

# Preparation of Pt/Al<sub>2</sub>O<sub>3</sub>-Cl Catalyst and Investigation of Operating Variables Effects on Isomerization Reaction

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(Received 25 May 2017, Accepted 09 March 2018)

[DOI: 10.22059/jchpe.2018.233982.1198]

## Abstract

A high chlorinated alumina catalyst obtained by treating Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.25 wt. % Pt) samples with two mixtures of CCl<sub>4</sub>/N<sub>2</sub> and CCl<sub>4</sub>/N<sub>2</sub>/H<sub>2</sub> was tested for the hydroisomerization of the C<sub>6</sub> alkane. The conversion of *n*-hexane feed was diluted with hydrogen performed with different H<sub>2</sub>/HC ratios at various temperatures, liquid hourly space velocities (LHSVs) and 3 MPa total pressure. The loaded catalyst in fixed bed reactor revealed an equitably great primary activity, however, conversion still decayed with time on flow stream. Adding CCl<sub>4</sub> to the hexane feed could not improve the durability with time on the outflow. The effects of temperature on conversion and isomer selectivity were studied at various H<sub>2</sub>/HC ratios and LHSVs. Superior conversion and selectivity were found for the catalyst at 160 °C and 120 °C at LHSV 1.2 h<sup>-1</sup>. Furthermore, effects of LHSV and low temperature were studied on conversion and product octane number derived from hexane isomerization, respectively. The highest octane number was observed at the low space velocity (1.2 h<sup>-1</sup>).

## Keywords

Catalyst;  
Chlorinated alumina;  
Isomerization;  
Light naphtha;  
Normal hexane.

## 1. Introduction

In recent years, environmental concern has increased because of air pollution and destruction of the environment by growing use of vehicles in the world. For this reasons, restrictions and regulations have been imposed on petroleum refining companies to introduce new sp-

ecifications for fuels. In this case, regulations on the contents of sulfur, olefins, and aromatics, as well as vapor pressure are increasingly stringent due to recent environmental restrictions. Treatment processes should be considered as a solution to increase the fuel quality and reduce its harmful impacts on the environment [1-5].

The light paraffin isomerization is a significant industrial engineering process to acquire branched alkanes employed like octane boosters in liquid gasoline [2-9]. So, isoparaffins are noticed as a

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means to the utilization of aromatic and oxygenate materials, whose maximum grasp are exposed to attend for environmental protection [10-15]. The isomerization route is a catalytic reaction which includes reordering of molecular construction of a hydrocarbon deprived of gaining or losing of any of its constituents. In this process, light naphtha, i. e., C5-C6 fractions, were used to produce the gasoline with high octane numbers. The main purpose of light naphtha isomerization process is to raise the octane number of light naphtha and decrease benzene quantity [16-20]. The isomerization processes are commonly using bifunctional catalysts which have both metallic and acidic tasks. Three kinds of money-oriented catalysts for light naphtha isomerization are provided from zeolite, chlorinated alumina and sulfated zirconia sources. The latter catalysts are characterized by the effect of their acidic behaviors [21-25]. The greatest active catalyst for the light naphtha isomerization is chlorinated alumina which is containing 0.2–0.5 Wt. % Pt, and 6–10 Wt. % Cl, broadly employed in the C6 alkanes isomerization processes. In this case, the process is usually achieved at 393–423 K, rather than 453–473 K for sulfated zirconia or 523K for zeolite catalysts. The lower temperature operation favors the selectivity to multi-branched isomers [10, 11]. On the other hand, makeup and feed gas drying devices are needed because of permanent deactivation of the catalysts via oxygenate mixtures like CO and H<sub>2</sub>O. Lengthy catalyst life for further than 3-5 years could be obtained using effective drying equipment. Also, incessant chloride addition is needed to possess high activity. The HCl in the off-gas could be neutralized by using the caustic scrubber. The regeneration of the catalysts are not possible [26-27]. In the present work, isomerization of Lavan Petroleum light naphtha with prepared Pt/Al<sub>2</sub>O<sub>3</sub>-Cl catalyst in different operating conditions has been investigated to achieve high selectivity and conversion toward isomers products isomers.

## 2. Experimental

### 2.1 Materials

Aluminum nitrate and sodium carbonate used for the preparation of gamma alumina support were purchased from Sigma-Aldrich Company. Hexachloroplatinic acid (34.0 wt. % Pt) was used (Carlo Erba, Iran) as a platinum source for prepara-

tion of catalyst samples. Carrier gas used in all experiments were 99.999% helium (Roham Co., Iran). Other gases such as H<sub>2</sub> and N<sub>2</sub> (99.999%) were supplied by Alvand Co. (Iran). CCl<sub>4</sub> (99.8%) used as a chlorinating agent in the isomerization process was supplied by Merck Co.

### 2.2 Support preparation

The distilled water (300 ml) was warmed to 70°C in a 1-liter round-bottom flask. Next Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (10.5 g) and Na<sub>2</sub>(CO<sub>3</sub>) (5 g) were each dissolved in 400 ml distilled water separately. The sodium carbonate and aluminum nitrate solutions were poured simultaneously into 200 ml deionized water using burette. The latter solutions were mixed vigorously to make an aluminum hydroxide gel.

The reaction temperature was set at 70 °C. After occurring the precipitation, pH was adjusted to 8 with sodium carbonate. Finally 350 ml of sodium carbonate was added to the round-bottomed flask. The formed colloidal solution was heated and aged at 80 °C so long as constant mixing for 4 hours. The pH of the filtrate was about 11. Afterwards, the white gel was rinsed several time with deionized water at 70-75 °C until the filtrate pH reached nearly 5.5, and shaped into small extrudes. The prepared alumina support (about 3 mm long and 1.5 mm in diameter) was dried at room temperature, and then oven dried at 80 °C for 1 hour (h). The sample was calcined at 650 °C for 2 h.

### 2.3 Catalyst preparation

The prepared gamma alumina samples were loaded with 0.25 wt % platinum by wet impregnation method using an aqueous solution of hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O). The impregnated samples were left overnight at room temperature and then dried in an oven at 100 °C for 2 h. The catalysts were dried and calcined at 520 °C under air atmosphere for 2 h. The temperature was reduced to 250 °C with changing air to nitrogen. The calcined samples were then revived by hydrogen at the same temperature for 6 h, while nitrogen was gradually changing to hydrogen. Since acidity of the catalysts are not sufficient for isomerization reaction, the samples were treated using different chlorination procedures: CCl<sub>4</sub>/N<sub>2</sub> (mole ratio 1:10, 1:12, with total flow rate 30

ml/min at 180 °C for 3 h) and  $\text{CCl}_4/\text{N}_2/\text{H}_2$  (mole ratio 2:8:2, with total flow rate 30 ml/min at 300 °C for 3 h). The prepared catalysts were characterized before testing for isomerization. The outcomes are given in Table 1. The catalyst sample with a higher chlorine content was used for normal hexane isomerization tests.

**Table 1.** Prepared catalysts characteristics.

Characteristics	Quantity	Unit
Pt	0.25	wt %
Cl	2- 4	wt %
Density	0.74	$\text{g}/\text{cm}^3$
Surface area	196	$\text{m}^2/\text{g}$
Total pore volume	0.53	$\text{cm}^3/\text{g}$
Average pore diameter	10.42	nm

BET analysis was done using a Micromeritics ASAP 2000 equipment. The adsorption isotherm was measured at the liquid nitrogen temperature at 196 °C and after treatment of the samples for 2 h at 350 °C in a vacuum of  $5 \times 10^{-3}$  Torr. The pore distribution was determined by the BJH method with data of the desorption branch [25]

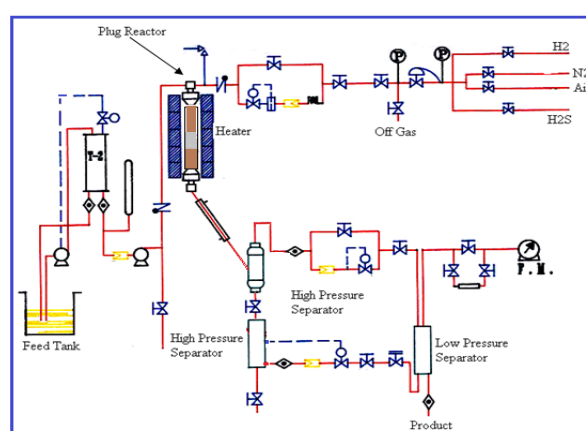
## 2.4 SEM and TEM analysis

Scanning electron microscopy measurements (SEM) for the catalyst were carried out with Mira\ Tescan Irost electron microscope operating at 15 KV. Transmission electron microscopy (TEM) measurements for the catalyst sample reduced at 250 °C for 2 h were performed with Philips CM30 300 KV electron microscope operating at 150 KV. Catalyst sample powders dispersed in ethanol were coated on a grid, which was then introduced to the microscope column. The microscope column was evacuated to less than  $1 \times 10^{-6}$  Torr. The size of the metal particles that are visible in the photograph is measured manually.

## 2.5 Normal hexane isomerization and product analysis

The isomerization experiments were made in a plug-flow reactor. Fig. 1 depicts a typical illustration of the experimental set-up. The catalyst (6.7 g) diluted with the same value of inert alpha alumina extrudates was loaded in the mid-region of the reactor under a pure nitrogen atmosphere. Bottom and top zones of the reactor were filled

with the same type of alpha alumina extrudates. Before reaction, the reactor was heated slowly to the desired temperatures under hydrogen. Feed and hydrogen were heated and mixed in the top zone (as preheater) of the reactor and introduced into the catalyst bed. Gaseous mixture from the reactor was first directed into a condenser, where it was cooled, and thereafter into a high-pressure separator, where the liquid isomers and unreacted n-hexane were separated from hydrogen and gaseous products. The high-pressure separator was a two-part jacketed vessel equipped with two needle valves, one after each part which was cooled by a circulating bath to enable the sampling of liquid products with the least disturbance on the pressure in the system via closing the middle valve when the bottom part was filled. After establishment of the steady-state conditions of the reactor were established, the liquid products were collected, while the gases were analyzed by GC-MS. Products were analyzed using GC-2550TG (Teif Gostar Faraz, Iran) equipped with Teknokroma (China) capillary column (length: 100 m; internal diameter: 0.25 mm; film thickness:  $0.50 \mu\text{m}$ ) and the flame ionization detector (FID) and the gaseous mixtures by Agilent (6890, USA) using thermal conductivity detector (TCD). The column temperature was set to 35 °C for 50 min, Injection port temperature to 200 °C and detector temperature to 200 °C. The n-hexane conversions ( $[(x(n\text{-C}_6)_{\text{in}} - x(n\text{-C}_6)_{\text{out}}) / x(n\text{-C}_6)_{\text{in}}] \times 100$ ) were calculated.



**Figure 1.** The typical plan of the set-up used in this work.

The prepared catalytic was tested in a laboratory scale reactor set-up. The performance of the catalyst was tested under different operating condi-

tions (temperature,  $H_2/HC$  and LHSV) which are indicated in Table 3. Experiments was done in constant pressure of 30 bar gage.

### 3. Results and Discussion

#### 3.1 Prepared catalysts and feed

Alfa alumina used in the top and bottom part of the reactor had no activity since it did not show any transformation of the feed (*n*-hexane) to the corresponding isomers. Catalysts characteristics are mentioned in Table 1. The feed used for isomerization was normal hexane. Composition and physical properties of the feed are given in Table 2.

The SEM picture was applied to specify the particle size of platinum on the support. As the SEM picture of the platinum-containing chlorinated alumina catalyst shows (Fig. 2a), only the morphology of alumina support is detectable on the picture not the clusters of platinum.

The TEM image of the catalyst, which was loaded by 0.25 wt % Pt, is shown in Fig. 2b. The black dots appearing on the support matrix are assumed as metallic particles consisting of Pt. particle sizes of the Pt clusters is found to be in the range of 2-3.5 nm.

**Table 2.** Feed characteristics.

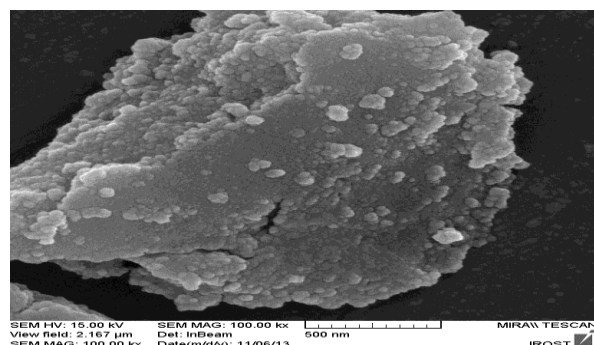
Feed characteristics	Quantity	Unit
Normal pentane ( <i>n</i> -C <sub>5</sub> )	0.13	wt %
3-methyl pentane (3-MC <sub>5</sub> )	0.27	wt %
Normal hexane ( <i>n</i> -C <sub>6</sub> )	98.74	wt %
Normal cyclopentane ( <i>n</i> -CC <sub>5</sub> )	0.48	wt %
Benzene	0.38	wt %
Density	0.65	g/cm <sup>3</sup>
Reid vapor pressure (RVP)	13.52	Psi
Molecular weight	68.15	g/mol
Water content	70	ppmw

#### 3.2 Catalytic studies

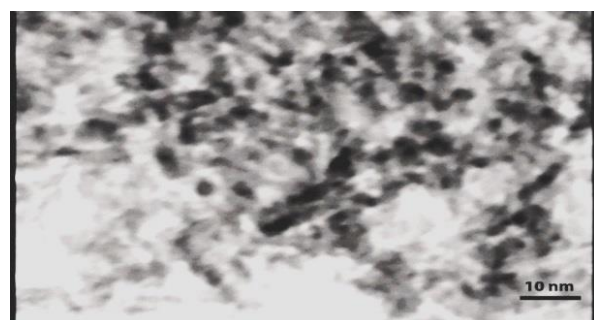
Three parameters were investigated for hydroisomerization process to study their effects on the conversion of *n*-hexane and selectivity to corresponding isomers. Temperature ranges were selected according to the standard situations exert in an industrial refining isomerization unit with Pt/Al<sub>2</sub>O<sub>3</sub>-Cl catalyst. Temperatures over 180 °C were not considered because it has been shown

that at great temperatures the contribution of cracking reactions in the process rises, which directs to the loss of respected isomeric blend with regard to the formation of light hydrocarbons [26]. The amount of hydrogen/feed proportion and space velocity effect studied on *n*-hexane isomerization were chosen on the base of the initial finding seeing the possibilities and limitations of the testing set-up in which experiments were conducted. The pressure was reserved fixed at 30 barg gage. The operating parameters investigated in this work are summarized in Table 3.

The *n*-hexane hydroisomerization reactions were carried out over the reduced catalyst at different  $H_2/HC$  and LHSVs (see Table 3) in the temperature range 120–180 °C in steps of 10 °C. It is found that 2-methyl pentane (2-MP), 3-methyl pentane (3-MP), 2,3-Dimethyl butane (2,3-DMB) and 2,2-Dimethyl butane (2,2-DMB) are always the major products indicating the skeletal rearrangement of *n*-hexane. Smaller amounts of cracked products were also observed irrespective of the catalytic tests conditions. The formation of these products indicates that the skeletal rearrangement in *n*-hexane isomerization is predominant.



**Figure 2a.** SEM-picture of the Pt/Al<sub>2</sub>O<sub>3</sub>-Cl catalyst.



**Figure 2b.** TEM image of the Pt/Al<sub>2</sub>O<sub>3</sub>-Cl catalyst.

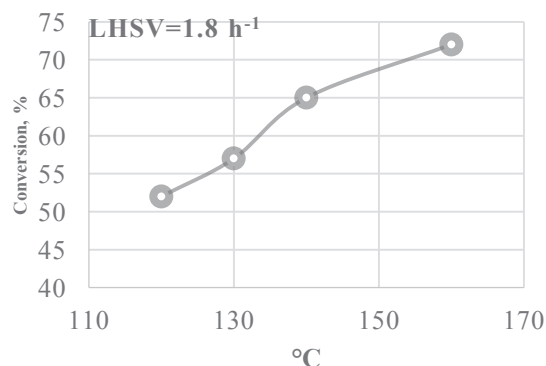
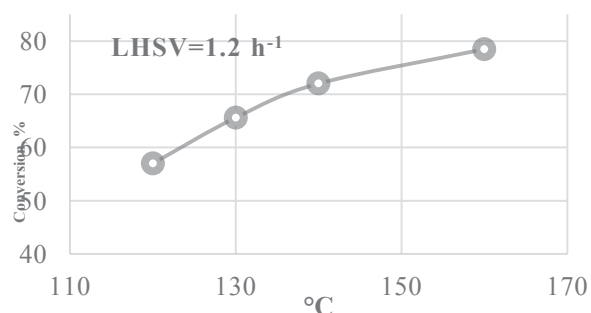
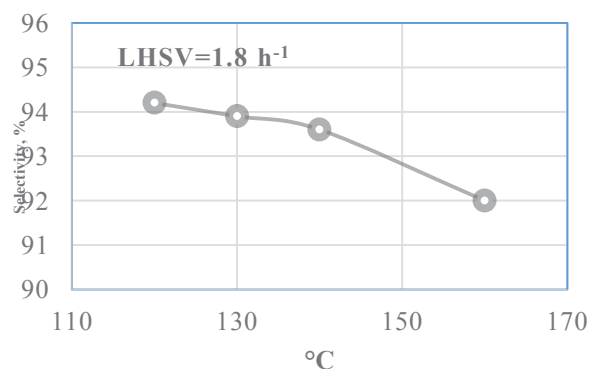
**Table 3.** Operating conditions of catalytic isomerization reaction

Run No.	T (°C)	H <sub>2</sub> /HC	LHSV (h <sup>-1</sup> )
1	180	0.95	1.5
2	160	0.7	1.8
3	160	1.2	1.2
4	160	0.7	1.2
5	150	0.95	1.0
6	150	0.95	2.0
7	150	1.5	1.5
8	140	0.7	1.8
9	140	1.2	1.2
10	140	1.5	1.5
11	130	0.7	1.8
12	130	1.2	1.2
13	130	1.5	1.5
14	120	0.7	1.8
15	120	1.2	1.2
16	120	1.5	1.5

### 3.3 Effect of temperature on conversion and selectivity

The effect of temperature on *n*-hexane conversion in the LHSVs 1.2 and 1.8 is displayed in Figs 3 and 4. It is found that the *n*-hexane conversion rises with temperature growth over the LHSVs studied. The maximum conversions of *n*-hexane at both the LHSVs are observed at 160 °C for the reaction temperatures studied. However, the isomerization selectivity in *n*-hexane conversion over the catalyst is shown to decrease with increasing reaction temperature and is found to be a minimum at 160 °C. Figs. 5 and 6 show isomer selectivity over various temperatures at LHSVs 1.2 and 1.8 h<sup>-1</sup> in hexane isomerization. It is found that the decrease in selectivity results from the increase in side reactions at higher temperatures in hexane isomerization. The results in complying with the work reported by Ref. [9]. In the case of LHSV=1.2 and LHSV=1.8 h<sup>-1</sup>, with increasing temperature to 160 °C, it is found that the DMBs selectivity to be a minimum at 160 °C with the corresponding values of 33% and 32.7%, respectively. The maximum activity and selectivity observed on the catalyst used may be due to the metal–acid synergism between metallic (Pt) particles, as evidenced by TEM (particle size: 2.5-3.5 nm), and the acid sites of the support which can be accounted for in terms of chlorine content increasing the Lewis acidity present on the alumina support [11, 26, 27]. Also, effects of temperature on cracking products in hexane isomerization at two LHSV values were shown in Figs. 7 and 8. These figures revealed that the LHSV values have a

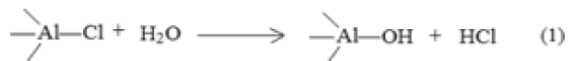
negligible effect on percent of cracked products in hexane isomerization.

**Figure 3.** Effects of temperature on hexane isomerization at LHSV=1.8 h<sup>-1</sup>**Figure 4.** Effects of temperature on hexane isomerization at LHSV=1.2 h<sup>-1</sup>**Figure 5.** Variation of isomerization selectivity versus reaction temperature, LHSV=1.8 h<sup>-1</sup>

### 3.4 Effect of time-on-stream (TOS) in isomer products

Figs. 9 and 10 illustrate the changes in volume % of various products, such as 2-methyl pentane, 3-methyl pentane, 2, 2dimethyl butane, 2, 3dimethyl butane, with time at 140 °C and 150 °C.

The sequel pointed that the catalysts had large activity at early life. It is noticeable that the volume % of products decreased by time. The 3 key types of deactivation are coke fouling, poisoning, and sintering. They may happen distinctly or concurrently. However, the main reason is often the exclusion of acid sites because of some Cl was released as of the catalytic area. Addition of  $\text{CCl}_4$  to feed of light naphtha enhanced both the initial stability and conversion with time in stream. Most of the studies carried out on the deactivation of isomerization catalysts have focused on the effect of coke deposition on their performance and those devoted to the effect of water on the activity of the catalyst are scarce. The presence of water in the combined feed can be a crucial factor accelerating the deactivation of the chlorinated Pt/ $\text{Al}_2\text{O}_3$  catalyst. Though, precipitation of heavy coke on the catalyst surface in the isomerization process is the other cause that may severely disable the catalyst too. The presumably precipitated coke on the catalyst area was measured at the end of the last run in order to clarify which one of the two factors caused the deactivation. The result showed that there was about 0.01wt% coke on the catalyst surface. Thus, this negligible amount of coke indicates that water was the only deactivation factor poisoning the chlorinated Pt/ $\text{Al}_2\text{O}_3$  catalyst. The continuous loss of chlorine of the catalyst during isomerization suggests that the presented water as an impurity in the combined feed was adsorbed dissociatively. Then,  $\text{H}_2\text{O}$  converted chloride species to hydroxyl groups (reaction 1) within the temperatures of isomerization reaction according to the literature [13, 26].



### 3.5 Temperature and LHSV Effects on conversion and product octane number

The LHSV effects on light naphtha conversion studied over the catalyst at 120 °C and 130 °C are depicted in Fig. 11. It is found that the conversion of light naphtha declines by increasing LHSV. The result is in a good agreement with the work reported previously [14-15]. Fig. 12 shows the effects of temperature on products octane number obtained from hexane feed treated over the catalyst at different LHSVs. It is found that increasing temperature over the range 160-180 °C increases

the octane number of products which controls fuel anti-knocking characteristic. The highest octane number was succeeded at LHSV 1.2  $\text{h}^{-1}$ . The octane number of the products was calculated using the following equation:

$$\text{Octane number} = \frac{\sum (\text{volume percent} \times \text{RON})}{100} \quad (2)$$

where RON is research octane number.

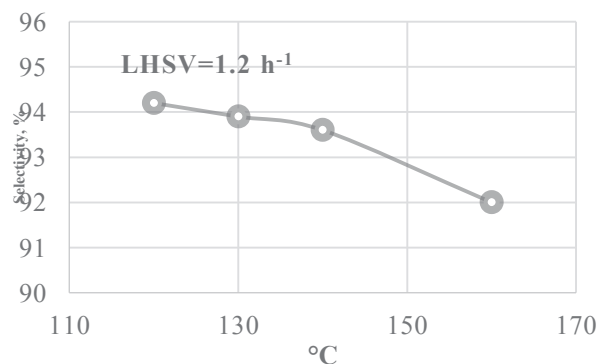


Figure 6. Influence of reaction temperature on isomerization selectivity in LHSV=1.2  $\text{h}^{-1}$

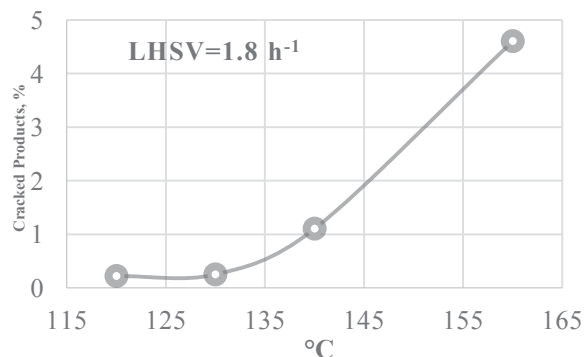


Figure 7. Effects of temperature on cracking products in hexane isomerization at LHSV=1.8  $\text{h}^{-1}$

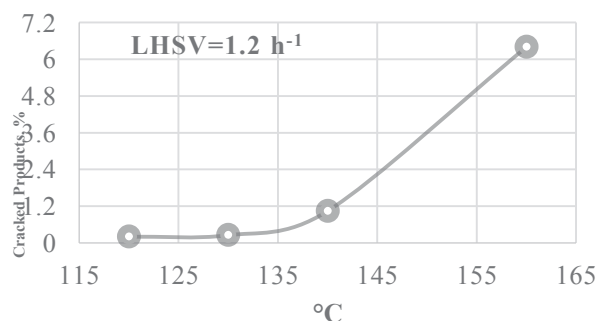


Figure 8. Effects of temperature on cracking products in hexane isomerization at LHSV=1.2  $\text{h}^{-1}$

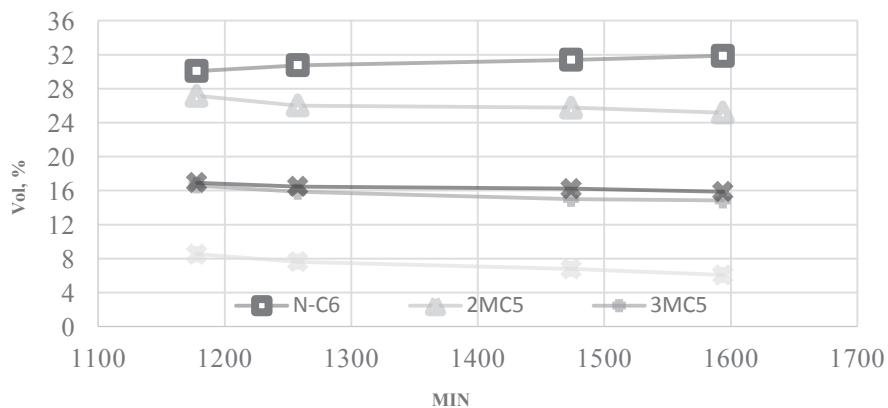


Figure 9. Effect of TOS on the individual isomer products at 140 °C

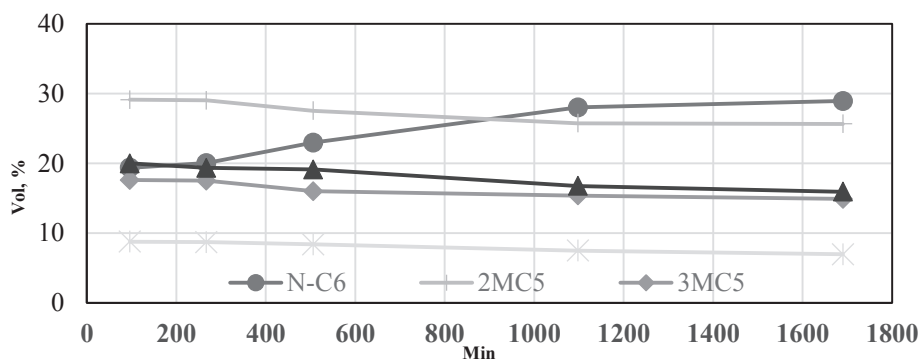


Figure 10. Effect of TOS on the individual isomer products at 150 °C.

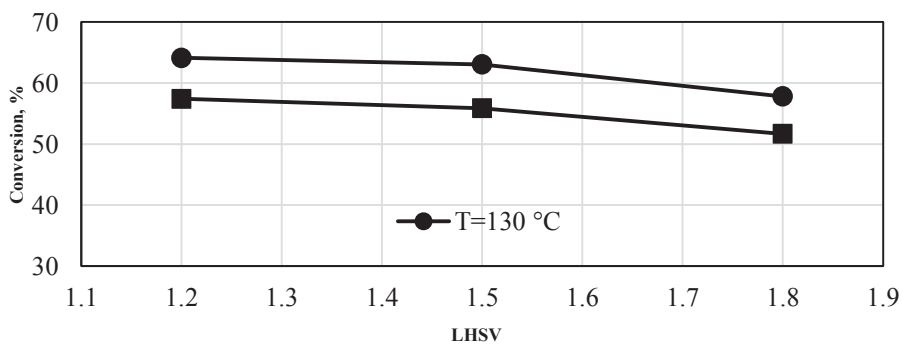


Figure 11. Effect of LHSV on hexane conversion

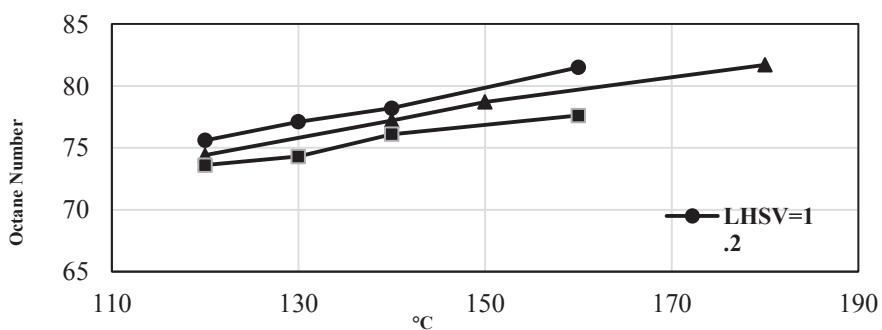


Figure 12. Effect of temperature on octane number of products in different LHSV

## 4. Conclusions

Experimental tests were performed in an experimental reactor setup at different temperatures, LHSV, and hydrogen to hydrocarbon molar ratios. A feed composed of hydrogen and light naphtha with the water content of about 80 ppmwt were passed above bed catalyst. It is concluded that light naphtha conversion upon Pt/Al<sub>2</sub>O<sub>3</sub>-Cl decreased at the beginning of the run (Experiment No. 1, T=140 °C and LHSV=1.2 h<sup>-1</sup>) to the end of the run (Experiment No. 16, T=130 °C and LHSV=1.5 h<sup>-1</sup>). Hence, these results clearly show that the catalyst was deactivated by time. It is supposed that decrease in the conversion can be due to the loss of chlorine of the catalyst caused by the water poisoning or the deposition of heavy coke on the catalyst active sites. The latter seems less likely since the low temperature of the operation did not favor such a heavy coke formation.

The most important factor was H<sub>2</sub>/HC, then temperature and velocity, whereas temperature quadratic effect besides interactions between temperature and H<sub>2</sub>/HC and velocity were less influential, but still significant. The maximum conversion from light naphtha, 80.06 wt. % was achieved at H<sub>2</sub>/HC = 1.2, LHSV = 1.2 and 160 °C.

## Acknowledgments

The encouragement and financial funding are providing by Semnan University, Zip code: 35131-19111, Tel/Fax: +98 2333654120, Semnan, Iran and Research institute of petroleum industry (RIPI), 1485733111 Tehran, Iran.

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