

Modelling and optimization: Isomerization reaction rate using response surface methodology with two kinetic model over bi-porous catalysts

Accepted Manuscript

## Abstract

A response surface methodology (RSM) with three levels and four variables was used to model and optimize the n-heptane isomerization kinetic process over Pt-HZSM-5/HMS catalysts in a fixed bed micro reactor. Thirty sets of isomerization rate tests were performed at different conditions of H<sub>2</sub> flow rate (20-45 ccmin<sup>-1</sup>), n-heptane flow rate (2-4.5 cch<sup>-1</sup>), temperature (200-350 °C), and the weight percent of HZSM-5 (10-40%). It was observed that the amounts of HZSM-5 into Pt-HMS structure has the greatest effect on the reaction rate. The surface and contour plots confirm that the rates do not considerably change versus temperature, n-heptane and H<sub>2</sub> flow rates. The amount of 0.24 molg<sup>-1</sup>s<sup>-1</sup> is the highest reaction rate obtained in the 4.5 cch<sup>-1</sup> n-heptane and 45 cc min<sup>-1</sup> H<sub>2</sub> flow rates. The response surface methodology was effective for predicting and optimizing this process. The modelling results also confirm both power-law model and Langmuir–Hinshelwood mechanism are in good agreement with the experimental data.

**Keywords:** n-Heptane isomerization; Kinetics; Langmuir–Hinshelwood model; RSM-CCD.

## 1. Introduction

The high use of fossil fuels has caused many concerns due to the high release of toxic pollutants during their combustion. These dangerous pollutants are the cause of many adverse effects on organisms [1-5].

Isomerization reaction of hydrocarbons has attracted a renewed attention due to the production of environmentally friendly products without production of pollutants such as aromatics and maintaining the octane number of the fuel. This catalytic reaction starts with linear hydrocarbons to produce mono- and multi-branched hydrocarbons with high octane numbers [1-5].

The catalytic design is a main step in the isomerization reaction of n-paraffins. There are several reports about the application of different catalysts in this process. The reports [1, 6] show hybrid systems have interesting features, high activity and thermal stability in the various catalytic reactions. Accordingly, they have been considered in many researches.

In our previous research [1], the activities of platinum catalysts supported on hexagonal mesoporous silica (HMS) were modified with HZSM-5 accomplished for the n-heptane (n-C<sub>7</sub>) isomerization. A number of characterization analyses were done in this work, including X-ray diffraction (XRD), X-ray fluorescence (XRF), temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD), Fourier-transform infrared spectroscopy (FTIR), H<sub>2</sub> chemisorption, nitrogen sorption, and thermo gravimetric analysis (TGA). Furthermore, the performance of these catalysts was studied in terms of production and selectivity to isomeric, cracking and hydrogenolysis products at various temperatures and time process [1]. Continuing this work, the kinetics of this reaction over Pt-HZSM-5/HMS catalysts were studied.

Several reports exposed that there are various parameters that can affect the rate of the isomerization reaction. Some of these parameters are as catalytic structures, reaction conditions as temperature and pressure, the volumetric flow rates of reactants and etc. [1-6].

Examining the variables affecting the isomerization reaction at the same time requires spending a lot of time, money and materials [7]. Based on this, theoretical methods with modelling tools are used in addition to experimental methods such as Response Surface Method (RSM). Here, this combined mathematical and statistical method is used to optimize the results for discovering the maximum of isomerization reaction rate and establish a relationship between the response and the independent variables [8-11].

The volumetric flow rates of n-heptane and hydrogen, weight percent of HZSM-5 zeolite in catalysts structures and temperature were studied as important independent variables in this work. To investigate the kinetics of n-heptane isomerization reaction on the synthesized catalysts, power law and Langmuir–Hinshelwood models were used.

## **2. Experimental methods**

### **2.1. Catalyst preparation**

According to the preparation method of Pt-HZSM-5/HMS catalysts [1], 7 g ethanol was dissolved and stirred with tetraethyl ortho silicate (5 g). Then, dodecylamine (1.2 g) in 0.5 cc of hydrochloric acid (1 M) and 15 cc of distilled water with various amounts of HZSM-5 were added to the first solution with stirring for 6 hour. Then, the solid sediment was washed, filtered, and heated in an oven at 110 °C overnight. The Pt impregnated HZSM-5/HMS catalysts (0.6 wt%) were calcined at 300 °C for 4 h [1].

The amounts of zeolite are 10 to 40 wt%. For convenience, the nomenclature used to identify these catalysts are as PZH-x (x=10, 20, 30 and 40 wt% of HZSM-5).

## 2.2. Kinetic unit

A continuous reactor was used to do the experiments. The n-heptane was inserted to reactor using an automatic syringe pump and mixed with hydrogen gas at different temperatures (isothermal conditions). The micro reactor was connected to a gas chromatograph (Agilent Technologies 7890A-FID) analyzing the products during the reaction time. The average accuracy of applied instruments and the uncertainties of measurements are  $\pm 0.0001$ . The rates for this reaction were measured by Equation 1:

$$r \text{ (mol. g}^{-1} \cdot \text{s}^{-1}) = \frac{\text{n-C}_7 \text{ flow rate} \times \text{n-C}_7 \text{ density} \times \text{conversion(\%)}}{\text{n-C}_7 \text{ molar weight} \times \text{weight of catalyst} \times \text{impregnated metal}} \quad (1)$$

## 2.3. Design of experiments

Design of experiments and response surface methodology (DOE/RSM) model was investigated for the volumetric flow rates of H<sub>2</sub> (A: cc min<sup>-1</sup>), n-C<sub>7</sub> (B: cc h<sup>-1</sup>), temperature (C: °C) and the HZSM-5 content (D: %) as central factors. The independent variables and their ranges were presented in Table 1. Each of these parameters has three levels (low (-1), central (0) and high (+1)) [12]. RSM using Central composite design (CCD) was used to design the results (Table 1).

**Table 1.** The results obtained from central cubic design.

Parameters		Levels		
		Low (-1)	Center (0)	High (+1)
A: H <sub>2</sub> flow rate (F <sub>H2</sub> : ccmin <sup>-1</sup> )		20	32.5	45
B: n-C <sub>7</sub> flow rate (F <sub>C7</sub> : cch <sup>-1</sup> )		2	3.25	4.5
C: Temperature (T: °C)		200	275	350
D: Weight of HZSM-5 (W: %)		10	25	40

RUN	Parameters				Responses
-	A	B	C	D	rate (molg <sup>-1</sup> s <sup>-1</sup> )
1	32.5	3.25	125	25	0.14
2	45.0	2.00	350	40	0.02
3	32.5	3.25	275	25	0.10
4	32.5	0.75	275	25	0.01
5	45.0	4.50	200	40	0.24
6	32.5	3.25	275	25	0.10
7	32.5	3.25	275	55	0.22
8	32.5	3.25	425	25	0.12
9	32.5	3.25	275	25	0.10
10	20.0	4.50	350	40	0.12
11	32.5	3.25	275	25	0.10
12	32.5	3.25	275	25	0.10
13	32.5	3.25	275	25	0.10
14	45.0	2.00	350	10	0.05
15	45.0	4.50	350	40	0.04
16	20.0	2.00	350	40	0.08
17	7.5	3.25	275	25	0.09
18	45.0	2.00	200	40	0.13
19	45.0	2.00	200	10	0.16
20	20.0	2.00	350	10	0.09
21	20.0	2.00	200	40	0.15
22	20.0	4.50	200	10	0.03
23	32.5	3.25	275	5	0.02
24	20.0	4.50	350	10	0.01
25	57.5	3.25	275	25	0.18
26	45.0	4.50	200	10	0.06
27	32.5	5.75	275	25	0.17
28	20.0	4.50	200	40	0.10
29	20.0	2.00	200	10	0.15
30	45.0	4.50	350	10	0.04

A second order polynomial function versus coded factors (Table 2) was used to fit the responses.

Fisher's test (F-value) and probability value (p-value) were investigated with the analysis of variance (ANOVA) for estimating the statistical importance of the parameters and their interactions and associated probability level.

**Table 2.** Final equation in terms of independent parameters.

Actual Equation= $a + bA + cB + dC + eD + fAB + gAC + hAD + iBC + jBD + kCD + lA^2 + mB^2 + nC^2 + oD^2 + pABC + qABD + rACD + sBCD + tA^2B + uA^2C + vA^2D + wAB^2$					
Coefficient	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
rate	+0.1007	+0.0230	+0.0397	-0.0049	+0.0504
Coefficient	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>
rate	+0.0144	-0.0186	-0.0033	+0.0076	+0.0265
Coefficient	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i>	<i>o</i>
rate	-0.0091	+0.0037	-0.0072	+0.0027	+0.0009
Coefficient	<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>	<i>t</i>
rate	-0.0059	+0.0028	-0.0128	-0.0085	-0.0504
Coefficient	<i>u</i>	<i>v</i>	<i>w</i>		
rate	-0.0308	-0.0327	-0.0220		

The importance of measuring coefficients was shown by T-test. The model fitness was compared using the coefficient of determination ( $R^2$ ) [12].

The kinetic parameters were obtained using the power law (PL) and the Langmuir–Hinshelwood (LH) models [6].

### 3. Results and discussions

#### 3.1. ANOVA analysis

Table 1 provides the matrix used to design the mathematical model in accordance with the experimental and predicted data. The ANOVA analysis according to the cubic equations was presented in Table 2. The linear effects of coded variables (such as single, dual interactions, square interactions, triple interactions, cubic interactions) on the output results were presented in Table 3. The fitness and the significance of the model were obtained with the low P-value (0.0219) and high F-value (4.65). 2.19% chance

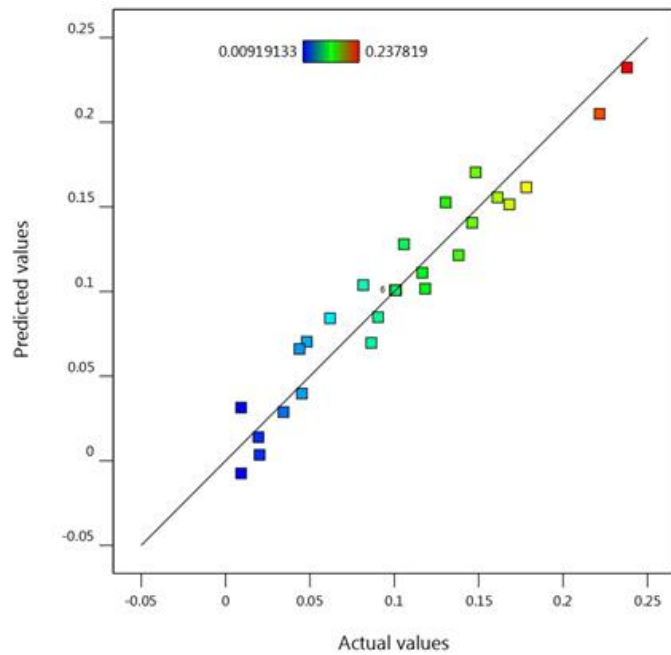
The low P-value (0.0219) and high F-value (4.65) for the used model confirm the fitness and the significance of the model response. The F-value can be influenced by noise only with a probability of 2.19%. A level of  $\alpha=0.05$  shows the variables as B, D, AC, BD,  $A^2B$ ,  $A^2D$  are important in the used model. Insignificant terms are more than 0.10 amount [12-16].

**Table 3.** Analysis of variance results for quadratic model.

Source	Sum of Square	Degree of freedom	Mean Square	F-Value	P-Value	
Model	0.0939	22	0.0043	4.6500	0.0219	significant
A: F <sub>H2</sub>	0.0042	1	0.0042	4.6000	0.0691	-
B: F <sub>C7</sub>	0.0126	1	0.0126	13.7700	0.0075	-
C: T	0.0002	1	0.0002	0.2130	0.6584	-
D: W	0.0203	1	0.0203	22.1200	0.0022	-
AB	0.0033	1	0.0033	3.6100	0.0993	-
AC	0.0056	1	0.0056	6.0500	0.0434	-
AD	0.0002	1	0.0002	0.1903	0.6758	-
BC	0.0009	1	0.0009	1.0000	0.3496	-
BD	0.0112	1	0.0112	12.2200	0.0101	-
CD	0.0013	1	0.0013	1.4500	0.2675	-
A <sup>2</sup>	0.0004	1	0.0004	0.4133	0.5408	-
B <sup>2</sup>	0.0014	1	0.0014	1.5400	0.2544	-
C <sup>2</sup>	0.0002	1	0.0002	0.2177	0.6550	-
D <sup>2</sup>	0.0000	1	0.0000	0.0225	0.8849	-
ABC	0.0006	1	0.0006	0.6136	0.4591	-
ABD	0.0001	1	0.0001	0.1332	0.7260	-
ACD	0.0026	1	0.0026	2.8500	0.1352	-
BCD	0.0012	1	0.0012	1.2700	0.2966	-
A <sup>2</sup> B	0.0136	1	0.0136	14.7800	0.0063	-
A <sup>2</sup> C	0.0050	1	0.0050	5.5000	0.0515	-
A <sup>2</sup> D	0.0057	1	0.0057	6.2000	0.0415	-
AB <sup>2</sup>	0.0026	1	0.0026	2.8100	0.1377	-
AC <sup>2</sup> , AD <sup>2</sup> , B <sup>2</sup> C, B <sup>2</sup> D, BC <sup>2</sup> , BD <sup>2</sup> , C <sup>2</sup> D, CD <sup>2</sup> , A <sup>3</sup> , B <sup>3</sup> , C <sup>3</sup> , D <sup>3</sup>	0.0000	0	-	-	-	-
Residual	0.0064	7	0.0009	-	-	-
Lack of Fit	0.0064	2	0.0032	-	-	-
Pure Error	0.0000	5	0.0000	-	-	-
Cor Total	0.1003	29	Sum of squares is Type III - Partial			

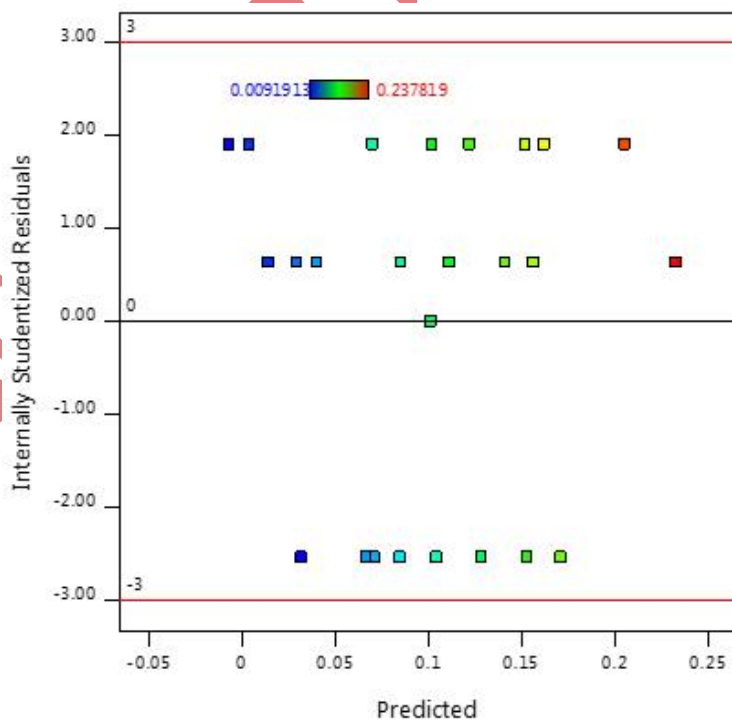
The model shows the  $R^2=0.94$ . Fig. 1 confirms a good fitness of the predicted and actual data for n-C<sub>7</sub> isomerization reaction. Also, the standard deviation of the residuals [13-16] was measured as the Root Mean Square Error (RMSE=0.03). Another key factor for model study is the signal to noise ratio ( $S/N > 4$ ). The results display  $S/N = 9.04$  that shows the cubic model can directly design the space. The Lack of Fit for the responses was measured 0.0064. The lack of fit is more important than the pure errors. Because the pure error is naturally removed and does not affect the model.





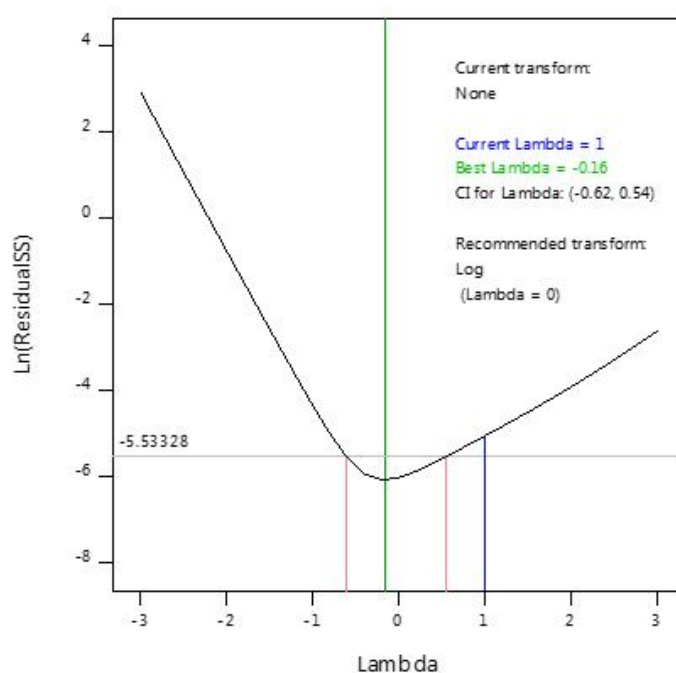
**Fig. 1.** Predicted values of reaction rate with RSM versus actual reaction rates.

The points in Fig. 2 are in the constant range [17], accordingly the model well fit the experimental data.



**Fig. 2.** The residuals versus predicted values plot for the model.

To determine the most appropriate reaction rate according to the response data, Box-Cox plot is presented in Fig. 3. No specific transformation is recommended for this model, because the 95% confidence interval around the best lambda value (the minimum point of the curve = -0.16) is 1 [17].



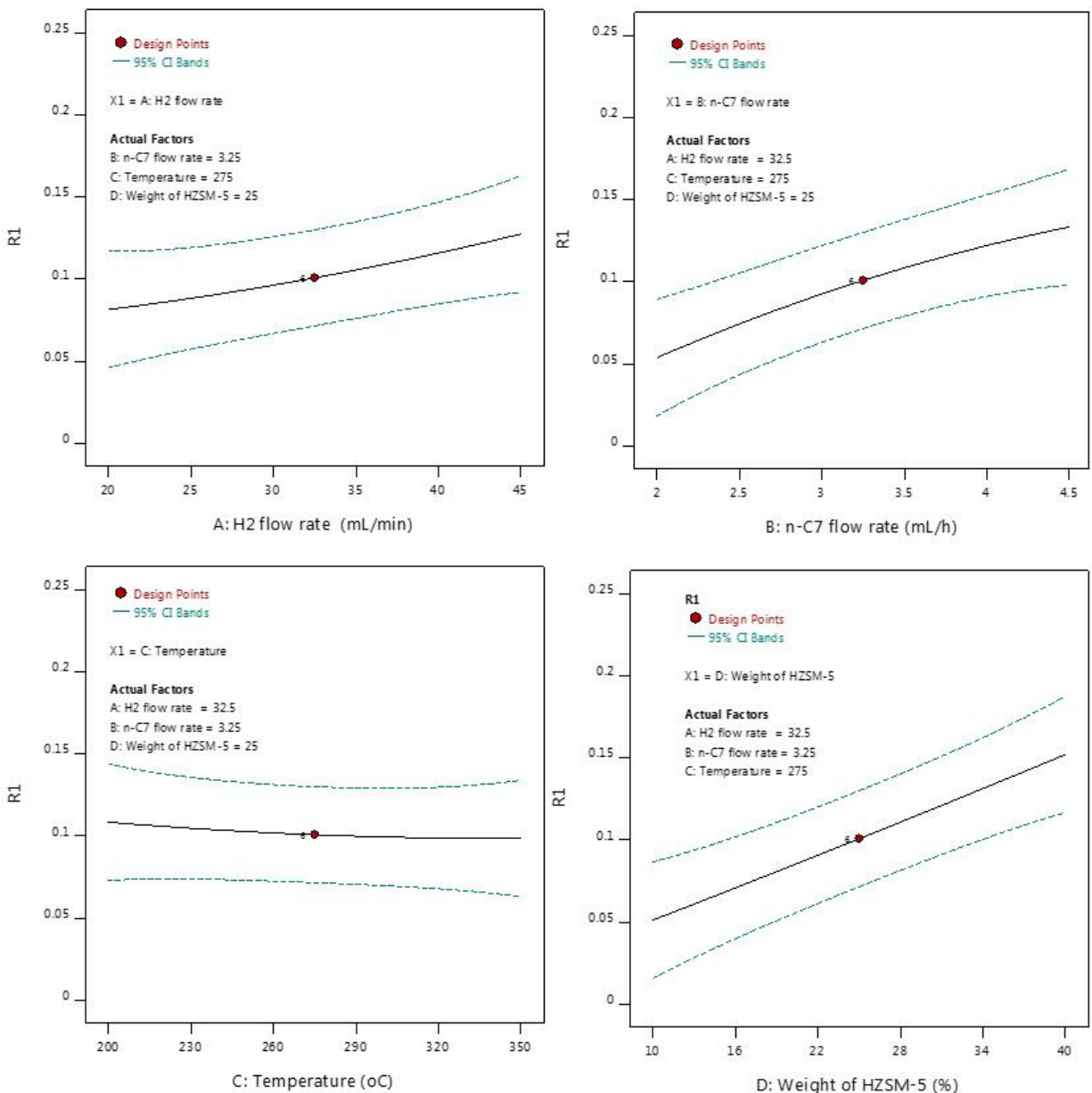
**Fig. 3.** Box-Cox plot for the model.

Fig. 4 shows one-factor plots. The other parameters are constant at mean values. Increased  $n\text{-C}_7$  flow rate and HZSM-5 content have significant influences on the reaction rate ( $P < 0.05$ ).

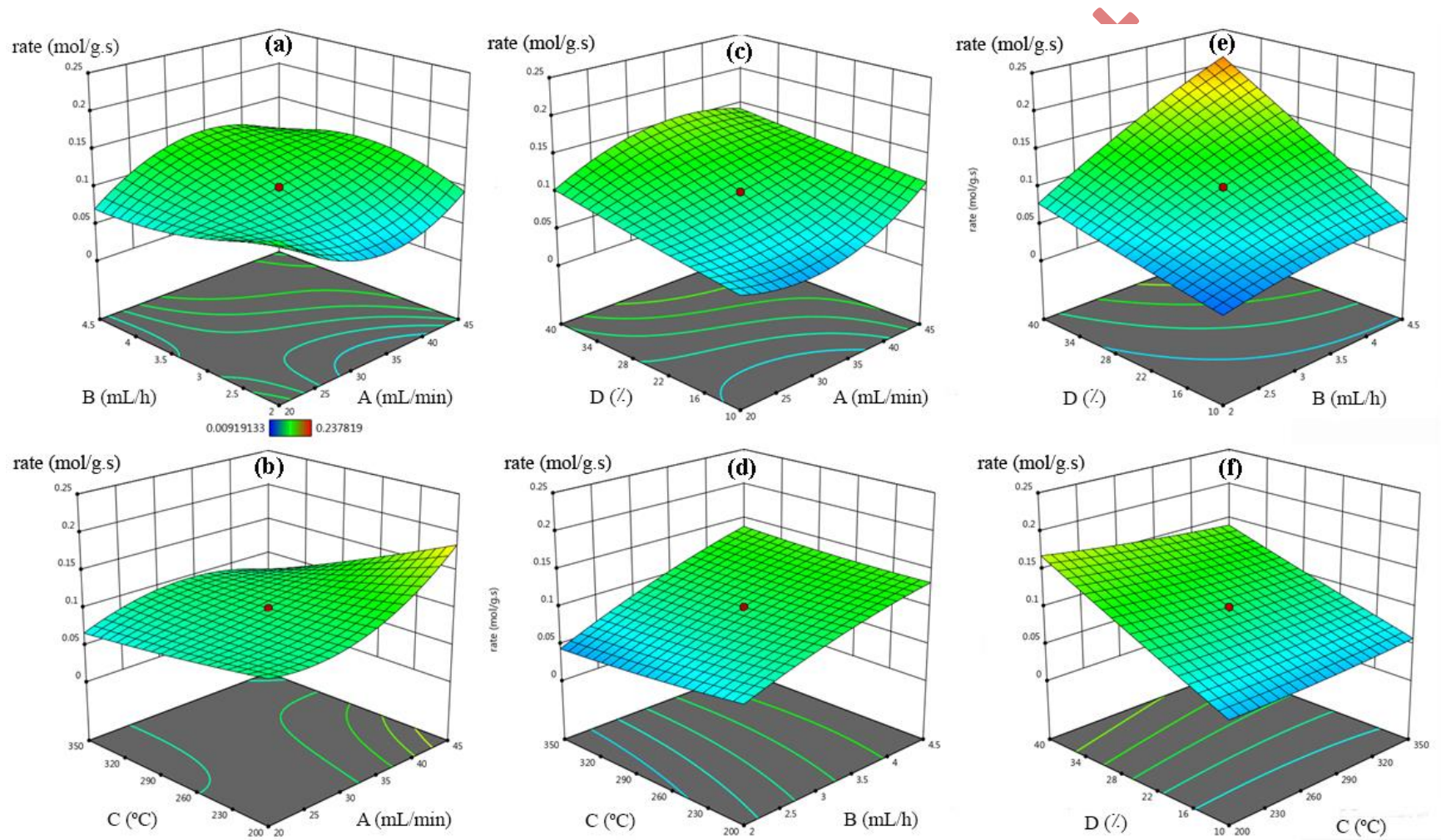
The combined effects of operating parameters (Table 1) for the isomerization reaction were investigated using RSM 3D plots (Fig. 5). Fig. 6 show the contour graphs. Between two variables, the C and D were kept constant in the central values (A: 32.5, B: 3.25, C: 275, and D: 25). The simultaneous effect of  $F_{\text{H}_2}$  and  $F_{\text{C}_7}$  at 275 °C and 25 wt% of HZSM-5 as surface presentations were shown in Fig. 5a. Other pairs of parameters were also shown in this figure while some parameter pairs were kept constant.

Consistent with the surface and contour graphs, the highest amount of rate ( $0.24 \text{ mol g}^{-1} \text{ s}^{-1}$ ) was found in the high amounts of  $F_{\text{C}_7}$  ( $4.5 \text{ cch}^{-1}$ ) and  $F_{\text{H}_2}$  ( $45 \text{ ccmin}^{-1}$ ). Increasing the  $F_{\text{H}_2}$  to  $45 \text{ ccmin}^{-1}$

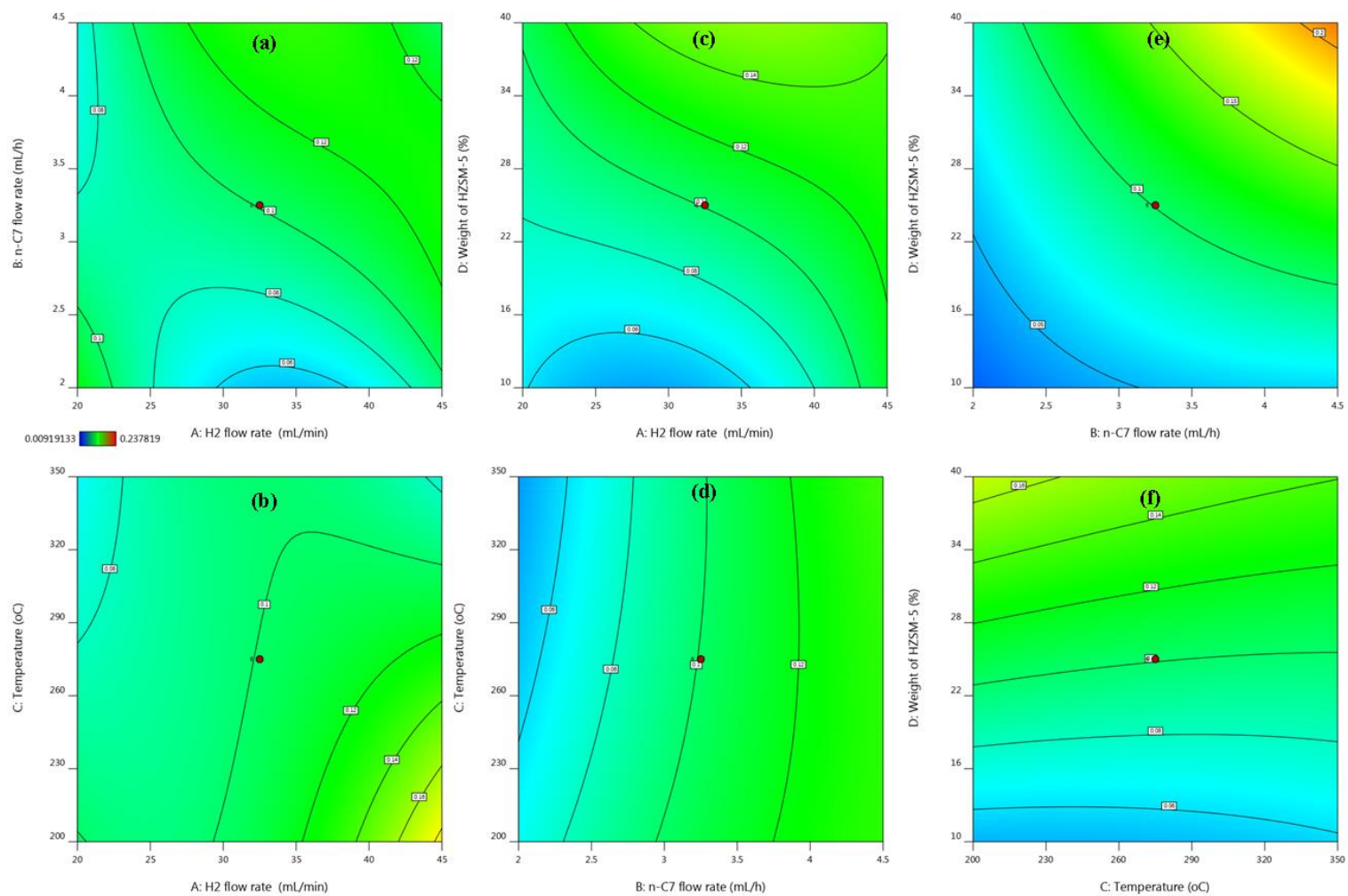
at a highest and constant amount of  $F_{C7}$  ( $4.5 \text{ cch}^{-1}$ ) supports the reaction rate at near  $200 \text{ }^\circ\text{C}$  for the PZH-40 catalyst, whereas this amount diminished to  $r=0.13 \text{ mol g}^{-1}\text{s}^{-1}$  at  $F_{C7} = 2.00 \text{ cch}^{-1}$ .



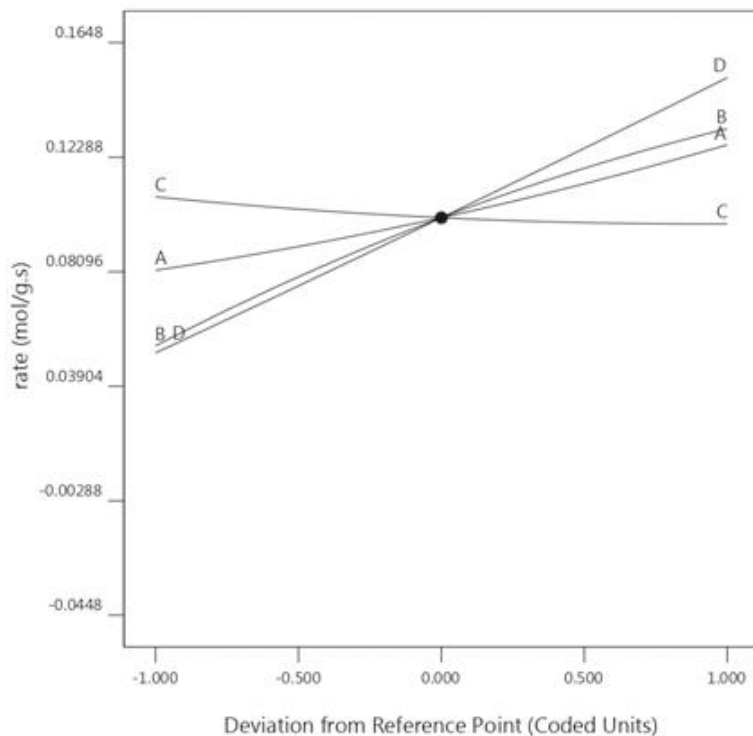
**Fig. 4.** One factor plots.



**Fig. 5.** 3D response surface plots for the reaction rates according to the combined effects of operating variables, (a) AB, (b) AC, (c) AD, (d) BC, (e) BD, and (f) CD at the central points.



**Fig. 6.** Contour plots for the reaction rates according to the combined effects of operating variables, (a) AB, (b) AC, (c) AD, (d) BC, (e) BD, and (f) CD at the central points.



**Fig. 7.** Perturbation plots of model factors (A:  $F_{H_2}$ , B:  $F_{C_7}$ , C: T, D: W) for isomerization reaction. Between these parameters, the HZSM-5 amount and temperature are the most influencing factors on this process (Fig. 7).

**Table 4.** Best points for the reaction rate of n- $C_7$  isomerization.

	rate	$F_{C_7}$	$F_{H_2}$	T	W
CCD results	0.24	4.50	43.25	200.00	40.00
real results	0.24	4.50	45.00	200.00	40.00

The specific optimal conditions were shown in Table 4 shows the optimal situations for the input and predicted data. The obtained data confirm that RSM predicts the data with a very low deviation of 0.03%.

A desirability function by mathematical optimization was measured to define the best situations for each factor combination. The objective of this work is to maximize the reaction rate as a response. Fig. 8 shows the optimal conditions for maximizing the reaction rate determined by the desirability function with numerical optimization. According to this, a temperature of 200.48 °C,

$F_{H_2} = 41.90 \text{ ccmin}^{-1}$ ,  $F_{C_7} = 4.48 \text{ cch}^{-1}$ , and  $W = 39.74\%$ , with a reaction rate of  $0.238 \text{ molg}^{-1}\text{s}^{-1}$  are the optimal conditions. The desirability value was given as one.

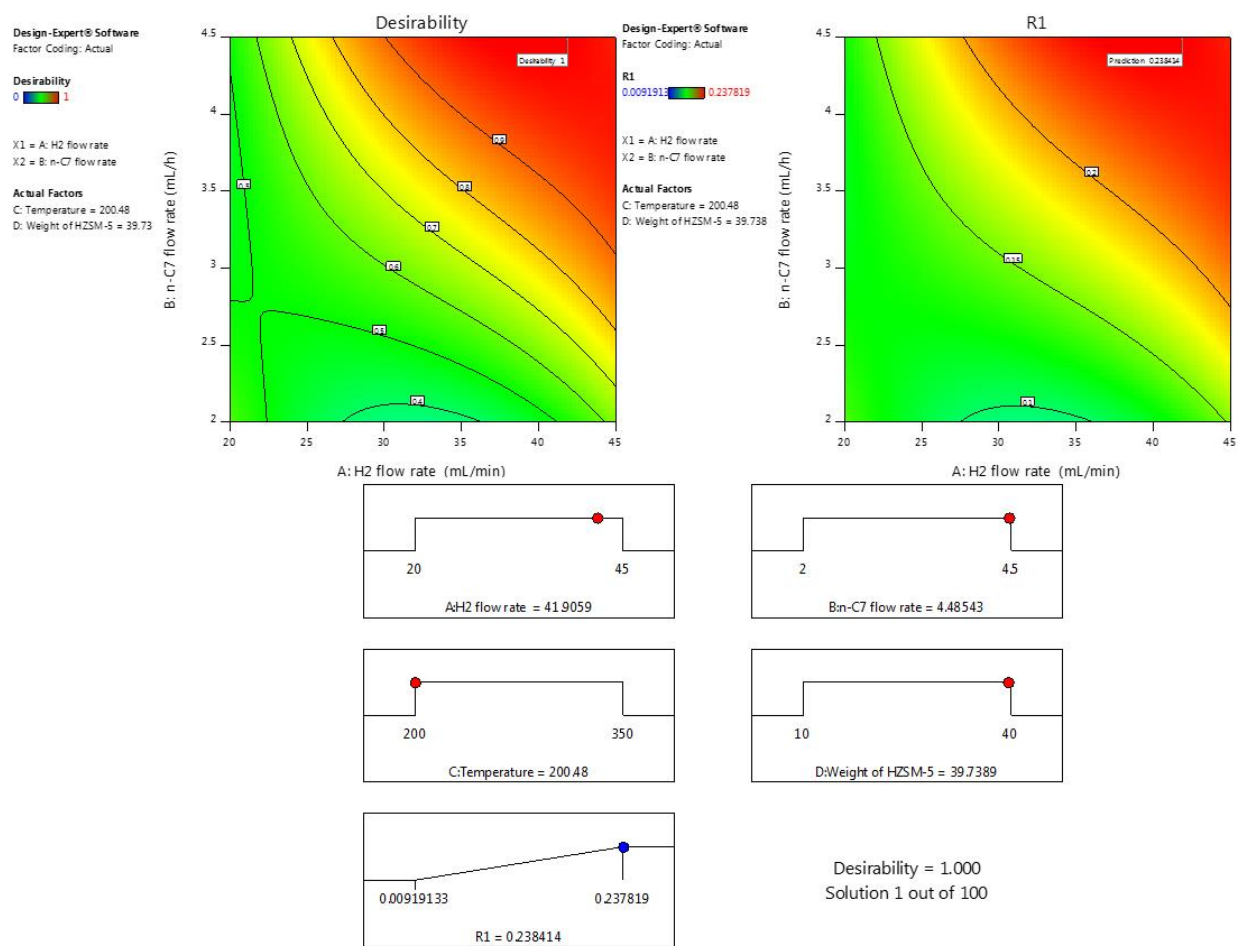


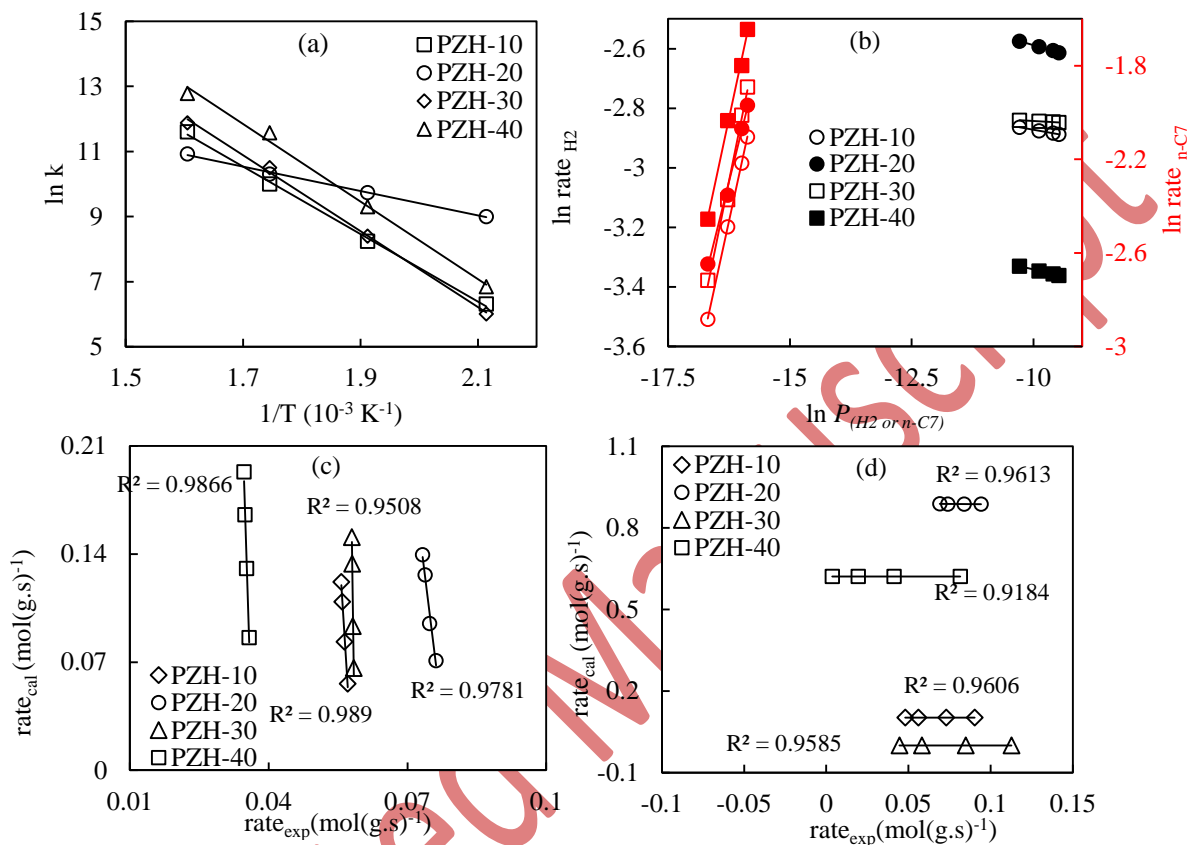
Fig. 8. Numerical optimization by desirability function.

### 3.2. Power law and Langmuir–Hinshelwood models

Power law and Langmuir–Hinshelwood models have been studied under the mentioned conditions. The estimated parameters versus the equations of these models were listed in Table 5. The activation energies ( $\sim 31 - \sim 99 \text{ kJmol}^{-1}$ ) were measured from Arrhenius plots for this process (Fig. 9a and Table 5).

Power law model (Equation 2) obtains the  $H_2$  reaction order =  $-0.01 - -0.09$  and the  $n-C_7$  order =  $0.47 - 1.03$  (Fig. 9b and Table 5).

$$r \text{ (mol g}^{-1}\text{s}^{-1}\text{)} = A e^{-\frac{E_{\text{app}}^{\text{act}}}{RT}} P_{\text{H}_2}^n P_{\text{C}_7}^m \quad (2)$$



**Fig. 9.** (a) Arrhenius plots, (b) double-log plots of the reaction rates versus the partial pressures of n-heptane and hydrogen, (c) estimated data by power law and (d) estimated data by Langmuir–Hinshelwood models.

The hydrogen orders propose low treatment of catalytic surfaces by hydrogen atoms and the dissociative and strong adsorption of n-heptane. The obtained data show the rate of this process drops with  $P_{\text{H}_2}$ . The fitness of these models were presented in Fig. 9c & d by regressions of the predicted and experimental results.



**Table 5.** the results obtained from power law and Langmuir–Hinshelwood models.

T (°C)	Orders	PZH-10	PZH-20	PZH-30	PZH-40
Power law results					
200	$n_{H_2}$	-0.07	-0.08	-0.02	-0.09
250	$n_{H_2}$	-0.06	-0.06	-0.03	-0.06
300	$n_{H_2}$	-0.03	-0.05	-0.01	-0.05
350	$n_{H_2}$	-0.03	-0.05	-0.01	-0.04
200	$m_{C_7}$	0.47	0.67	0.60	0.57
250	$m_{C_7}$	0.60	0.71	0.62	0.93
300	$m_{C_7}$	0.77	0.72	0.80	0.96
350	$m_{C_7}$	0.96	0.84	1.03	0.98
	$E_{app}^{act}$ (kJmol <sup>-1</sup> )	86.22	31.09	96.89	99.07
Langmuir–Hinshelwood results					
K	$E_{app}^{act}$ (kJmol <sup>-1</sup> )	95.2	54.2	99.8	100.6
	A (mol(gs) <sup>-1</sup> )	1.1×10 <sup>-5</sup>	1.1×10 <sup>-9</sup>	2.7×10 <sup>-5</sup>	9.0×10 <sup>-7</sup>
$K_{C_7}$	$-\Delta H_{ads-C_7}$ (kJmol <sup>-1</sup> )	27.2	15.6	87.5	52.6
	$A_{C_7}$ (atm <sup>-1</sup> )	1.2×10 <sup>-11</sup>	1.2×10 <sup>-12</sup>	2.7×10 <sup>-5</sup>	9.2×10 <sup>-9</sup>
$K_{H_2}$	$-\Delta H_{ads-H_2}$ (kJmol <sup>-1</sup> )	4.5	7.1	7.1	7.1
	$A_{H_2}$ (atm <sup>-1</sup> )	1.4×10 <sup>-2</sup>	2.7×10 <sup>-2</sup>	2.7×10 <sup>-2</sup>	2.7×10 <sup>-2</sup>

The correlation coefficients ( $R^2$ ) confirm that the results conducted from these models are appropriate. However, the Langmuir–Hinshelwood model is a more realistic model and predicts better results according to its mechanism (Equation 3).

$$r = \frac{A e^{-\frac{E_{app}^{act}}{RT}} \cdot P_{C_7} \cdot P_{H_2}}{\left( \left( \frac{1}{A_{C_7} e^{-\frac{\Delta H_{ads-C_7}}{RT}}} \right) + P_{C_7} \right) \cdot \left( \left( \frac{1}{A_{H_2} e^{-\frac{\Delta H_{ads-H_2}}{RT}}} \right) + P_{H_2} \right)} \quad (3)$$

The valuations of  $R^2$  for this model (>0.9) show the good fitness between experimental and predicted results (Fig. 9d). The activation energies are in the range of ~54 to 100 kJ mol<sup>-1</sup> that are in good agreement with previously reported results [6].

The lowest amount of activation energy and in other words the fastest reaction was obtained by PZH-20 catalyst (Table 5).

$A_{H_2}$  (the pre-exponential factor of hydrogen adsorption) is greater than  $A_{C_7}$  that it shows the faster adsorption of hydrogen than n-heptane. So, the n-heptane adsorption heat ( $\Delta H_{ads-C_7}$ ) is higher than hydrogen ( $\Delta H_{ads-H_2}$ ).

#### **4. Conclusion**

The effects of HZSM-5 content in catalytic structure, temperature and volumetric flow rates of n-heptane and hydrogen on the reaction rates of n-heptane isomerization were investigated over Pt supported HZSM-5/HMS catalysts. The effect of these independent parameters on reaction rate was determined using thirty different runs of the response surface method. Based on the obtained results, the rate of this reaction can be successfully predicted with RSM. The highest volume flow rates of n-heptane ( $4.5 \text{ cch}^{-1}$ ) and hydrogen ( $45 \text{ ccmin}^{-1}$ ) result in the highest reaction rate ( $0.24 \text{ molg}^{-1}\text{s}^{-1}$ ). The HZSM-5 content in the structure of PZH-x catalysts is the most effective parameter on the reaction rate of n-heptane isomerization. Other parameters, especially temperature, do not have meaningful effect on the rate of this reaction.

#### **Acknowledgement**

The Study was supported by Kosar University of Bojnord with the grant number “NO.0102051736”.

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