HYDROISOMERIZATION OF *n*-ALKANE OVER ZEOILTE SUPPORTED CATALYST

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ABSTRACT

The conversion of *n*C5-*n*C7 over 0.32wt%Pt/HY-Zeolite catalyst was studied with temperature range 240-270ºC, liquid hourly space velocity range 1-3h^{-1}, hydrogen to n-alkane mole ratio 8-24 and atmospheric total pressure. The effect of the P_{H2}, P_{nC5}, P_{nC6}, and P_{nC7} orders on the overall reaction rate was studied. For *n*C7, the reaction order with respect to hydrogen varied between -0.998 and -0.948 while with respect to *n*C7 varied between 0.154 and 0.156. For *n*C6, the reaction order varied between -0.811 and -0.808 while with respect to *n*C6 varied between 0.332 and 0.337. For *n*C5, the reaction order with respect to hydrogen varied between -0.652 and -0.620 while the reaction order with respect to *n*C5 was varied between 0.336 and 0.339. The values of apparent activation energy were obtained and found to be varied between 110 and 111 kJ/mol for *n*C7, 120 to 122 kJ/mol for *n*C6, and 145 to 148 kJ/mol for *n*C5.

الخلاصة

تم دراسة تحول البنتان الأعتيادي ،الهكسان الأعتيادي والهبتان الأعتيادي على العامل المساعد من نوع زيولايت والحاوي على نسبة 0.32% وزنا من البلاتين والمحضر بطريقة الترطيب . تم إجراء التجارب بضغط جوي في منظومة مختبريه تحتوي على مفاعل ذو حشوة ثابتة وبدرجات حرارة بين 240 -270°م وباستخدام سرع فراغية بين 1- 3 سا$^{-1}$ وبنسب مولية للهيدروجين إلى البنتان والهكسان والهبتان بين 8 - 24 . درس تأثير مرتبة التفاعل بالنسبة للهيدروجين والبنتان والهكسان والهبتان الأعتيادي بالنسبة لتفاعل الهبتان الأعتيادي لوحظ ان مرتبة التفاعل بالنسبة للهيدروجين تتراوح بين -0.998 و -0.948، بينما كانت مرتبة التفاعل بالنسبة للهبتان الاعتيادي تتراوح بين 0.154 و 0.156 . بالنسبة لتفاعل تحول الهكسان الأعتيادي كانت مرتبة التفاعل بالنسبة للهيدروجين تتراوح بين -0.811 و -0.808، بينما كانت مرتبة التفاعل بالنسبة للهكسان الاعتيادي تتراوح بين 0.332 و 0.337. بالنسبة لتفاعل تحول البنتان الأعتيادي كانت مرتبة التفاعل بالنسبة للهيدروجين تتراوح بين -0.652 و -0.620، بينما كانت مرتبة التفاعل بالنسبة للبنتان الاعتيادي تتراوح بين 0.336 و 0.339. تم دراسة قيم طاقات التنشيط و وجدت بانها تتراوح بين 110-111 كيلوجول/مول بالنسبة للهبتان الاعتيادي ، 120-122 كيلو جول/مول بالنسبة للهكسان الاعتيادي ، و 145 - 148 كيلو جول/مول بالنسبة للبنتان الاعتيادي ،

KEYWORDS

Isomerization, HY-Zeolite, Heptane, Hexane, Pentane

INTRODUCTION

Hydroisomerization of light alkanes is becoming extremely important as an alternative for octane upgrading. Since the branched alkanes products have high research octane numbers (RON) and burn cleanly they are the only acceptable alternative as octane booster. The interest in improving the environmental protection and to promote the efficiency of the automotive motors encourages the formulation of new catalysts and development of new processes for gasoline. Considering that branched-chain alkanes posse the greatest octane numbers, the use of gasoline containing higher content of these compounds is one alternative to obtain fuel with high antiknock characteristics [Kuchar et al.,1993]. Usually, branched chain alkane can be obtained by isomerization reaction employing bifunctional catalysts formed by metal supported over acid zeolite [Kouwenhoven and Zijll, 1971]. The isomerization is a catalytic processes involveing rearrangement of the molecular structure of a hydrocarbon without gain or loss of any of its components [Meyers,1996]. The interest in the isomerization process heightened with the phase out of tetraethyl lead in 1970's, following the phase out of leaded gasoline due to the introduction of Clean Air Act Amendments of 1990 in the USA and similar legislation in other countries.

The aim of this work is to provide:

(1) An integrated experimental data on the skeletal isomerization of *n*C5, *n*C6 and *n*C7 on zeolite catalysts in a continues reaction unit containing a fixed bed of a catalyst and at atmospheric pressure;

(2) A study on the effect of operating conditions (Temperature, LHSV, (H_2/$nC_{5,6,7}$) mole ratio, n-alkane and H_2 partial pressures) on the isomerization rate and selectivity;

(3) A comparison between the conversion of *n*-C5, *n*-C6, and *n*-C7 over platinum loaded zeolite

EXPERIMENTAL

Catalyst Preparation

HY-zeolite as a powder was mixed with montmorillonite clay as binder. The preferred binder content is between (15-30 wt %) as noticed by Allain et al.(1997) and Cañizares et al.(2000) . The resulting mixture was mixed with water to form a paste. An extrudates with 3~5 mm length and about 2 mm diameter were formulated and dried over night at 110°C. The value of Pt required to obtain acid reaction as the limiting step is between 0.15-2wt%, as reported by Lanewala et al.(1967), Ribeiro et al.(1982), and Runstraat et al.(1997a). In this study a Pt/HY-zeolite catalysts with 0.32wt% Pt were prepared using impregnation method. To prepare a 0.32wt% Pt/HY-Zeolite catalyst the impregnation process requires proper solution of hexchlorplatinic acid. The impregnated extrudates were then dried at 110°C over night and calcinated at 300°C for 3 hours in a furnace with dry air. The calcinated catalyst were then reduced with hydrogen at 350°C for 3 hours [Runstraat et al.,1997a, Exner et al., 1989]. The impregnation process was carried out under vacuum and the solution was added as drop wise with mixing for homogenous distribution at fixed temperature 40°C.

TEST METHODES

Catalyst Composition

The analysis of platinum in the prepared catalyst was achieved using atomic absorption spectrophotometer type (PYE UNICAM SP9) at Ibn-Sina State Company.The surface area and pore volume tests where done by the Petroleum Research and Development Center. It is found that the surface area decreases to 545.96 m^2/gm after adding the binder and formulate the particles, while it falls down to 435.59 m^2/gm with the pore volume 0.3735 ml/gm after adding platinum.

GC Analysis

The separation and analysis of reaction product into their components were carried out by gas chromatographic analysis on packed model 438Aa-VSA from Agilent Technologies Company. All the gas chromatograph analysis was done in AL DURA refinery.

PROCEDURE AND CONDITION

Thirty cubic centimeters of fresh catalyst was charged to the reactor between two layers of inert materials. The charged reactor was flushed with nitrogen to purge the air from the system. Meanwhile, the reactor is heated to the desired temperature. After reaching the reaction temperature, the nitrogen valve was closed. A pre-specified flow rate of feedstock was set on, vaporization of the feed occurs in the evaporator, and the vapor feed is mixed with the hydrogen and nitrogen in the mixing section at a specified flow rates .The mixture entered the reactor from the top, distributed uniformly by the inert materials and reacted on the catalyst charged inside. The product gases passed through down to the condenser and the final condensates were collected only after steady state operation was established and initial products were discarded. **Figure 1** shows the catalytic hydro-conversion unit process flow digrame.

The isomerization reaction conditions, employed are temperature 240-270ºC, liquid hourly space velocity of 1-3 h^{-1}, hydrogen to n-alkane mole ratio 8 to 24 and the total pressure kept atmospheric. *n*C5, *n*C6 and *n*C7 partial pressures were kept constant at 7.3 kPa while hydrogen pressure varied between 47.7-90.2 kPa using nitrogen as a make-up gas varied between 3.75-46.3 kPa to obtain the final reaction pressure of atmospheric. Another set of experiments were done by keeping the hydrogen partial pressure constant at 90.2 kPa while *n*C5, *n*C6 and *n*C7 partial pressures varied between 3.6-11 kPa, and the nitrogen partial pressure varied between 0-7.4 kPa to give the final reaction pressure of atmospheric pressure.

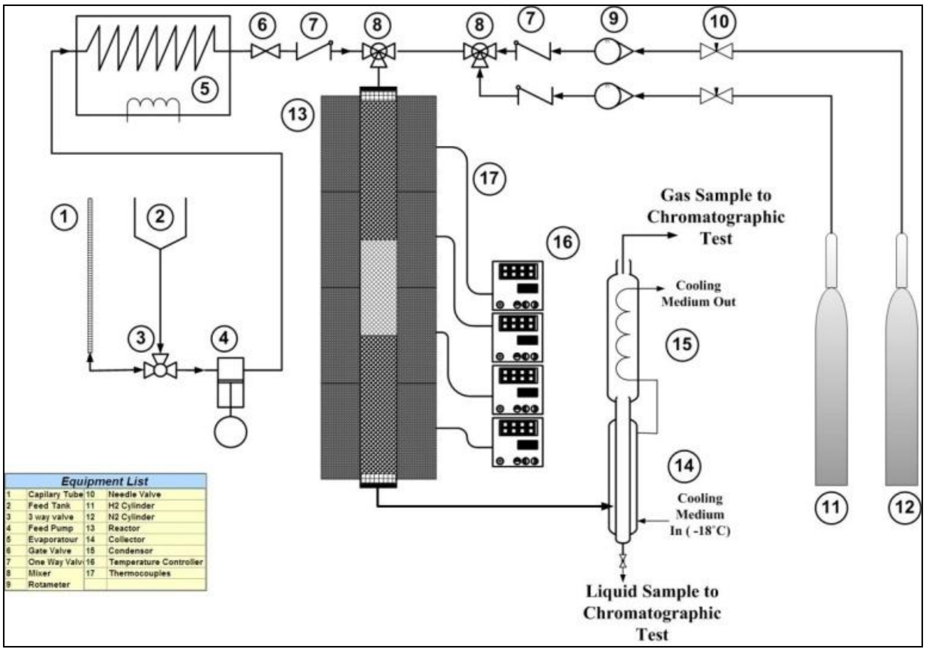

Figure 1 The catalytic hydro-conversion unit process flow digrame

RESULTS & DISCUSSION

Effect of Temperature

Figures 2, shows that the increasing of temperature of isomerization process at a constant LHSV increases the conversion of n-pentane, n-hexane and, n-heptane ,that is due to the number of sites that can be used for the reaction increased when the temperature increases, in agreement with Ahari et al.(2006), Asuquo et al.(1997), Martens et al.(2000) and and Narbeshuber et al. (1997).

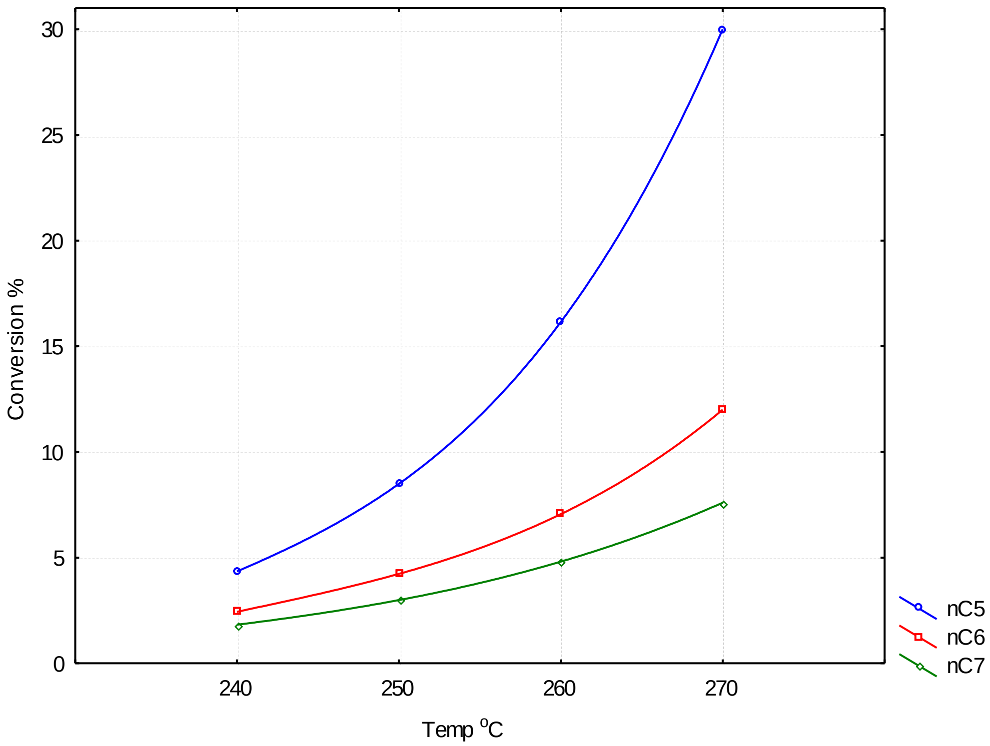

Figure 2 Conversion of nC5, nC6, and, nC7 at different temperature and LHSV=1hr-1

EFFECT OF LHSV

Figures 3 shows the changes of *n*C5,*n*C6 and, *n*C7 conversion as a function of a space time(1/LHSV). As LHSV decreases the conversion increases. This means that increasing in the residence time, which leads to offer a plenty of contact time of feed stock with catalyst inside the reactor. All results indicate that low LHSV is favored for isomerization process.

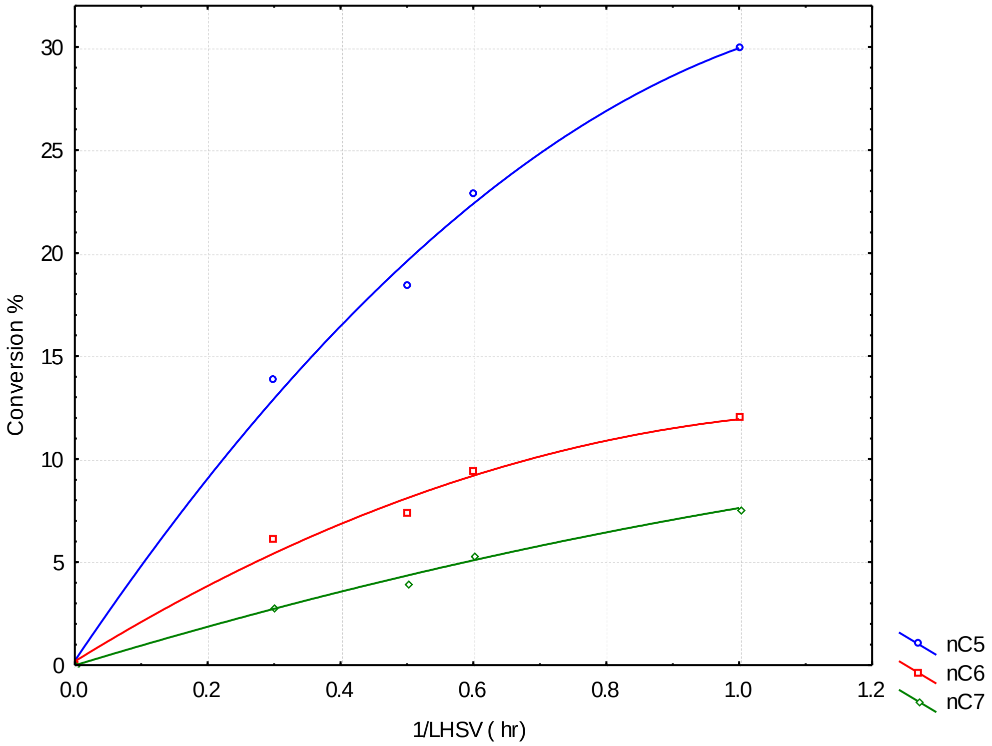

Figure 3 Conversion of nC5, nC6, and, nC7 at different contact time and T=270˚C

Rate of Reaction

According to the differential method, the rate of reaction can be estimated by finding the slop of the line tangent to the curve which represents the relationship between n-alkane conversion and (W/F_{Ao}) at any given point. **Figures 4 - 5** shows the plots of %conversion vs. the(W/F_{Ao}) for nC5, nC6, and nC7.

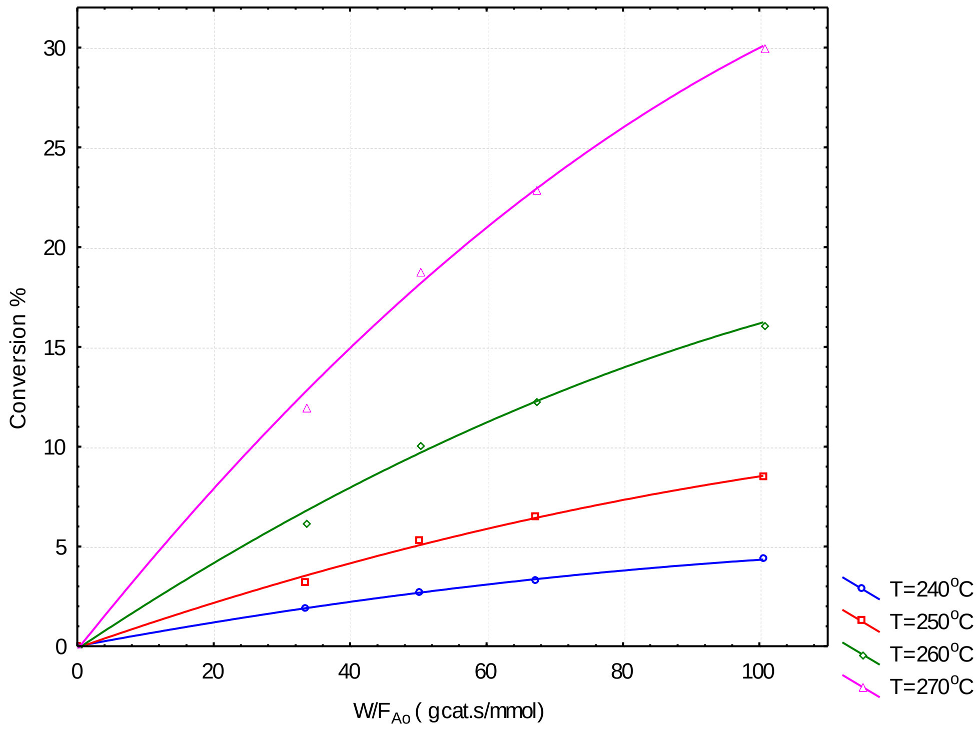

Figure 4 Experimental conversion of nC5 vs W/FAo

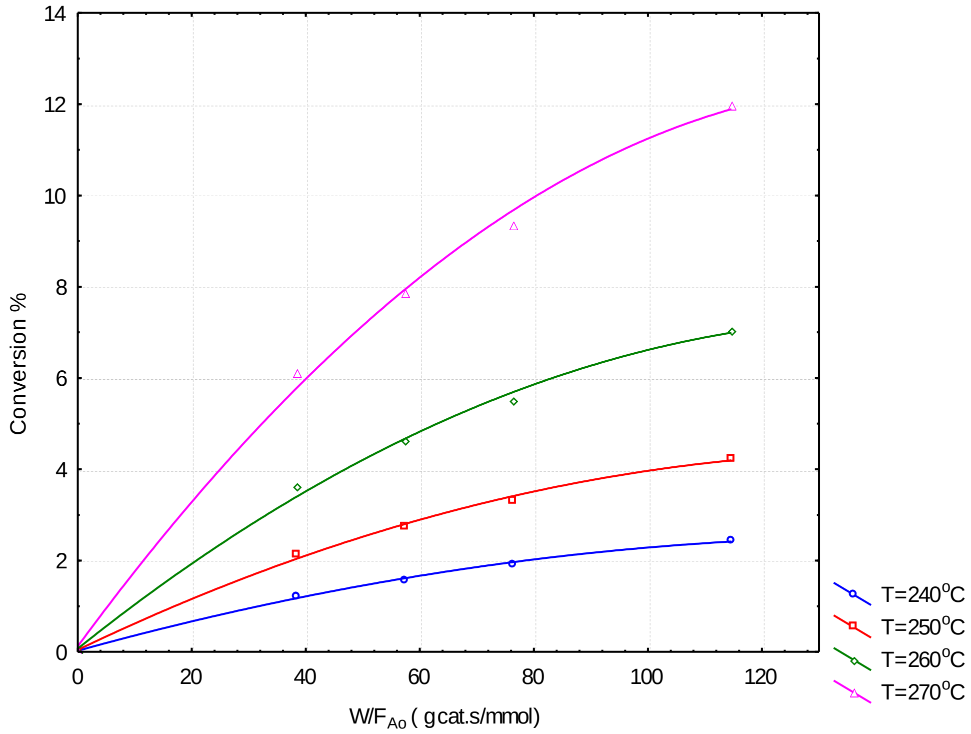

Figure 5 Experimental conversion of nC6 vs W/FAo

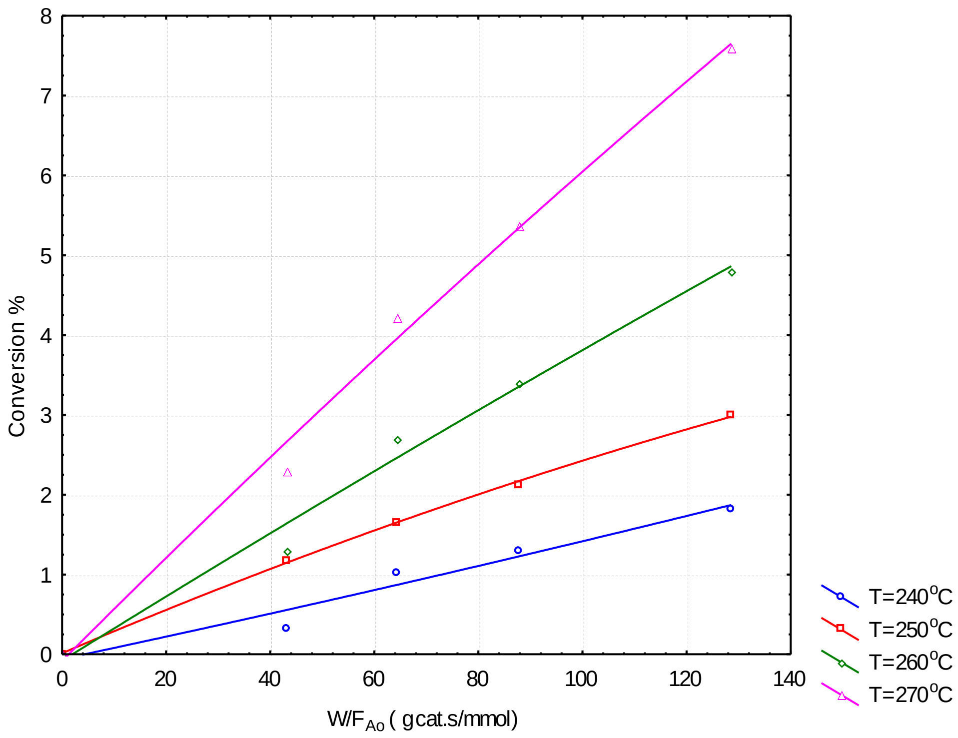

Figure 6 Experimental conversion of nC7 vs W/FAo

The Apparent Activation Energy Measurements

The activation energy (E_{act}) is usually determined by measuring the rate of reaction (***r***) as a function of temperature and fitting the data to Arrhenius equation.

$$r = z\exp(-E_{act}/RT) \qquad (1)$$

Rewriting equation (**1**) gives equation (**2**):

$$\ln(r) = \ln(z) - \frac{E_{act}}{RT} \qquad (2)$$

Table 1 shows the apparent activation energies for *n*C5, *n*C6, and *n*C7 conversions over the temperature range 240-270°C. These values are determined from the slopes of the straight lines of plots of figures 7 to 9 and according to equation (**2**).

Table 1 Apparent activation energy(kJ/mol) for C5,C6and C7

LHSV hr^{-1}	*n*-C5	*n*-C6	*n*-C7
1	145	119.9	110
1.5	147	120.9	110
2	148	122	110
3	148	122	111

As shown in Table 1 the apparent activation energy decreases with decreasing LHSV, since the rate of reaction increases with decreasing space time. Also, these values are decreases as the carbon number increases. The difference in the apparent activation energies possibly resulted from the different adsorption enthalpy since the experimentally determined activation energy consists of the sum of the true activation energy and the adsorption enthalpy. Additionally, variation of temperature and n-alkane partial pressures can lead to a variation of surface coverage which corresponds to a higher or lower degree of adsorption sides occupied and therefore different adsorption energy is observed

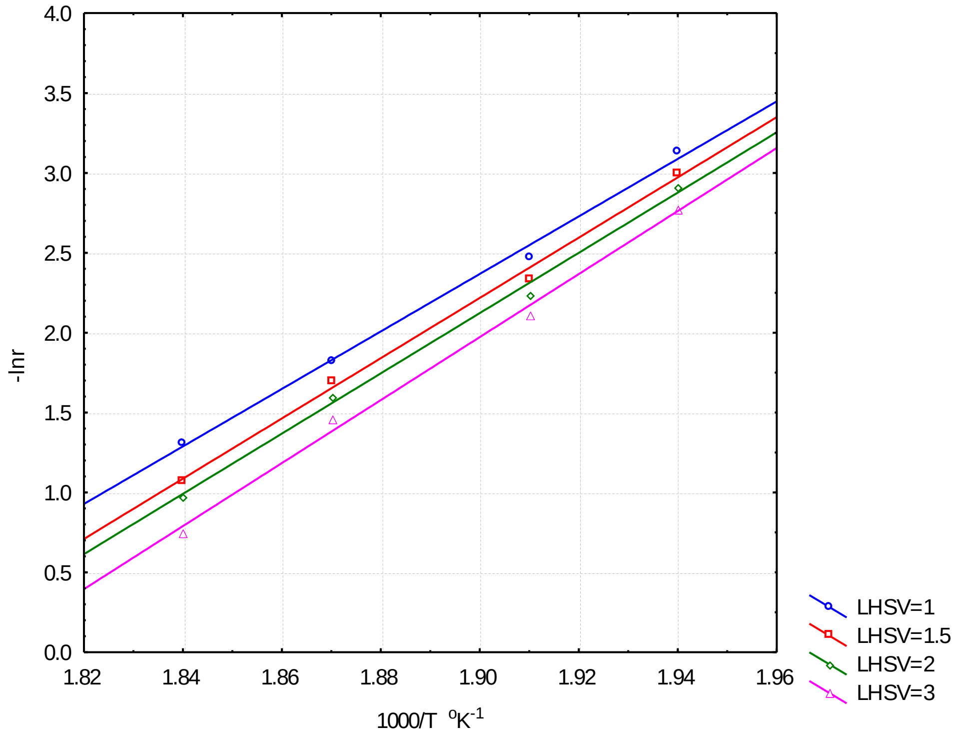

Figure 7 Arrhenius plots for isomerization process of nC5

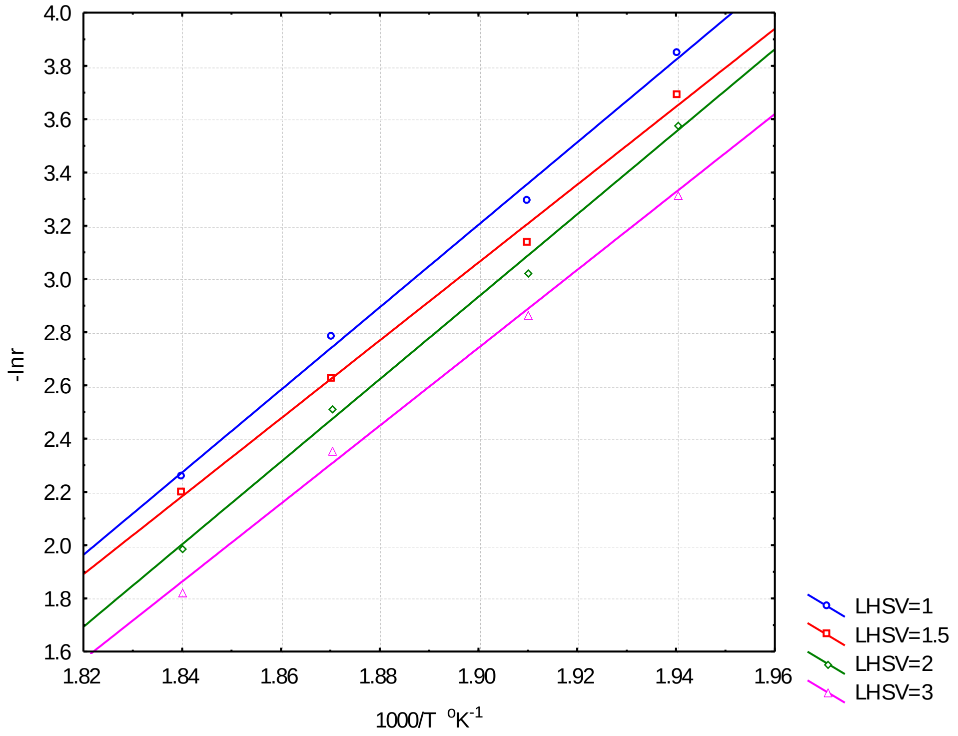

Figure 8 Arrhenius plots for isomerization process of nC6

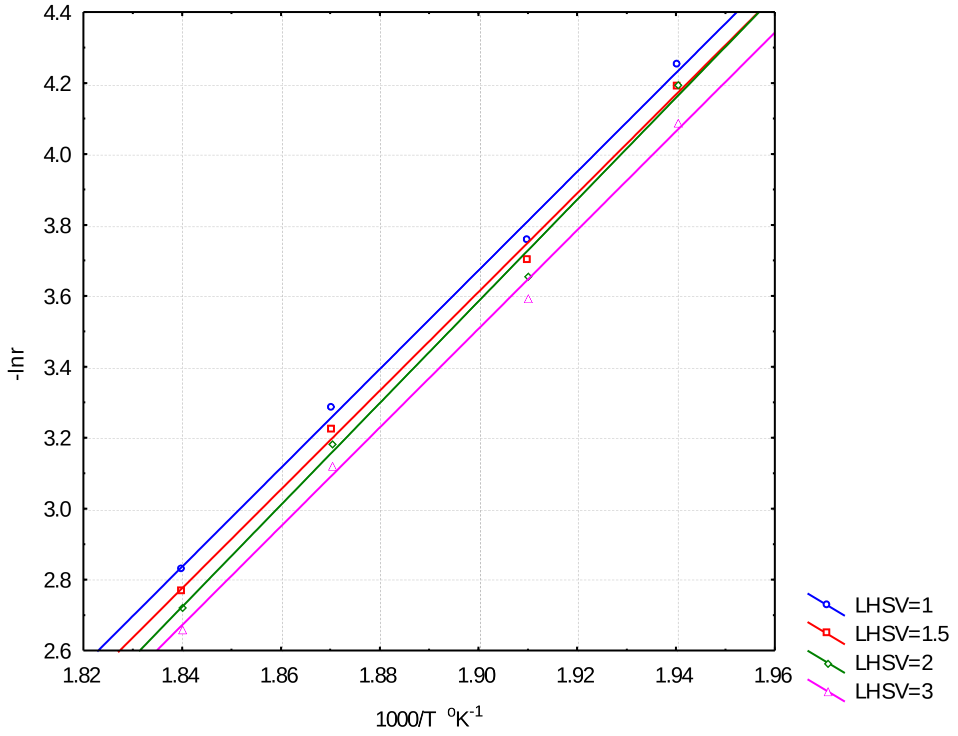

Figure 9 Arrhenius plots for isomerization process of nC7

The reaction order with respect to hydrogen and n-alkane pressure

The effect of deactivation on common empirical kinetic parameters, namely the reaction order with respect to n-alkane (***m***) and hydrogen (***n***) and the apparent activation energy ($E_{act,app}$) is represented in equation 3 [Alvarez et al.,1996]:

$$TOF = k_{re}\ P^{m}_{n-alkane}\ P^{n}_{H2} \qquad (\mathbf{3})$$

Where, TOF is the turnover frequency and is defined as the rate of reaction per acid site [Runstraat et al., 1997b], k_{re} is effective reaction rate coefficient. From equation 2.1 it can be gathered that m and n are function of $P_{n\text{-alkane}}$ and P_{H2} ranging from 0 to 1 for (***m***) and -1 to 0 for (***n***). However, in many studies the absolute values of ***m*** and ***n*** is found both ***m***<-***n*** and ***m***> -***n***. These differences are usually attributed to deactivation effects [Alvarez et al.,1996, Santen et al.,1997].Since the TOF is defined as the rate of reaction of n-alkane per acid site, equation (**3**) can be rewritten into the following empirical form:

$$-r = k\ P^{m}_{n-alkane}\ P^{n}_{H2} \qquad (\mathbf{4})$$

Where, ***k*** is constant and equal to the effective reaction rate coefficient multiplied by the number of acid site. Rewriting equation (**4**) gives equation (**5**):

$$\ln(-r) = \ln k + m \ln P_{n-alkane} + n \ln P_{H2} \qquad (\mathbf{5})$$

The order of reaction with respect to hydrogen at given temperature can be calculated by simulating the reaction at different hydrogen partial pressure and fixed n-alkane partial pressure. According to equation (**5**), plotting ln(-***r***) vs. ln($\mathbf{P_{H2}}$) must gives a straight line with slop equal to ***n***. The order of reaction with respect to n-alkane was achieved by simulation the reaction in variable n-alkane partial pressure and constant hydrogen partial pressure. According to equation (**5**), plotting ln(-***r***) vs. ln($\mathbf{P_{n\text{-}alkane}}$) should gives a straight line with slop equal to ***m***.

Alkane Order Measurement

Table 2 shows the order of reaction with respect to nC5, nC6, and nC7 at different temperature. As shown in table 2, no significant change in the reaction order was detected when the temperature increases from 240-270°C. The values of the reaction order with respect to n-alkane are arranged in the following manner:

$$\mathbf{C_7 < C_6 < C_5}$$

Table 2 Reaction order with respect to n-alkane(m) at different temperature

Temp °K	*n*-C5	*n*-C6	*n*-C7
513	0.339	0.337	0.156
523	0.338	0.335	0.155
533	0.335	0.332	0.154
543	0.336	0.332	0.154

The most likely reason for slight change in the order of reaction may be due to the active sites elimination resulted from deactivation increase with increasing $P_{n\text{-}alkane}$. This is enhanced by the fact that coking involves bimolecular reactions. The extent to which (***m***) is decreased depends on the rate of deactivation which itself is a function of, among other things, temperature and catalyst characteristics. Hence the variation in the deviations from the intrinsic (***m***) values caused by deactivation.

Hydrogen Order Measurement

The orders of reaction with respect to hydrogen (***n***) are tabulated in **table 3**. These values are vary with the n-alkane carbon number, and arranged in the following order:

$$C_5>C_6>C_7$$

Also, it seems that these values are slightly affected when the temperature rises from 240 to 270°C, the decrease of ***n*** values can be attributed to the change in the number of active sites resulting from coke deposition. The steady state level of deactivation increases with decreasing P_{H2}. These results show that the effect of deactivation on hydrogen order is stronger than on the n-alkane order, indicating that the rate of deactivation is more sensitive to P_{H2} than to $P_{n\text{-alkane}}$. The reason for this is probably that a decrease of P_{H2} not only results in a higher concentration of alkene, but also in a lower rate of decoking reaction.

Table 3 Reaction order with respect to hydrogen (n) at different temperature

Temp °K	*n*-C5	*n*-C6	*n*-C7
513	-0.652	-0.811	-0.998
523	-0.640	-0.809	-0.981
533	-0.631	-0.810	-0.968
543	-0.620	-0.808	-0.948

Selectivity and Product Distribution

n-Heptane

Figure 10 shows the distribution of three main products : methylhexane and ethylpentane (monobranched isomers(**MB**)); dimethylpentane (dibranched isomers(**DB**)); and cracked products(**CP**), as a function of the total conversion.

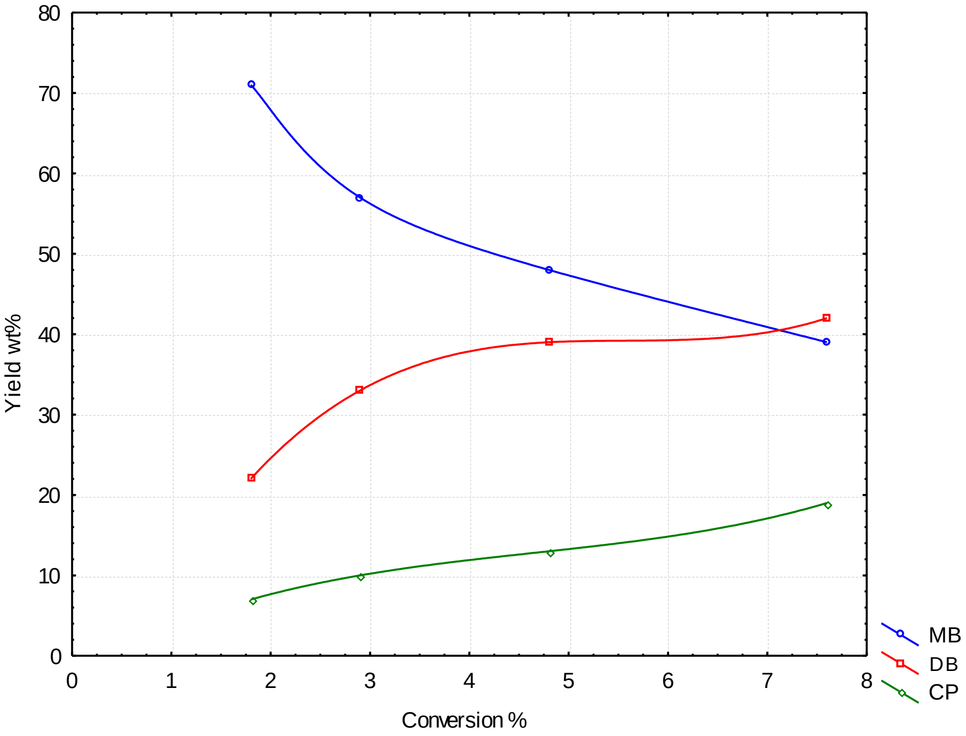

Figure 10 Product distribution for nC7 conversion (LHSV=1hr-1)

Figure 11 shows that Methylhexane constitute over 97% of the mono branched products,and that 2- and 3- methylhexane seems to be in a ratio close to equilibrium value that is around 1.2 (**figure 12**) .

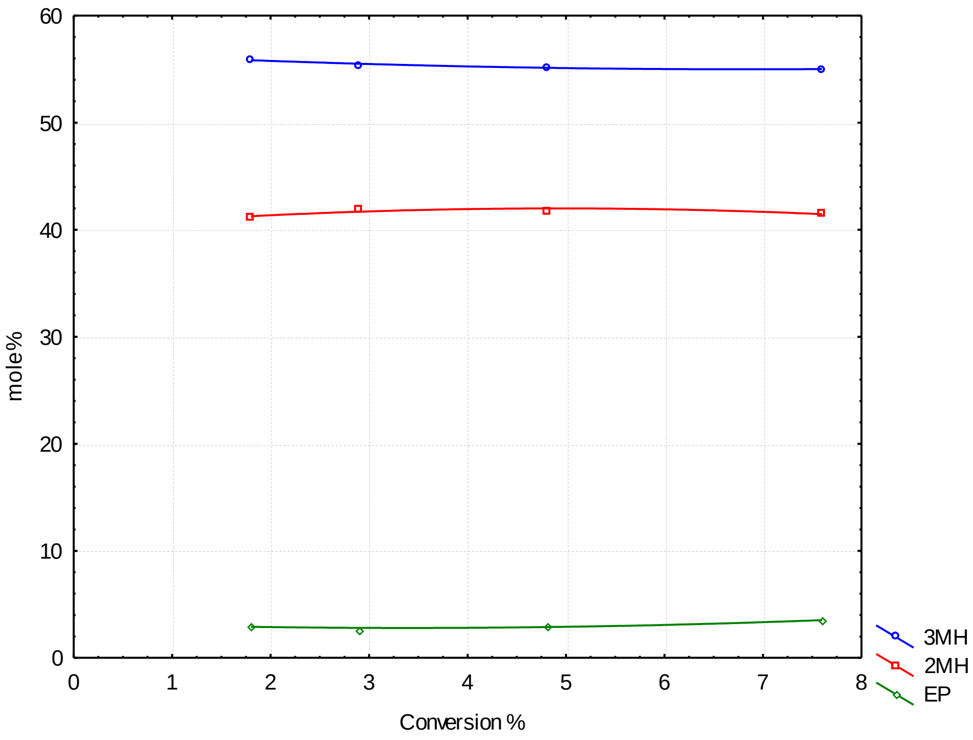

Figure 11 Distribution of monobranched isomers for nC6 conversion (LHSV=1 hr-1)

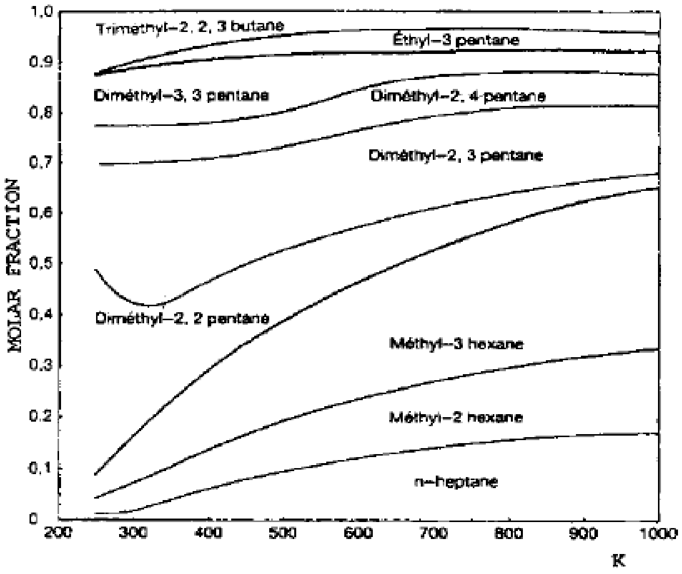

Figure 12 Thermodynamic equiliberium for Heptane isomerization (Pins et al. 1984)

The dibranched isomers distribution changes also very noticeably with the conversion (**figure 13**). 2,3-Dimethylpentane is initially highly favored but disappears for the benefit of 2,2- and 3,3-dimethylpentanes. 2,2,3-Trimethylbutane formed with negligible amount, moreover, its only formed like cracking products for very high conversion. This results are in agreement with the results published by Giusepp et al.(1986).

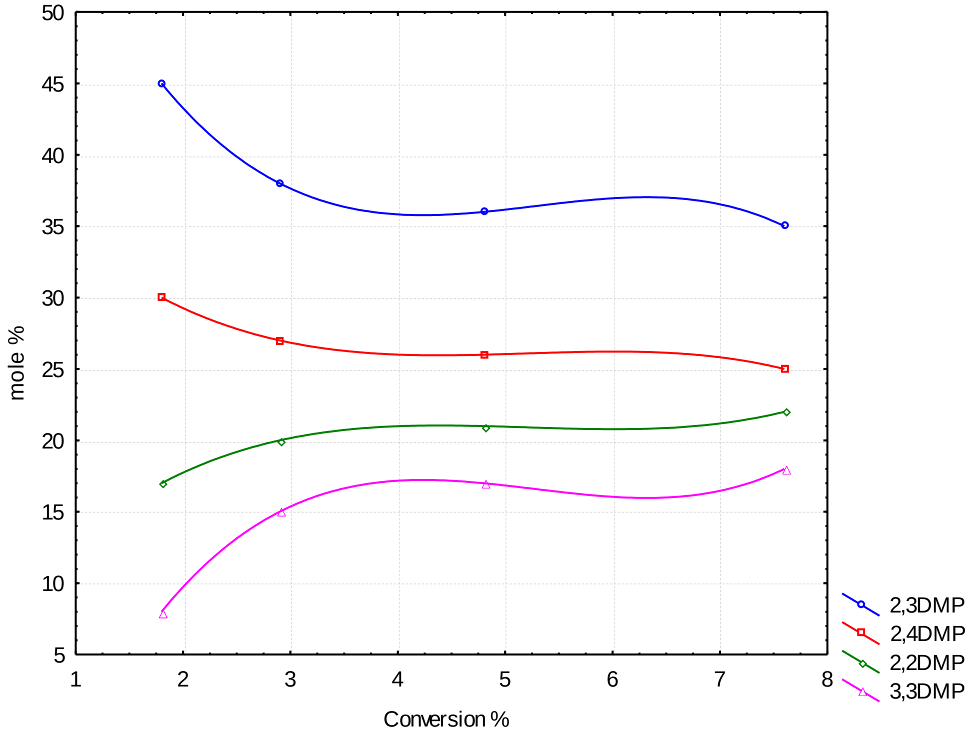

Figure 13 Distribution of dibranched isomers for nC7 conversion (LHSV=1 hr-1)

n-Hexane

Figure 14 shows the distribution of three main products: methylpentane (monobranchedisomers(**MB**)); dimethyl-butane (dibranched isomers (**DB**)); and cracked products(**CP**), as a function of the total conversion.

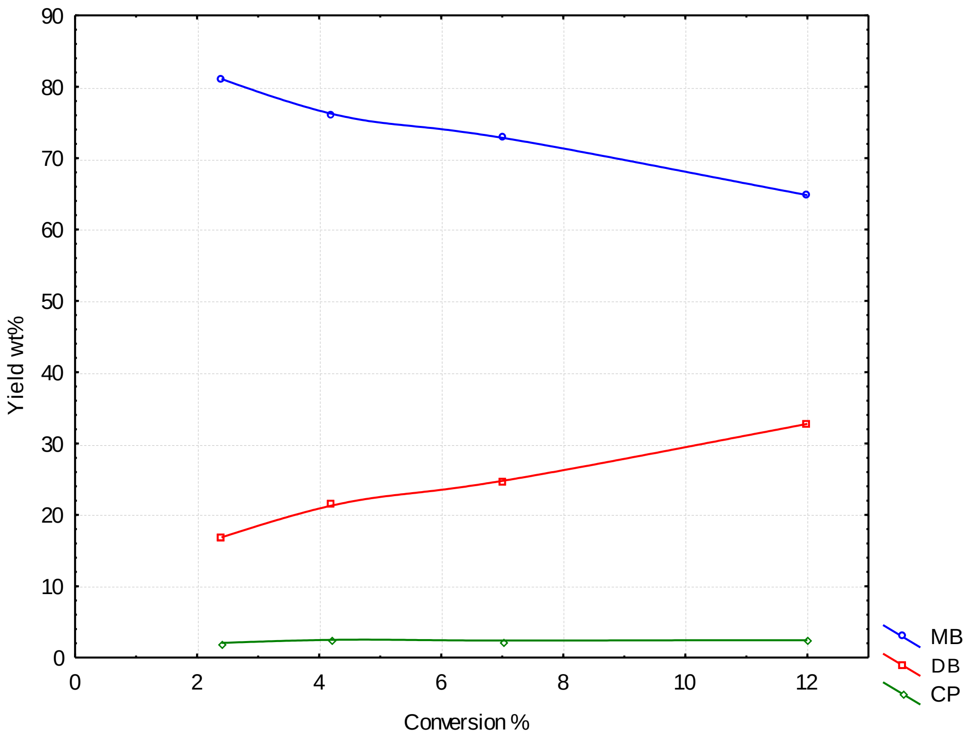

Figure 14 Product distribution for nC6 conversion (LHSV=1hr-1)

Figure 14 shows that the monobranched isomers are the main products. **Figure 15** shows that the 2-methylpentane (2MP)/ 3-methylpentane(3MP) ratio is found to be around the thermodynamic equilibrium value (~1.6) (**figure 16**).

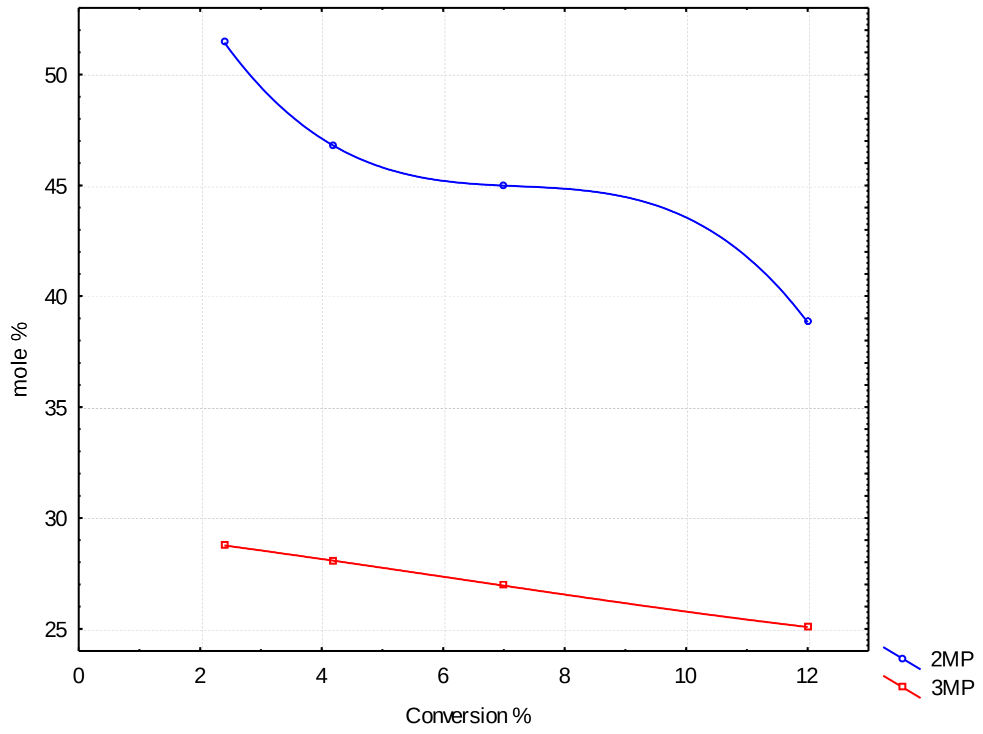

Figure 15 Distribution of monobranched isomers for nC6 conversion (LHSV=1 hr-1)

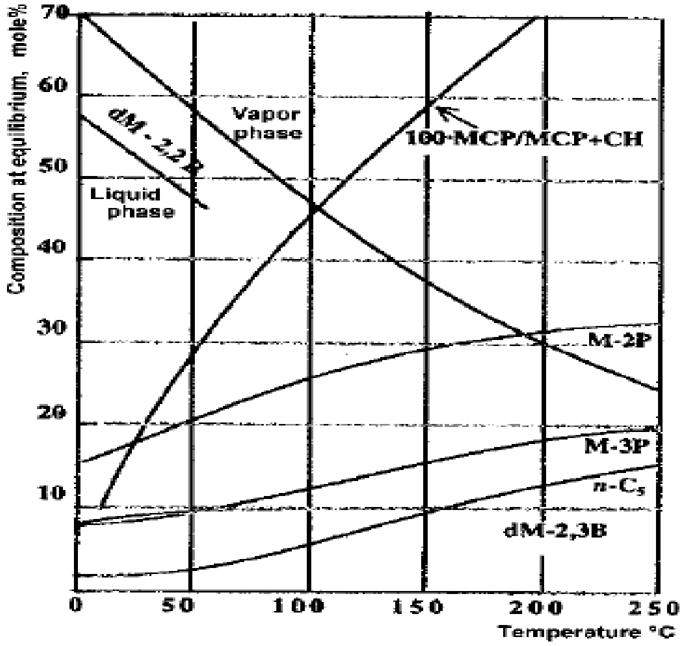

Figure 16 Thermodynamic equiliberium for Hexane isomerization(Serge, 2003)

The ratio of 2-methylpentane (2MP) /2,3-dimetylbutane (2,3DMB) is also reached the thermodynamic equilibrium value as seen in **figure 17**. Further more 2,3DMB should be formed more rapidly than 2,2DMB since 2,3DMB formation involves tertiary cation [Allain et al.,1997]. However, the transformation of 2,3DMB to 2,2DMB is slow because it is required the passage through a tertiary carbocation which is less stable.

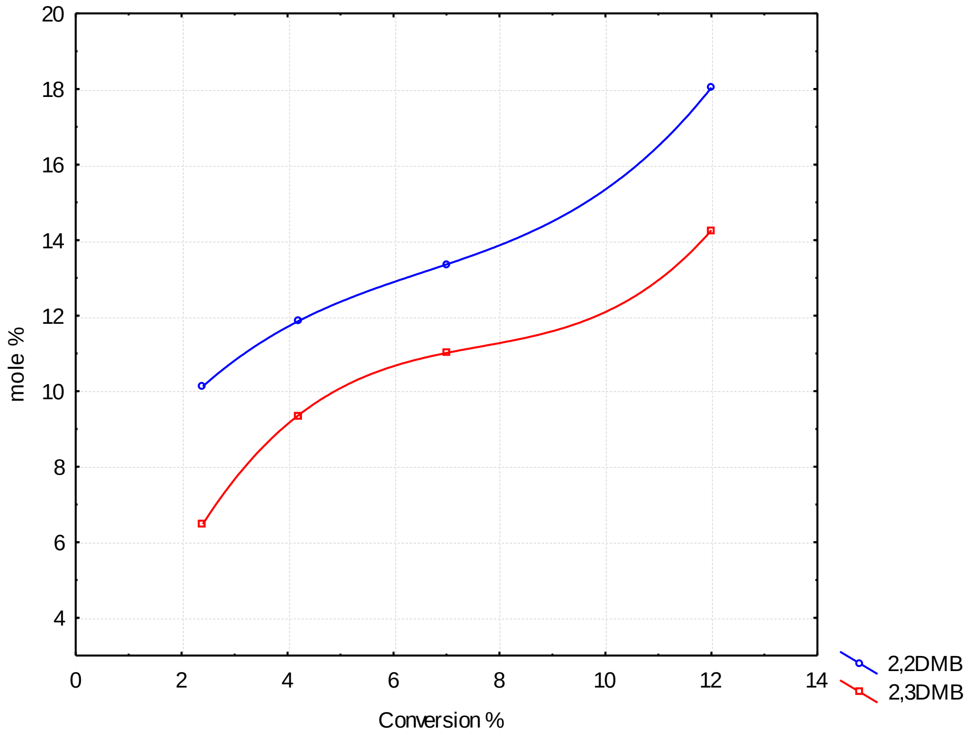

Figure 17 Distribution of dibranched isomers for nC6 conversion (LHSV=1 hr-1)

n-Pentane

Figure 18 show that the iso-pentanes is the main product for n-pentane conversion over Pt/HY-Zeolite, the n-pentane molecules are easily penetrated into the catalyst pore so that the conversion is higher than that for n-hexane and n-heptane reaction.

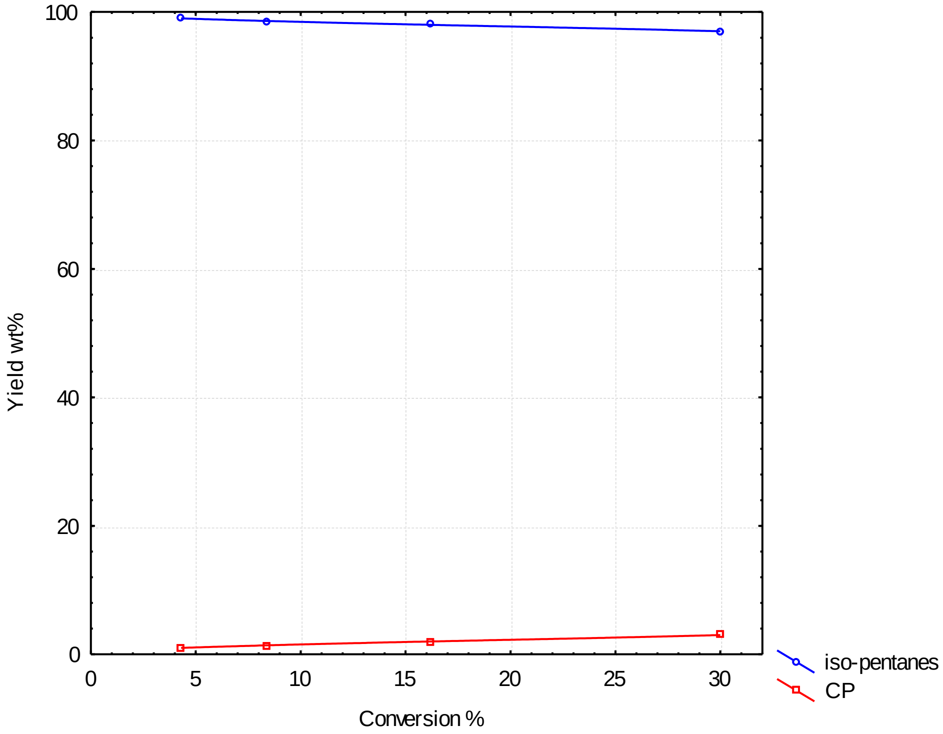

Figure 18 Product distribution for nC5 conversion (LHSV=1hr-1)

CONCLUSION

- It was observed that the isomerization of n-heptane occurs as follows:

  nC7↔(3MH,2MH,EP)↔(2,3DMP,2,4DMP)↔(2,2DMP,3,3DMP)

  and the that the isomerization of n-hexane occur as follows:

  n-C6↔(2MP,3MP)↔(2,3DMB)↔(2,2DMB)

- The conversion of n-pentane, n-hexane, and n-heptane increases as pressure of n-alkane increases and hydrogen pressure decreases. This leads to positive order with respect to n-pentane, n-hexane, and n-heptane , and negative order with respect to hydrogen.
- It was observed that the values of apparent activation energy for hydroisomerization of n-pentane, n-hexane, and n-heptane over the prepared catalyst take the following order

  E_{act} of *n*-Heptane < E_{act} of *n*-Hexane < E_{act} of *n*-Pentane

  And the apparent activation energy decreases with decreasing LHSV since the rate of reaction increases with decreasing space time
- the selectivity to iso-alkanes increases as the n-alkanes chain become shorter. This illustration can be seen in **Figure 19** show a comparison between the selectivity of n-pentane, n-hexane, and n-heptane to the total isomers as a function of temperature. Okuhara (2004) reported that if the number of carbon

atom is 7 or higher, the β-scission of the carbenium ion can take place to form alkenes and carbenium ion with less number of carbon atoms. As a result, a smaller hydrocarbon chains are formed. This is one of the important reasons for the low selectivity in the isomerization of n-heptane especially when the reaction temperature increases. **Figure 20** show a comparison between the selectivity of n-pentane, n-hexane, and n-heptane to the cracked products as a function of temperature.

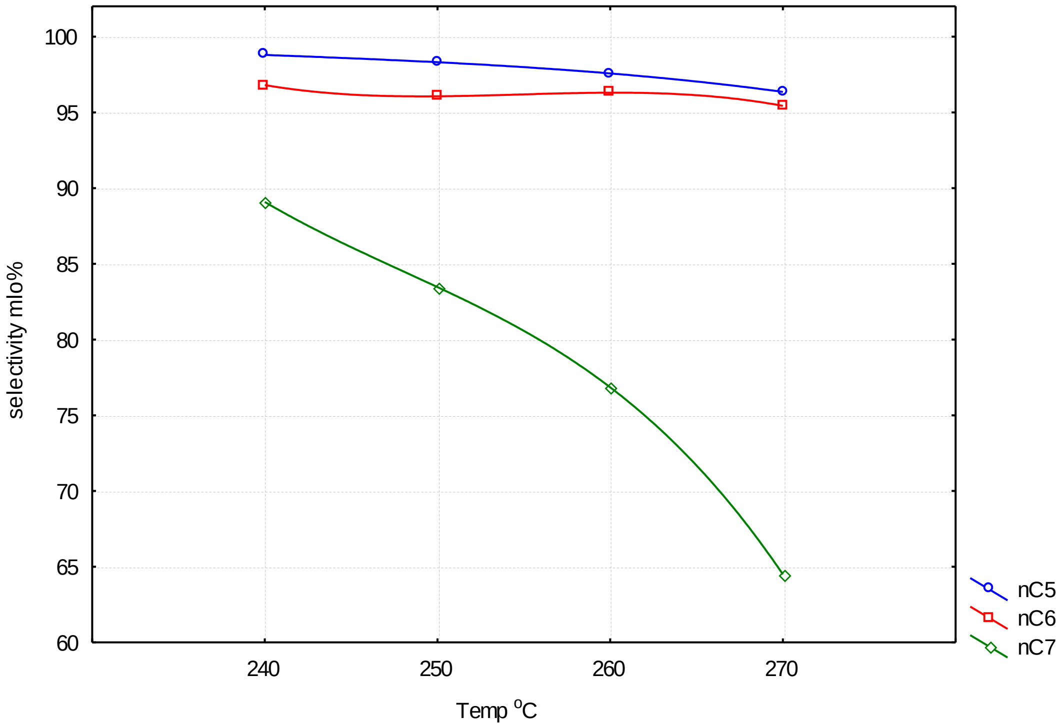

Figure 19 Selectivity to total isomers for nC5, nC6, and nC7 at different temperature (LHSV=1 hr-1)

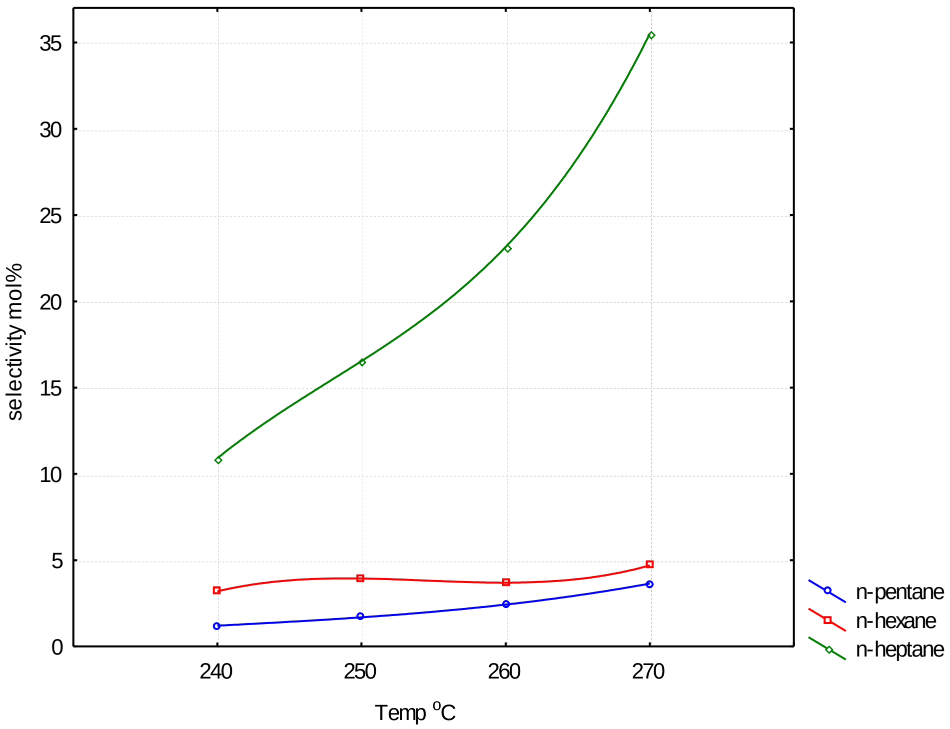

Figure 20 Selectivity to cracked products for nC5, nC6, and nC7 at different temperature (LHSV=1 hr-1)

REFERENCES

- Jafar Sadeghzadeh **Ahari**, Kayvan Khorsand, Azita A Hosseini, Amir Farshi ," EXPERIMENTAL STUDY OF C5/C6 ISOMERIZATION IN LIGHT STRAIGHT RUN GASOLINE (LSRG) OVER PLATINUM MORDENITE ZEOLITE", Pet. & Co. 48 (3), 42-50, 2006.

- **Allain** J. F., P. Magnoux, Ph. Schulz and M. Guisnet," *Hydroisomerization of n-hexane over platinum mazzite and platinum mordenite catalysts kinetics and mechanism*", App. Cat. Vol.152, (2) , 221-235,1997
- **Alvarez**, F., Ribeiro, F.R., Perot, G., Thomazeau, C., Guisnet, M., Jour.of Cat., Vol. 162,(2, 179-189), 1996.
- **Asuquo** R.A.,G.Eder-Mirth, K. Seshan, J. A. Z. Piterse, and J. A. Lercher " *Improving the stability of H-mordenite for n-butane isomerization*" , Jour.of Cat.,168,292-300(1997).
- **Cañizares** P., A. Durán, F. Dorado and M. Carmona, App.Clay Sci.Vol.16, 273-287,2000

- **Exner** H., E. Nagy, F. Fetting, and L. Gubicza, conf. of app. Chem. Vol 2 420-425(1989).
- **Giuseppe** E. Glannetto, Guy R. Perot, and Michel I., *Ind. Eng. Chem. Prod. Res. D8V.* 1986, 25, 481-490
- **Kouwenhoven** H.W. and W.C. Van Zijll Langhout, ,.*Chem .Eng. Prog*., v.67, p.65, 1971

- **Kuchar** P. J., J. C. Bricker, M. E. Reno, R. S. Haizmann, Fuel Pro. Tech., Vol.35, . 1-2, 183-200,1993

- **Lanewala** M. A., P. E. Pickert and A. P. Botton, Journal of CatalysisVolume 9, Issue 1, September 1967, Pages 95-97.
- **Meyers**, A. Robert, "*Handbook of Petroleum Refining Process*." McGraw Hill, New York (1996).
- **Martens** G.G., G.B.Marin, J.A.Martens, P.A. Jacobs, and G.V. Baron" *A fundemental kinetic model for hydrocracking of C8 to C12 alkanes on Pt/US-Yzeolites*", jor.of cat.195,253-267 (2000).
- **Narbesshuber** Thomas F., Axel Brait, Kulathuyiedr Seshan, and Johannes A. Lercher "*Dehydrogenation of light alkanes over zeolite*" , jor. of cat. 172,127-136(1997).
- **OKUHARA** Toshio, *Skeletal Isomerization of n-Heptane to Clean Gasoline*,jour. Of jap.petr.inst. 47,(1),1-10, 2004
- **Pine** L. A., P. J. Maher, W. A. Wachter," *Prediction of cracking catalyst behavior by a zeolite unit cell size model*" Jour. of Cat., Vol. 85, .2, 466-476,1984.
- **Ribeiro** F., C. Marcilly, M. Guisnet, Jour. of Cat., Vol. 78, 2, , Pages 267-274,1982.
- **Runstraat** A. van de, J. A. Kamp, P. J. Stobbelaar, J. van Grondelle, S. Krijnen, and R. A. van Santen, Jour. of Cat. 171, 77–84 (1997a)

- **Runstraat** A. van de, Joop van Grondelle, and Rutger A. van santen, Ind. Eng. Chem. Res.,36,3116-3125. (1997b)
- **Santen** R. A. van, Runstraat A. van de, J. van Grondelle, , Jour.of Cat., Volume 167, .2, Pages 460-463 ,1997.
- **Serge** Raseev, "***Catalytic processes in petroleum refining***", *New York* 2003.