IRANIAN JOURNAL OF CATALYSIS

Optimization of main parameters affecting activity and octane number produced from catalytic isomerization of n-heptane using response surface methodology

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Received 19 February 2023; received in revised form 24 May 2023; accepted 29 June 2023 (**DOI: 10.30495/IJC.2023.1980650.1994**)

ABSTRACT

In this work, the Response Surface Methodology (RSM) was investigated by applying the Design of the Experiment in normal heptane isomerization. The design was guided to three surface responses on the dependency of normal heptane conversion, isomerization selectivity, and research octane number on the reaction temperature (200 - 350 °C), the weight percentage of protonated Zeolite Socony Mobil–5 (HZSM-5) zeolite in catalyst structure (10 - 40 weight percent) and time on stream (1 - 6 h). The Analysis of Variance for Pt-supported micro/mesoporous catalysts indicated that the reaction temperature was the prominent significant variable in normal heptane conversion, the development of isomers, and research octane number followed by weight percent of HZSM-5 and time on stream. The optimum research octane number predicted from the response surface analysis is ~ 61 at the reaction temperature of 350 °C, weight percent of HZSM-5 of 25%, and time on stream of 1 h.

***Keywords**: Analysis of Variance, Design of Experiment; n-Heptane isomerization; Response Surface Methodology; Research octane number*

1. Introduction

Catalytic isomerization involves mono- or multi-branched isomerization of hydrocarbons to improve the quality and combustion properties of gasoline. It increases the research octane number (RON) of linear hydrocarbons, which is a good substitute for polluting aromatics [1, 2]. The properties of pretreated gasoline with isomerization reaction are influenced by different variables, including temperature, hydrogen pressure, time on stream (TOS), and catalyst type. Among these parameters, the catalyst type has been considered the most important factor [3]. Conventional isomerization at a laboratory scale is carried out in a fixed bed reactor at low temperature and 1 atm pressure using a bifunctional catalyst [2]. Platinum (Pt) metal has been reported to be effective in the isomerization process owing to its ability to reduce the deactivation of catalysts by coke, good hydrogen transfers, and also because it can be effective on acid sites [2, 3]. Pt performance can be performed in combination with other metals. For example, the alteration of the monometallic Pt-supported catalysts using a small amount of other metals such as Re [4, 5], Sn [4], W [6, 7], Mo [8], Cr [9, 10], Zr [6, 8], and etc. can change its attributes. However, the use of Pt-supported micro-mesoporous composites in the area of n-heptane isomerization has been more or less reported [2, 11-13].

The RON is an important property of gasoline quality, indicating an anti-knock index of gasoline to evaluate fuel performance under severe engine operation. Isomerization is one of many processes with low gasoline octane numbers and better environmental impacts. In the area of catalytic isomerization, the RON decreases during the decrease in C = C bonds of aromatics in the existence of hydrogen. It is used for monitoring the catalyst activity. The rate of RON is connected to the nature of the feed (hydrocarbon), operating conditions, and catalyst type [2-4]. The aromatics in fuel have been observed to be harmful to human health. This content is strongly correlated with the hydrogenation and the reaction conditions, but RON can be minimized by this process that changes by isomerization reaction and catalyst development reduces the decline in RON amount [2-4].

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However, our previous studies [2-4] have not considered the modeling of isomerization process with n-heptane as a function of various variables. Here the various variables affecting the activity and octane numbers produced by the isomerization reaction of n-heptane and minimize the aromatization activity over Pt-supported HZSM-5/HMS catalysts were analyzed and optimized by applying the Design of Experiment (DOE) of the response surface methodology (RSM). This method [9, 10, 14, 15] helps to reduce the number of runs and the time required for model-building and statistical analysis.

In 2021, Parsafard *et al.* [10] optimized the kinetic parameters for the isomerization reaction of n-heptane on the novel platinum-chromium/zirconium- hexagonal mesoporous silica. This research evaluated the simultaneous effect of process conditions such as reaction temperatures, Cr/Zr molar ratio, the n-C_7 flow rate, and the H_2 flow rate by using the response surface method.

Hasanudin *et al.* [16] were used the response surface method to study the effects of the process variables, such as temperature, contact time, and catalyst-to-feed ratio, on conversion, oil, gas, and coke yield. Their study showed that the RSM is a suitable method for estimating the hydrocracking process of palm oil to bio-gasoline and bio-aviation fuels using an MoN-bentonite catalyst.

Hamied *et al.* [17] were also investigated the kinetic modeling of light naphtha hydroisomerization over a Pt/Al_2O_3-Cl catalyst. They used a genetic algorithm stochastic optimization technique.

The influence of operating conditions such as temperature and time on stream and also a textural property of catalyst as the HZSM-5 amount on catalytic performance were collected from our reported work [2] over a 6-hour period based on the catalyst lifetime. These data were then applied to predict the influence of these conditions on the research octane number using the RSM approach (Design Expert software). Thus, the activity and RON were predicted under various conditions.

2. Experimental

2.1. Catalyst preparation

Pt-HZSM-5/HMS catalysts were prepared by the wet impregnation method. The HZSM-5 was impregnated using the precursor solutions of HMS via a method similar to that used by Parsafard et al. [2]. Prior to Pt impregnation, all catalysts were calcined at 600 °C for 6 h in air. The platinated catalyst samples were prepared by impregnation of the H_2PtCl_6 aqueous solution. After calcination of Pt catalysts at 300 °C for 4 h, these catalysts were loaded in the reactor (Pyrex fixed bed microreactor) for taking place the isomerization reaction. The used catalysts composed of dual functions includes of the Pt(0.6 wt %) species as active metallic sites, supported on HZSM-5/HMS composite with different HZSM-5. These prepared catalysts with different HZSM-5 weights (10, 20, 30 & 40 wt%) were named as PZH-10, PZH-20, PZH-30, and PZH-40, respectively. A detailed description of the catalyst preparation and structural investigation can be seen in the literature [2] and Supplementary Information section.

2.2. Experimental design and optimization

In this study, statistical examination of n-heptane conversion (equation 1), isoheptane selectivity (equation 2), and research octane number (equation 3) in isomerization reaction was performed using Design-Expert Software V.11.

$$\text{Conv.}(\%) = \text{the percentage of the total amount of n} - C_7 \text{ converted} \quad (1)$$

$$S_i(\%) = \frac{\text{n}-C_7 \text{ converted to isoheptane products}}{\text{total amount of n}-C_7 \text{ converted}} \times 100 \quad (2)$$

$$\text{RON} = \sum_{i=1}^{k} \mathbf{y_i RON_i} \quad (3)$$

where RON: is the measured octane number for total hydrocarbons, RONi: is the pure-component octane number for each molecule i, and yi: is the volume fractions of reaction products.

The Box-Behnken was utilized to study the interplay of process variables and to predict the optimum process condition for n-heptane isomerization by applying RSM. The reaction temperature (A: T, °C), time on stream (B: TOS, h), and the weight percent of HZSM-5 in catalyst structure (C: WZ, %) were utilized as independent variables. The reaction temperature is referred to the temperature used during the isomerization process, while time on stream refers to the time used during this reaction under hydrogen and n-heptane streams. The third variable is the weight percent of HZSM-5 (WZ) in the structure of composite catalysts. The range of these variables and their coded levels are listed in **Table 1**. These independent variables were coded to the (-1, 1) interval. These variables were selected based on the findings of the earlier study that has been reported in Ref. [2]. The quadratic equation model is used according to the equation below [18]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{n} \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

Where $\boldsymbol{y}$ is the measured response, $\boldsymbol{\beta_0}$ is the intercept term, $\boldsymbol{\beta_i}$, $\boldsymbol{\beta_{ii}}$, and $\boldsymbol{\beta_{ij}}$ are the measure of the influence of the variables $\boldsymbol{x_i}$, $\boldsymbol{x_i^2}$, and $\boldsymbol{x_i x_j}$, respectively, and $\boldsymbol{\varepsilon}$ is the noise or error observed in the response.

3. Results and Discussion

3.1. n-Heptane conversion model and ANOVA analysis

The experiments were performed according to the designed matrix in **Table 1**. Multiple regression analysis was performed according to equation 4. Also, equation 5 represents the response surface model of *n*-heptane conversion.

$$Conv.(\%) = +76.73 + 19.37x_1 - 7.16x_2 + 1.78x_3 + 0.09x_1x_2 - 1.17x_1x_3 - 0.10x_2x_3 - 2.88{x_1}^2 - 2.33\,{x_2}^2 - 15.02{x_3}^2 \quad (5)$$

where, Conv. is the total percentage of the n-heptane (n-C_7) conversion of catalytic products.

According to the regression coefficients of equation 5, **Fig. 1** shows a suitable fit between the observed and the actual values (R^2=0.80). The fitness of this model was tested with ANOVA. From **Table 2**, the calculated Fisher test (F) value for n-heptane conversion model is 7.77, showing that this model is significant at the 95% confidence level.

Table 1. Central composite design matrix and experimental results.

	factors			responses		
RUN	x_1: [T, 200-350 °C]	x_2: [TOS, 1-6 h]	x_3: [WZ, 10-40%]	Conv.(%)	S_{iso}(%)	RON
1	275	6	40	53.05	5.47	21.83
2	200	3.5	10	39.10	22.10	3.48
3	275	1	40	70.05	4.95	28.70
4	275	3.5	25	75.61	16.43	34.66
5	350	3.5	40	76.20	0.11	46.87
6	275	3.5	25	64.46	19.79	35.98
7	350	6	25	87.25	8.09	54.31
8	200	1	25	55.95	33.80	16.15
9	275	3.5	25	92.34	14.19	34.66
10	200	3.5	40	44.20	18.79	9.20
11	350	3.5	10	75.80	6.80	30.93
12	200	6	25	43.95	26.63	12.84
13	275	3.5	25	75.61	16.43	33.77
14	350	1	25	98.90	9.20	61.45
15	275	3.5	25	75.61	16.43	34.66
16	275	6	10	48.90	11.24	12.79
17	275	1	10	65.50	15.2	16.95

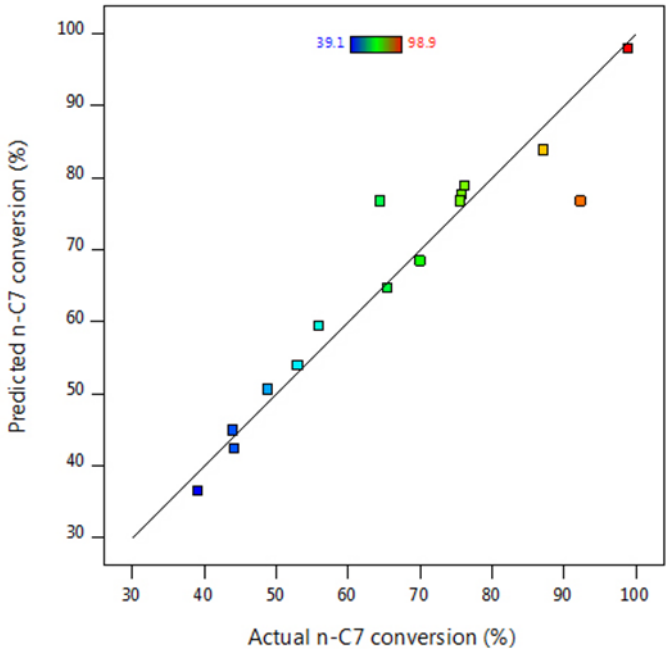

Fig. 1. Comparison between predicted and actual values for n-heptane conversion.

Table 2. ANOVA results for n-heptane conversion model.

Source	Sum of Squares	df	Mean Square	F-value	p-value ($\times 10^{-2}$)	
Model	4495.46	9	499.50	7.77	0.66	significant
x_1 (T)	3001.19	1	3001.19	46.66	0.02	
x_2 (TOS)	409.70	1	409.70	6.37	3.96	
x_3 (WZ)	25.20	1	25.20	0.39	55.12	
x_1x_2	0.03	1	0.03	0.00	98.32	
x_1x_3	5.52	1	5.52	0.08	77.80	
x_2x_3	0.04	1	0.04	0.00	98.08	
x_1^2	34.99	1	34.99	0.54	48.48	
x_2^2	22.91	1	22.91	0.36	56.94	
x_3^2	949.92	1	949.92	14.77	0.64	
Residual	450.29	7	64.33			
Lack of Fit	52.16	3	17.39	0.17	90.83	not significant
Pure Error	398.13	4	99.53			
Cor Total	4945.75	16				

The significance of regression coefficients for this model was shown according to their F- and p-values in **Table 2**. The lower p-value [19] with a higher F- value indicates the highly significant reaction temperature (x_1) in this model. The Lack of Fit F-value of 0.17 suggests the absence of Fit is not significant relative to the pure error. There is a 90.83% possibility that a Lack of Fit F-value this large could occur owing to noise. Non-significant lack of fit is good to fit the model.

Fig. 2 presents the 3-D graphical surface plot of n-heptane conversion of temperature and time on stream. This figure demonstrates that the high reaction temperature results in an increase in n-heptane conversion.

Moreover, it can reveal from **Fig. 3** of the 3D plot depicted in fixed TOS that increasing the temperature resulted in an increase in conversion.

3.2. Isomerization selectivity model and ANOVA analysis

The examinations of the reaction variables in the n-heptane isomerization were done in order to increase the isomerization selectivity of n-heptane. A predicted link between isomerization selectivity and the reaction variables in coded factors is given in equation 6.

$$S_{iso}\ (\%) = +16.65 - 9.64x_1 - 1.46x_2 - 3.25x_3 + 1.52x_1x_2 - 0.84x_1x_3 + 1.12x_2x_3 + 2.76{x_1}^2 +$$

$0.02\ {x_2}^2 - 7.46{x_3}^2$
(6)

where S_{iso} is the predicted values with RSM for the n-C_7 isomerization selectivity.

Also, the empirical model developed in equation 4 by applying a multiple regression method was fitted to the experimental data (**Fig. 4**).

Based on the determination coefficient (R^2=0.93), there is an acceptable agreement between the predicted and actual i-C_7 selectivity. In this model, the determination coefficient R^2 is higher than in the n-C_7 conversion model. Therefore, the i-C_7 selectivity model displays a better fit than the n-C_7 conversion model.

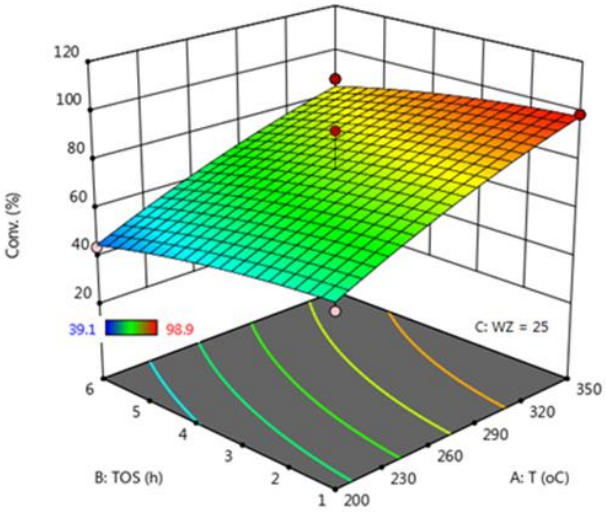

Fig. 2. 3D Response surface plot for the n-heptane conversion as function of temperature and time on stream at 25% weight of HZSM-5.

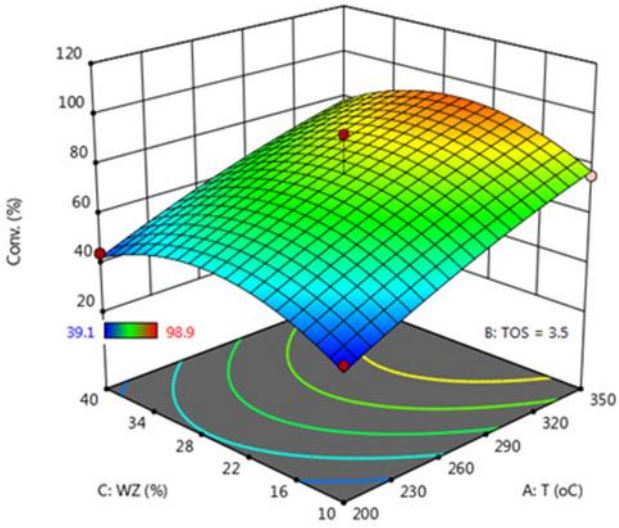

Fig. 3. 3D Response surface plot for the n-heptane conversion as function of weight of HZSM-5 and temperature at 3.5 h on stream.

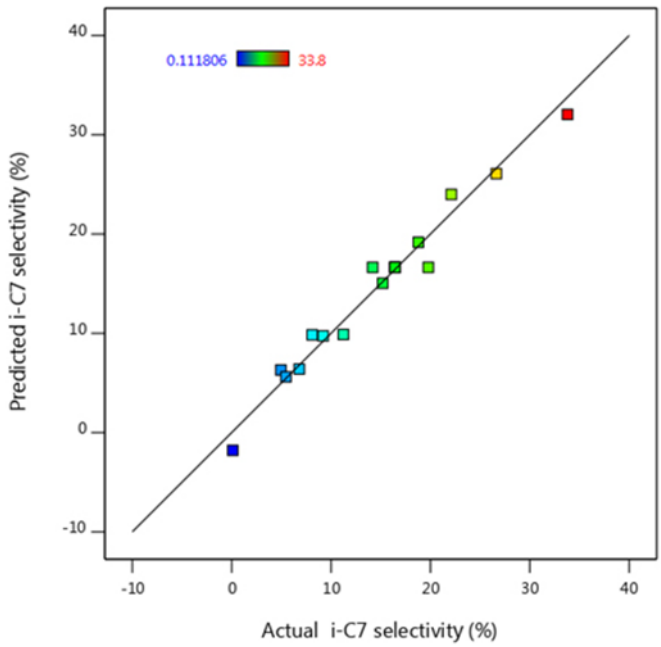

Fig. 4. Comparison between predicted and actual i-C_7 selectivity.

The suitability of the model can be concluded from **Table 3** with the examination of variance. The Model F-value of 25.62 implies the model is significant. The Lack of Fit F-value of 1.49 implies the Lack of Fit is not significant relative to the pure error. Also, P-values less than 0.05 indicate model terms are significant. In this case, A, C, A^2, and C^2 are significant in model terms. Values greater than 0.10 indicate the model terms are not significant. According to the obtained results, the reaction temperature is the highly influential parameter on the i-C_7 selectivity.

The 3D plot presented in **Fig. 5** shows the predicted i-C_7 selectivity over the reaction temperature and TOS at fixed WZ. It can be discovered from the Figure that low reaction temperature with almost low TOS results in a high i-C_7 selectivity. This is owing to the fact that linear chain hydrocarbons are well converted into branched hydrocarbons at low temperatures, which are thermodynamically advantaged. So, the low reaction temperature is selective to enhance isomerization activity.

Fig. 6 shows the 3D plots of the i-C_7 selectivity with the variables while one parameter is fixed. It can be observed a maximum point for i-C_7 selectivity when the HZSM-5 amount in catalyst structure (WZ) changes.

Table 3. ANOVA results Table for i-C_7 selectivity.

Source	Sum of Squares	df	Mean Square	F-value	p-value ($\times 10^{-2}$)	
Model	1120.33	9	124.48	25.62	0.02	significant
x_1 (T)	743.34	1	743.34	152.98	< 0.01	
x_2 (TOS)	17.16	1	17.16	3.53	10.23	
x_3 (WZ)	84.62	1	84.62	17.41	0.42	
x_1x_2	9.19	1	9.19	1.89	21.14	
x_1x_3	2.84	1	2.84	0.58	46.95	
x_2x_3	5.01	1	5.01	1.03	34.35	
x_1^2	31.99	1	31.99	6.58	3.72	
x_2^2	0.21×10^{-2}	1	0.21×10^{-2}	0.04×10^{-2}	98.40	
x_3^2	234.34	1	234.34	48.23	0.02	
Residual	34.01	7	4.86			
Lack of Fit	17.94	3	5.98	1.49	34.55	not significant
Pure Error	16.08	4	4.02			
Cor Total	1154.35	16				

3.3. Research octane number (RON) model and ANOVA analysis

The optimal values of the three used variables in the Pt-HZSM-5/HMS catalysts such that maximum RON is achieved with a maximum isomerization activity. The coefficients of this model were developed based on equation 4. The quadratic mathematical model of RON is represented in equation 7.

$$RON = +34.75 + 18.99x_1 - 2.68x_2 + 5.31x_3 - 0.96x_1x_2 + 2.56x_1x_3 - 0.68x_2x_3 - 2.00{x_1}^2 - 0.55\,{x_2}^2 - 14.12{x_3}^2 \quad (7)$$

The fitness of this model was also arbitrated from the determination of the correlation coefficient value, R^2. The R^2 value closer to unity indicates the better model and its better prediction to the real value. In this case, the value of R^2 = 0.97 demonstrates that there is an excellent agreement between the actual and predicted values of RON from the fitted model (**Fig. 7**).

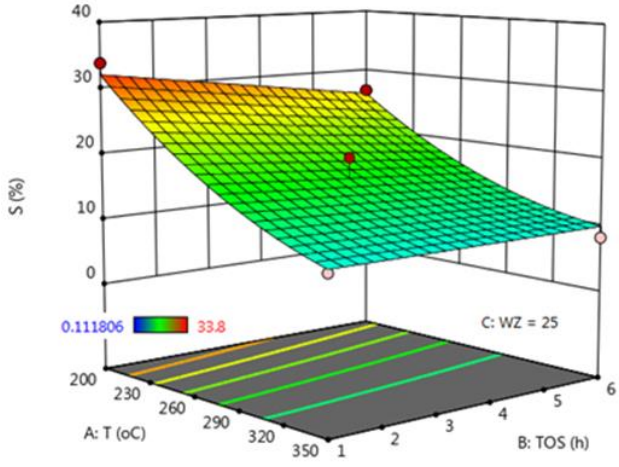

Fig. 5. Comparison between predicted and actual i-C_7 selectivity.

The F-computed value is a technique for checking the suitability of the RON model. In this study, the Fisher test value for the RON model calculated by ANOVA (**Table 4**) is 51.50, which implies that equation 7 has a good projection of the RON model as a response.

Usually, a p-value of less than < 0.05 is considered to be very significant and contributes primarily towards the responses. Based on **Table 4**, the reaction temperature (x_1) has the major impact on RON.

Fig. 8 represents that RON has been enhanced of up to 50 as the temperature increased up to 320 °C at operating conditions. This can be ascribed to this fact that increasing the reaction temperature preferred the creation of aromatics and other unsaturated hydrocarbons. This is while the TOS is not in support of RON. Probably owing to the deactivation of the catalyst after a period of time by coke deposition.

As shown in **Fig. 9**, decreasing the TOS results in an improvement of the RON. However, the increase of WZ amount indicates a Gaussian diagram with a maximum value. This observation is exactly in accordance with the results obtained in the previous work [2], owing to the specific structural interactions of the synthesized catalyst.

4. Conclusions

The effects of reaction temperature, time on stream, and weight of HZSM-5 in catalyst structure on catalytic n-heptane isomerization process were studied over Pt-HZSM-5/HMS catalysts. Central composite design joined with response surface methodology were utilized in this study. The applied models were examined by

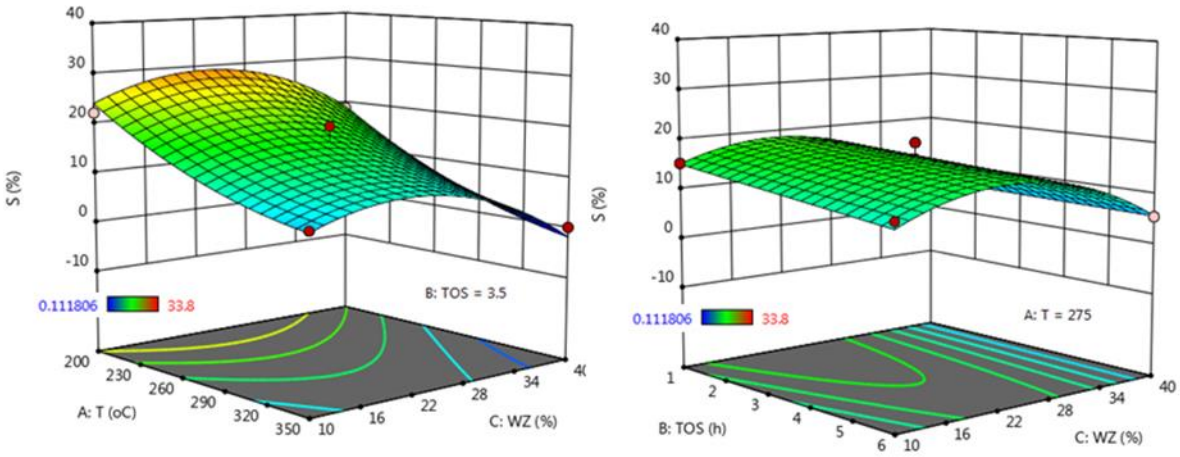

Fig. 6. 3D Response surface plots for the design of i-C_7 selectivity as a function of various parameters depicted at another fixed parameter.

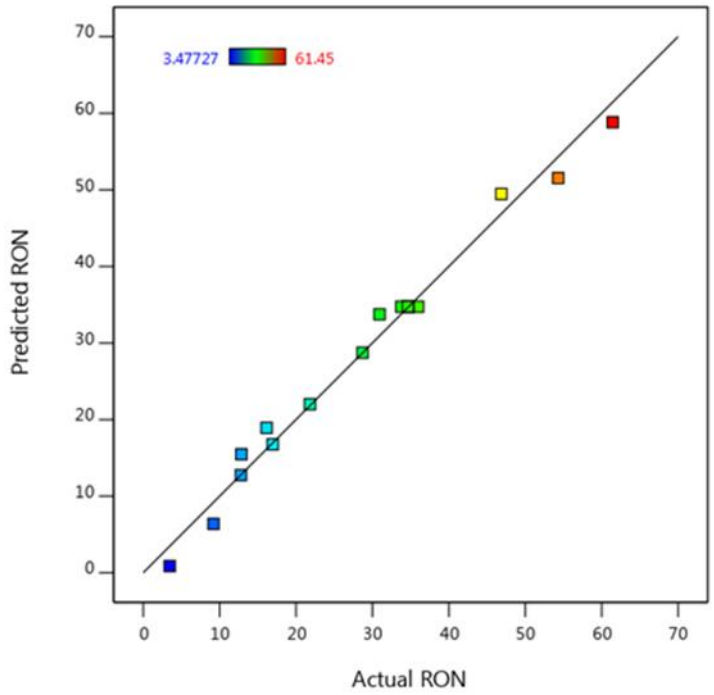

Fig. 7. Comparison between predicted and actual RON values.

Table 4. ANOVA results for RON.

Source	Sum of Squares	df	Mean Square	F-value	p-value ($\times 10^{-2}$)	
Model	4051.51	9	450.17	51.50	< 0.01	significant
x_1 (T)	2883.99	1	2883.99	329.96	< 0.01	
x_2 (TOS)	57.64	1	57.64	6.59	3.71	
x_3 (WZ)	225.27	1	225.27	25.77	0.14	
x_1x_2	3.67	1	3.67	0.42	53.76	
x_1x_3	26.12	1	26.12	2.99	12.75	
x_2x_3	1.84	1	1.84	0.21	66.03	
x_1^2	16.80	1	16.80	1.92	20.82	
x_2^2	1.30	1	1.30	0.15	71.16	
x_3^2	839.95	1	839.95	96.10	< 0.01	
Residual	61.18	7	8.74			
Lack of Fit	58.68	3	19.56	31.28	0.31	significant
Pure Error	2.50	4	0.62			
Cor Total	4112.69	16				

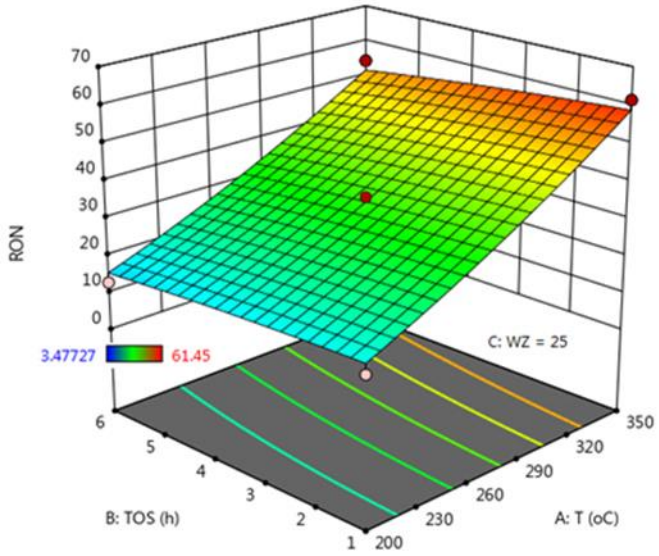

Fig.e 8. 3D plot of RON model under the variable TOS and temperature conditions at a fixed WZ.

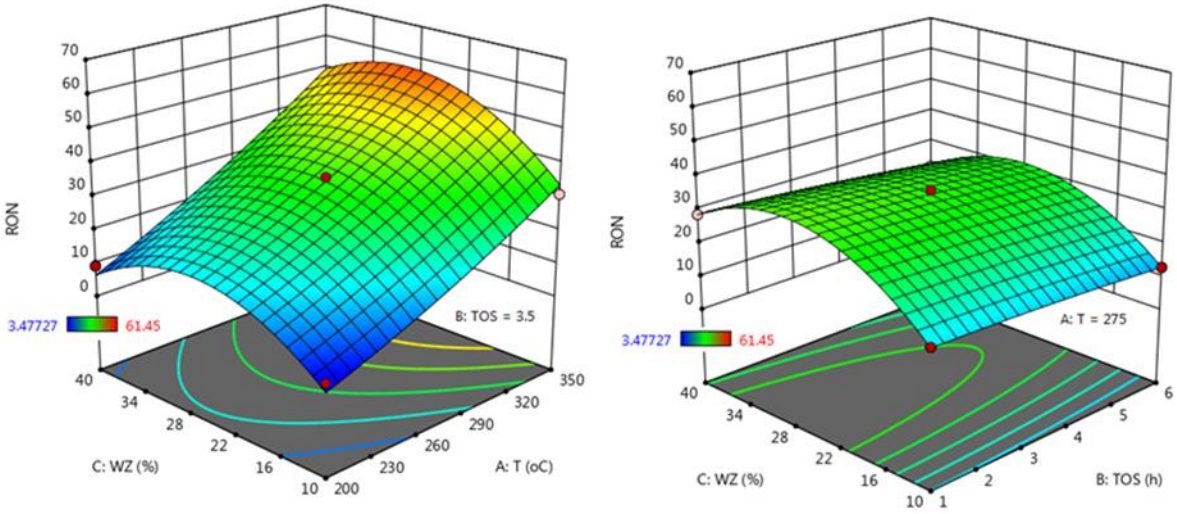

Fig. 9. 3D plot of RON model over the process conditions.

assessment of variance with 95%-degree confidence. The obtained results concluded that the equation models fitted well with the experimental outcomes for n-heptane isomerization to produce optimum n-heptane conversion, iso heptanes selectivity, and research octane number. Numerical results indicated that the maximum RON was ~61 at an optimum reaction temperature of 350 °C, TOS of 1 h, and WZ of 25%.

Acknowledgements

The study was supported by Kosar University of Bojnord with the grant number NO.0111251736.

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