actual variables for factor (i.e., A, B, and C). Note in Eqs. (1) and (2) that the terms with statistical significance were only considered in the models based on analysis of variance. The R² value equal to 0.982 for Eq. (1) indicates a very good fitting for the experimental data of ethylene. The R² value of Eq. (2) is 0.995, also indicating a fitting with high precision for the experimental data of propylene on specified factors.

2. Effect of Process Variables on the Yield of Main Products

The yields of ethylene and propylene in the catalytic cracking of naphtha over Fe-modified HZSM-5 catalysts as a function of reaction temperature are shown in Fig. 3. The yield of ethylene increases with the temperature increasing, while the yield of propylene initially increases with the temperature and reaches a maximum value at 650 °C, and then drops with the reaction temperature. The combined yield of ethylene and propylene increases monotonically with temperature and reaches a maximum value 43.26 wt% at 680 °C. Furthermore, the conversion of naphtha increases with the temperature.

Fig. 4 shows the yields of alkanes as a function of temperature. As shown, the yields of alkanes have the same trend with conversion; they increase with increasing the temperature. The yield of propane increases from 5 to 10.23 wt% when the temperature rises to 680 °C from 620 °C; therefore, it shows a high dependency on the reaction temperature.

**Fig. 4. The yield of alkanes as a function of temperature.**

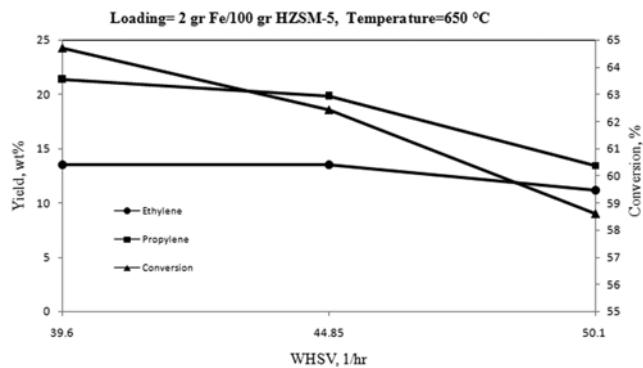


Fig. 5. The yield of ethylene, propylene and conversion of naphtha as a function of WHSV.

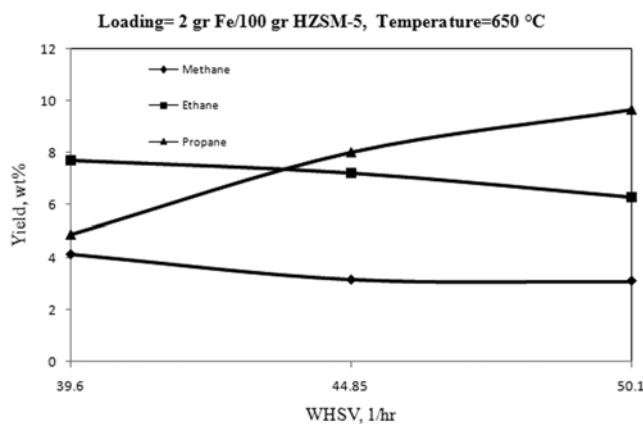


Fig. 6. The yield of alkanes as a function of WHSV.

The effect of WHSV on the conversion of catalyst and product distribution is presented in Figs. 5 and 6. The conversion over 6%Fe/HZSM-5 is relatively large at small values of WHSV and decreases moderately for high values of WHSV. Conversion of naphtha decreased from 64.7% to 58.61% when WHSV increased from 39.6 hr^{-1} to 50.1 hr^{-1} .

The product distribution as a function of WHSV changed significantly. From Fig. 5, the propylene yield shows an optimum at WHSV of 44.85 hr^{-1} and it reaches to 14.2 wt%. Propylene is produced from the secondary reactions. Therefore, decreasing of WHSV results in increasing the residence time and the time which the propylene remains in the reaction. Consequently, it causes the propylene to be cracked more in the process and produces lighter hydrocarbons. The yields of ethylene, methane and ethane monotonously decrease with the increase in WHSV, while the yield of propane shows a different trend. More propane is produced when the residence time is decreased.

The influence of loading amount of Fe over HZSM-5 catalyst on the yields of main products is shown in Fig. 7. The yields of ethylene and propylene over 2, 6, 10% Fe/HZSM-5 samples were apparently higher than unmodified HZSM-5 sample at 680 $^{\circ}\text{C}$. Both ethylene and propylene show an optimum at 6 wt%. Moreover, Fig. 7 shows that the conversion on HZSM-5 without any Fe loading is 61.2 wt%, while the conversion rapidly increased to 73.9 wt% with increasing the Fe loading up to 6 wt%, and then decreased slightly

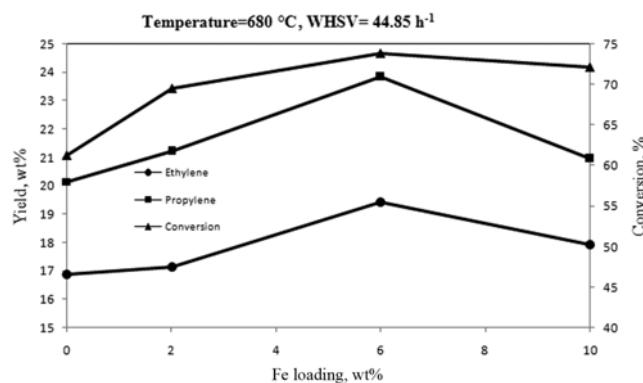


Fig. 7. The yields of ethylene and propylene and conversion of naphtha as a function of Fe loading.

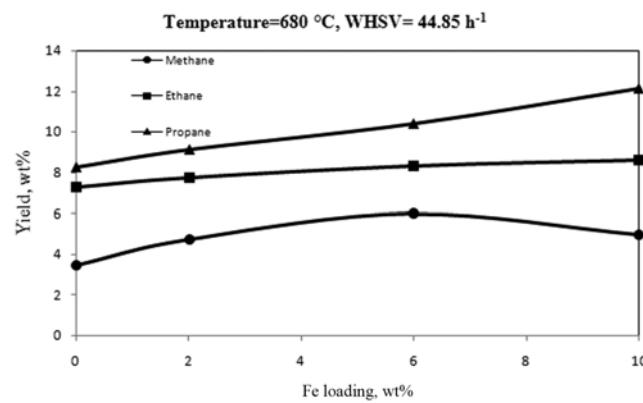


Fig. 8. The yield of alkanes as a function of Fe loading.

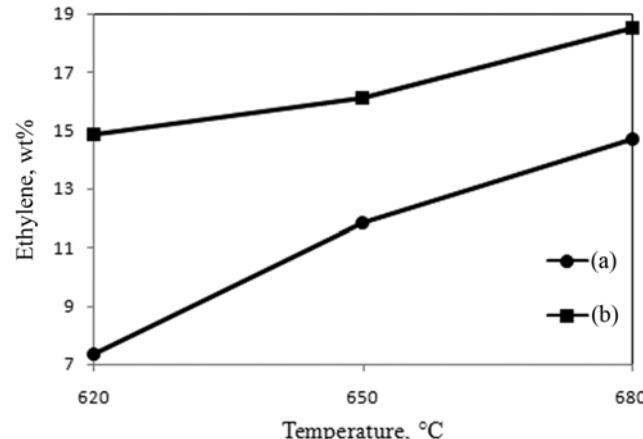


Fig. 9. The yield of ethylene in (a) Thermal Cracking, (b) TCC over Fe/HZSM-5 as a function of temperature.

to 72.14% at 10 wt% Fe. It indicates that high loadings of Fe favored the formation of alkanes, so that it resulted in lower amount of light olefins. As shown in Fig. 8, the yields of ethane and propane increase with increasing the loading and reach 8.58 and 12.15 wt%, respectively. Therefore, the catalytic performance of Fe/HZSM-5 depended significantly on the Fe loading. Methane also has the same trend of ethylene and propylene; it shows an optimum at 6 wt% Fe.

In Figs. 9 and 10 the yield of ethylene and propylene in thermal

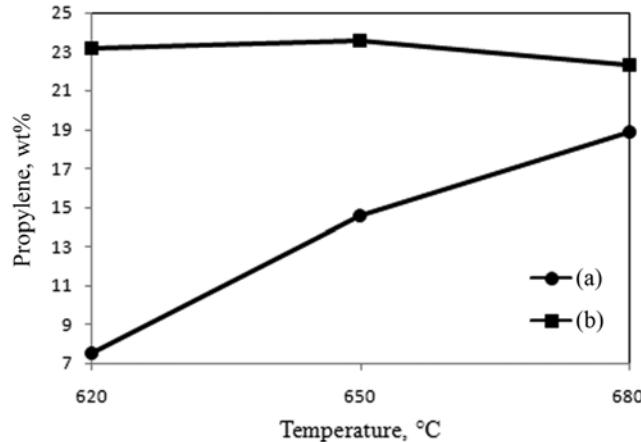


Fig. 10. The yield of propylene in (a) Thermal Cracking, (b) TCC over Fe/HZSM-5 as a function of temperature.

cracking and thermal-catalytic-cracking of naphtha over Fe/HZSM-5 catalyst is compared. The experimental conditions in both processes were the same (naphtha flowrate=1.32 gpm, S.R=0.5, WHSV=39.6 hr^{-1}). It is seen that catalyst has a significant effect on the yields of olefins. For instance, at $T=650$ °C the yield of ethylene and propylene in cracking of naphtha over Fe/HZSM-5 compared with thermal cracking 5.7 wt% increased. In thermal cracking at 680 °C, $C_2+C_3=33.59$ wt%, while it increases to 40.87 wt% in thermal catalytic cracking.

3. Contour Plots

Contour plots can be used to study the effect of process variables on the yield of ethylene and propylene in wider range of operating conditions. Furthermore, they can also be used for designing an optimum catalyst for the thermal catalytic cracking of naphtha. Eqs. (1) and (2) were used to construct the contour plots for the yields (in wt%) of ethylene and propylene against temperature, WHSV and Fe loading as shown in Figs. 11 and 12. In these figures the third factor is held at the midpoint.

From Fig. 11, the yield of ethylene is significantly increased with simultaneous increase of temperature. At low temperatures, the yield of ethylene as a function of both WHSV and Fe loading has an optimum. At 620 °C, the increase of WHSV results in increasing of ethylene yield and it reaches to a maximum at 15.18 wt% from 14.62 wt% at 43.13 hr^{-1} . Further increase of WHSV causes a sharp drop of 2.24 wt% in the yield of ethylene. This trend can also be seen for the change of ethylene yield by altering Fe loading. At 620 °C, the yield of ethylene has a sudden increase of 4.05 wt% by increasing of Fe loading from 2 to 7.54 wt%. It shows the effect of Fe active sites in the cracking of naphtha. The yield of ethylene decreased to 14.49 wt% from 15.37 wt% by further increase of Fe loading to 10 wt%. Fig. 11(c) clearly shows that a maximum yield of ethylene, 16.78 wt%, occurs at 6.84 wt% Fe and 43.05 hr^{-1} when the temperature is held constant at midpoint, 650 °C.

As shown in Fig. 12, the yield of propylene has an optimum amount with respect to temperature, WHSV and Fe loading. At moderate loadings, the yield of propylene reaches a maximum amount. At 6 wt% Fe and 42.29 hr^{-1} , the increasing of temperature up to 652 °C results in a maximum amount of propylene, 24.08 wt%. The increasing of WHSV or decreasing of residence time also has favor-

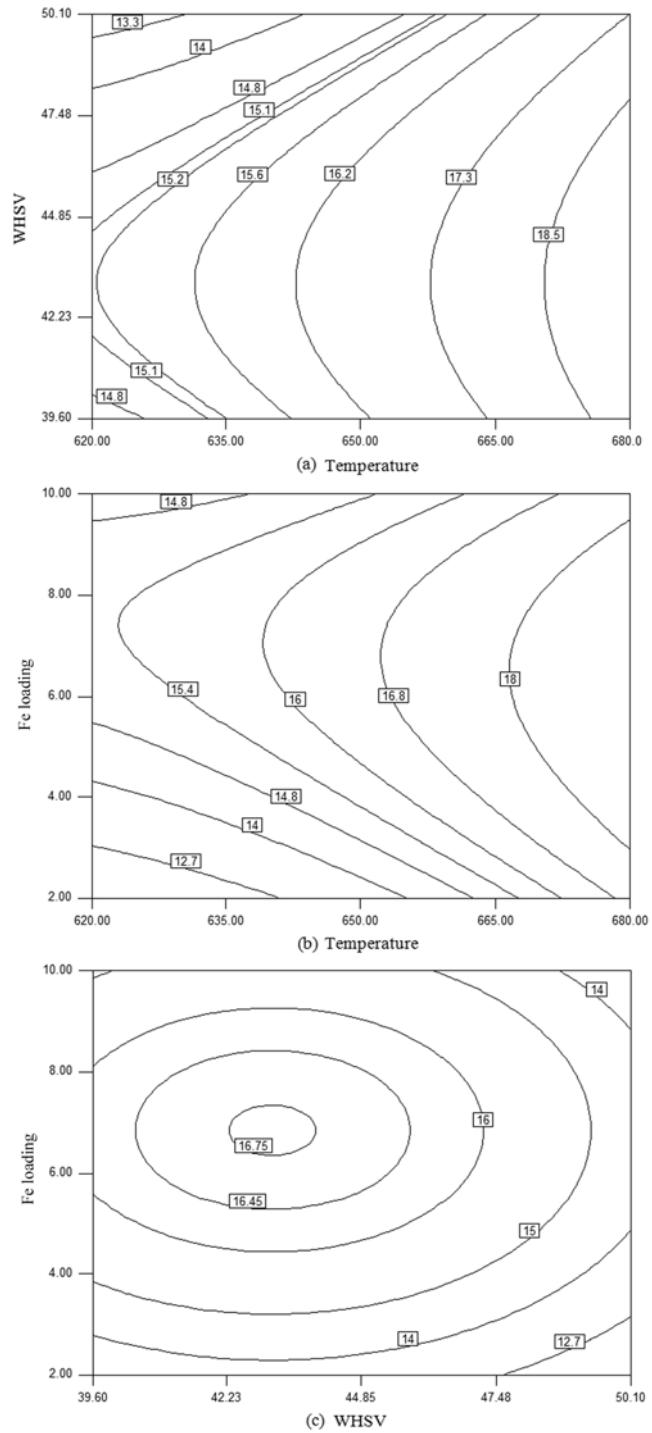


Fig. 11. Contour plots describing the response surface for ethylene as a function of (a) temperature vs. WHSV at Fe loading = 6 wt%, (b) temperature vs. Fe loading at WHSV = 44.85 hr^{-1} , (c) WHSV vs. Fe loading at temperature = 650 °C.

able effect on the yield of propylene. The yield of propylene increases when WHSV reaches to 42.29 hr^{-1} . Then it decreases significantly to 13.97 wt% by increasing of WHSV to 50.1 hr^{-1} .

These contour plots facilitate a straightforward optimization of single responses such as ethylene or propylene yield. However, considering the maximization of the yields of ethylene and propylene

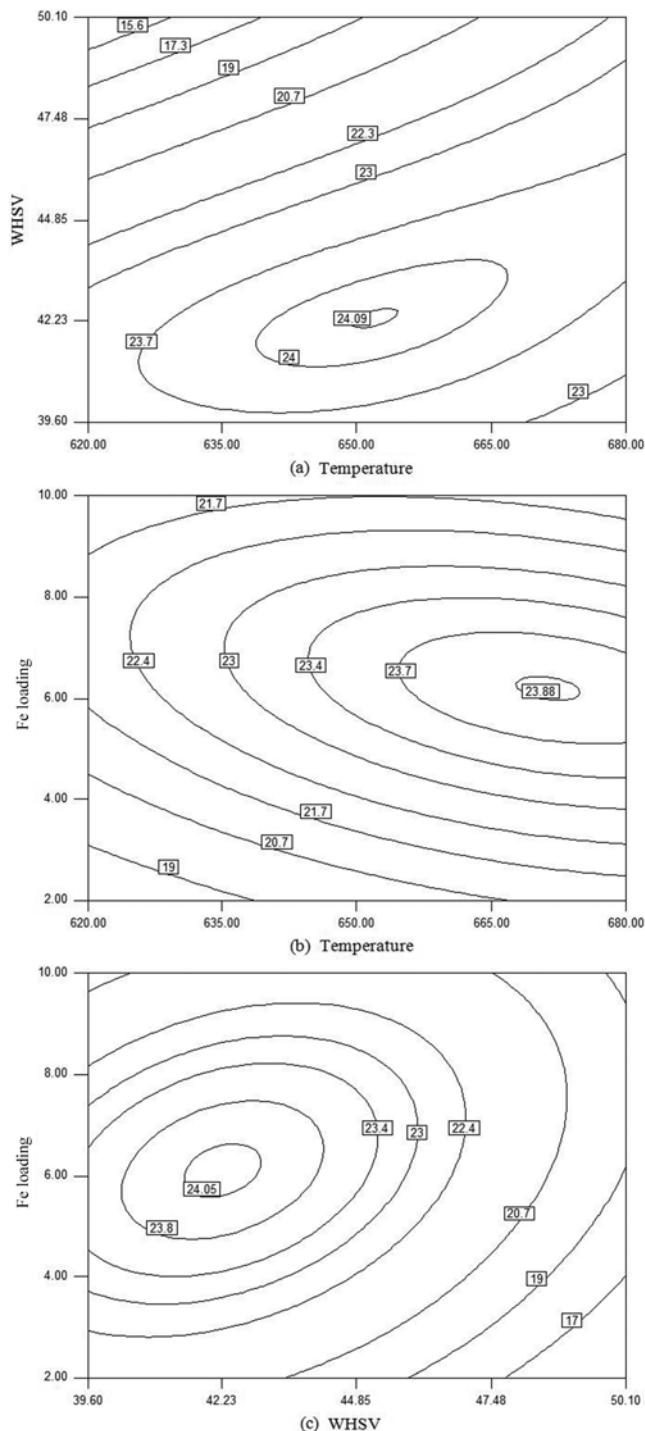


Fig. 12. Contour plots describing the response surface for propylene as a function of (a) temperature vs. WHSV at Fe loading=6 wt%, (b) temperature vs. Fe loading at WHSV=44.85 hr⁻¹, (c) WHSV vs. Fe loading at temperature=650 °C.

simultaneously is of primary importance. Eqs. (1) and (2) are used for analytical maximization of ethylene and propylene. The complete method of optimization used in this paper is clearly described in our previous works [14,15]. In our case the optimum was found at temperature=670.82 °C, WHSV=43.71 hr⁻¹ and Fe loading=6.01 wt%. This set gave the predicted ethylene yield=18.52 wt% and

propylene yield=23.95 wt%. This run was repeated three times to check the reproducibility of the optimum. No significant deviations were found from the values reported. This optimum point of multi-objective optimization is in accordance with the discussion given for the single response optimization. The value optimized for temperature was toward its upper limit to boost higher yield of ethylene and propylene. Temperature has an opposing effect on the yields of ethylene and propylene; high temperature maximizes ethylene production, while moderate temperature maximizes propylene production. The yield of ethylene and propylene had nearly the same trend as a function of WHSV and Fe loading. Both reach a maximum at nearly moderate WHSV or loading.

CONCLUSIONS

The successful application of response surface methodology for designing an optimum catalyst has been reported. Three key factors affecting the performance, namely temperature, WHSV and loading were selected and optimized using the Box-Behnken design method. ANOVA results show that the most significant factor affecting the yield of ethylene is temperature and the one affecting the yield of propylene is WHSV. Moreover, some higher interactions are proved to be significant and should be considered in the modeling of thermal catalytic cracking over Fe/HZSM-5.

Compared with the unmodified HZSM-5, Fe/HZSM-5 catalysts had higher yields of ethylene and propylene at the same operating conditions. The addition of Fe should be done up to a certain amount of Fe loading, as high loadings favored the formation of aromatics and resulted in reduction of the yield of light olefins. With increasing temperature, the yield of light olefins increases; however, the single trend of ethylene or propylene is different. Furthermore, the maximum amount of light olefins occurs at moderate WHSV. The optimization indicates that the maximum amount of light olefins reached to 42.47 wt%.

ACKNOWLEDGEMENT

The authors would like to thank the financial support from the Chemical Engineering Center in Tarbiat Modares University. The financial support by INSF is also gratefully acknowledged.

NOMENCLATURE

WHSV : weight hourly space velocity

TCC : thermal catalytic cracking

A : temperature [°C]

B : Fe loading (g Fe/100 g HZSM-5)

C : WHSV [hr⁻¹]

REFERENCES

1. B. G. Anderson, R. R. Schumacher, R. van Duren, A. P. Singh and R. A. van Santen, *J. Mol. Catal. A: Chem.*, **181**, 291 (2002).
2. Q. Shao, P. Wang, H. Tian, R. Yao, Y. Sun and J. Long, *J. Catal. Today*, **147S**, S347 (2009).
3. K. Keyvanloo and J. Towfighi, *J. Anal. Appl. Pyrol.*, **88**, 140 (2010).
4. Y. Wei, Z. Liu, G. Wang, Y. Qi, L. Xu, P. Xie and Y. He, *Stud. Surf.*

Sci. Catal., **158**, 1223 (2005).

5. S. M. Jeong, J. H. Chae and W.-H. Lee, *Ind. Eng. Chem. J.*, **40**, 6081 (2001).

6. K. K. Pant and D. Kunzru, *Chem. Eng. J.*, **87**, 219 (2002).

7. Y. Yoshimura, N. Kijima, T. Hayakawa, K. Murata, K. Suzuki, F. Mizukami, K. Matano, T. Konishi, T. Oikawa, M. Saito, T. Shiojima, K. Shiozawa, K. Wakui, G. Sawada, K. Sato, S. Matsuo and N. Yamaoka, *J. Catal. Surveys from Japan*, **4**, 157 (2000).

8. W. Xiaoning, Zh. Zhen, X. Chunming, D. Aijun, Zh. Li and J. Guiyuan, *J. Rare Earths*, **25**, 321 (2007).

9. L. Li, J. Gao, Ch. Xu and X. Meng, *Chem. Eng. J.*, **116**, 155 (2006).

10. J. Lu, Zh. Zhao, Ch. Xu, A. Duan and P. Zhang, *J. Catal. Lett.*, **109**, 65 (2006).

11. X. Li, B. Shen and Ch. Xu, *J. Appl. Catal. A: Gen.*, **375**, 222 (2010).

12. K. Wakui, K. Satoh, G. Sawada, K. Shiozawa, K. Matano, K. Suzuki, T. Hayakawa, Y. Yoshimura, K. Murata and F. Mizukami, *J. Catal. Lett.*, **84**, 259 (2002).

13. G. Jiang, L. Zhang, Zh. Zhao, X. Zhou, A. Duan, Ch. Xu and J. Gao, *J. Appl. Catal. A: Gen.*, **340**, 176 (2008).

14. K. Keyvanloo, J. Towfighi, S. M. Sadrameli and A. Mohamadalizadeh, *J. Anal. Appl. Pyrol.*, **87**, 224 (2010).

15. M. Sedighi, K. Keyvanloo and J. Towfighi, *Korean J. Chem. Eng.*, **27**(4), 1170 (2010).