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Kinetics Of C_5/C_6 Isomerization In Light Straight Run Gasoline Over Platinum Mordenite Zeolite

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ABSTRACT

This article is the result of comprehensive study about isomerization process of light paraffin, including: Mechanism of reaction, laboratory tests and determination of kinetic equations. At the first, the history of isomerization process is described and following that the types of methods and catalysts are considered, then the effective factors are pointed and experimental results of Geomechanical pilot on feed of a refinery in Iran will be considered. At the end, the final conclusion based on experimental results will be presented and finally the rate of equation will be offered. © 2006 Trade Science Inc. - INDIA

KEYWORDS

Isomerization;
Light naphtha;
Kinetics.

INTRODUCTION

Crude oil treatment is related to the first successful excavation in 1859(Titusville). Crude oil became available by oil rock exploration in western north of Pennsylvania and the refineries produce kerosene by using simple distillation of the first product have better quality than animal oil for light. After that, completion of oil excavation technologies developed to Russia and the other refineries can produce better quality fuel oil and kerosene in 1890.

As car increasing, the request for the high quality gasoline, also, increased and continuous distillation of crude oil is developed. During World WarP, iso-butane process and alkylation to produce airplane motor fuel became important. In this operation, n-butane isomerization was necessary.

In 1958, some processes suggested for isomerization of light straight run gasoline . Following refineries request in USA for increasing gasoline octane number with low cost. They found that the high oil cutoff shape is produced by atmospheric distilla-

tion directly that includes a large amount of n-paraffin (Bp: 27-71°C and Octane No.: 65-70).

The refiners produced two types of lead gasoline and mix the cut off in that to achieve good indicator. This is because of good capability of mixing n-paraffin and nonlinear paraffin in the presence of lead. World activity to remove additives such as Lead tetra ethyl and Lead tetra methyl to reduce air pollution of vehicles is the major target for using light paraffin isomerization. Replacing alcohols, aromatics and iso-paraffins with compounds with low octane number, slightly, can compensate decreasing octane number that causes by removing or reducing lead compounds.

Unfortunately, most of these compounds have been abolished, completely, in order to have hazardous environmental effects. So, the isomerization technology of light paraffin (C5/C6) to produce fuel for vehicles becomes important in recent years.

LSRG Isomerization Processes

Isomerization of Light Straight Run Gasoline leads to produce substituted alkenes that are important for producing gasoline with high octane number and low amount of aromatics and Lead

(Pb). This reaction proceeds via carbonium ion that requires strong acid media and equivalent temperature and is suitable for substituted isomers production. The catalysts including rare metals and solid acids and modified mineral soil in the presence of Pt have been used for C5/C6 isomerization at medium temperature (200-300°C).

Basically, two types of catalytic isomerization processes are used to convert n-paraffin to substituted molecules^[1,2,3]. The first method uses catalyst at low temperature (about, 93-204°C) that is sensitive to feed impurities such as Sulfur, Nitrogen, Oxygen compound and water.

The second uses Zeolite catalyst with lower activity, that can bear feed impurities, but it works at higher temperature than equivalent temperature (about 230-270°C). The impurities exists in LSRG feed, include gasoline, Olefin and higher and lower Carbon compounds. Since these reactions are occurred under hydrogen pressure, Benzene and saturated olefins and higher hydrocarbons will be hydro-

cracked. Lighter hydrocarbons are neutral. Feed main components are affected, partially, by secondary reaction (Hydrocracking) and the Hydrogen consumption is low.

After isomerization, reactor output cools and high-pressure hydrogen will be separated by instant vaporization and recycled to the beginning of the process.

Isomerate product should be stabilized to separate remained hydrogen and low amount of light products.

Instant pressure change can be used for decreasing the amount of stabilizer overhead gas.

The processes that are using zeolite catalysts require the operating temperature higher than equilibrium temperature and because of the thermo dynamical limitation per pass, lower isomerization occurs; thus for each pass, the octane number of product can not be more than 80 and this number can be increased by separating and recycling of remained Pentane.

Usually, the input feed introduces to Deisopentanizer to separate iso-pentane and to limit the equilibrium conversion in reactor.

Separation equipments can be added to recycle hexanes with low octane number to give higher octane number.

The catalyst can be regenerated per 5 or more years.

In the other type of isomerization process by using Chlorinated catalyst the dry feed and input hydrogen require and the amount of the Sulfur in the feed should be controlled.

The catalyst cannot be regenerated. Besides, system risk will be increased due to corrosion that is caused by any possible upset and humidity because of hydrochloric acid injection.

Regarding to process temperature (near equilibrium temperature), Octane number per pass, also, reaches to 85. If the higher octane number is necessary the n-pentane should be separated and recycled (figure-1)^[4].

The weaker in hexane compounds, regarding to Octane number is n-hexane and the best is Dimethyl butane (2, 3- Dimethyl butane is better than 2, 2-Dimethyl butane). Methyl pentane regarding to boil-

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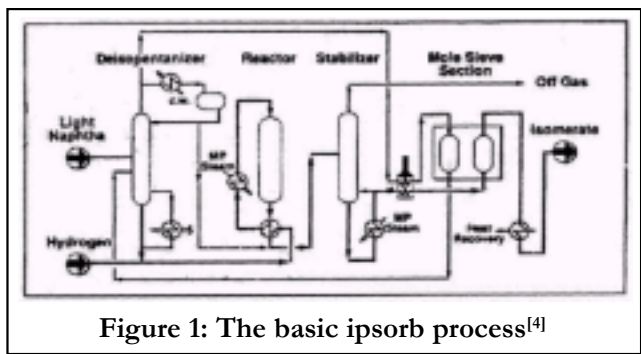


Figure 1: The basic ipsorb process^[4]

ing point and Octane number is medium.

Separation of dimethyl butanes from methyl pentane is required. The process is same as recycle process of pentane, but it needs a deisohexanizer column to separate dimethyl butane as a major cut off.

The column requires a lot of tray and high-recycled stream and high utility consumption^[5].

In addition to fractionation distillation separation lower octane number compounds can do by molecular sieves adsorption. In this method, only, linear n-paraffin adsorb, since they are alkane molecules with small dimension and can be transferred into by molecular sieves (5°A diameters), thus, the octane number is low because methyl pentane is not recycled.

Separating by fixed bed molecular sieves is preferred because their mechanical forces are not sufficient to move the bed. So, cyclic process is required for adsorption and desorption. N-Paraffin main components adsorb and the others are passed through adsorbent and liquefied as a product.

When bed reaches its defined design, then the feed flow path changes to another bed and hydrogen passes the bed through counter current to remove n-paraffins. The mixture of hydrogen and n-paraffins with fresh feed charged into isomerization reactor, reactor output cools and puts under instant pressure change to separate hydrogen from liquid hydrocarbons with molecular sieves. Light components separate from products in stabilizer and gives stabilized product with high octane number^[1, 6, 7].

Isomerization reaction mechanism

Isomerization process by using two-functional catalyst includes 3 stages are as follows:

- (1) Dehydrogenation
- (2) Isomerization
- (3) Hydrogenation

Stages 1 and 3 take place on metal function and stage 2 takes place on acid site bases.

At first, n-paraffins convert to olefins on metal center through dehydrogenation. Olefin transfers from metal centers to acid sites and adsorbs one proton (H^+) and then converts to substitution compound by rearrangement and releases proton to give olefin. Iso-olefines converts to iso-paraffines after penetration from acid centers to metal centers via dehydrogenation.

Isomerization reaction mechanism on zeolite catalyst depends on its acid center density, holes structure and operating condition^[8,9,10]. The pressure has less effect on little obstacles catalysts and it works the same as an ideal two-functional catalyst. As pressure increasing the improvement of the catalyst selectivity occurs in more obstacles catalysts. At atmospheric pressure, the catalyst activity will decrease, if the acid center's density decreases. If no acid center (AlO_4) exists, at high pressure, activity reaches the maximum. The less acid centers density, the higher ratio of Si/Al and the more stable catalyst.

The differences between reactions under atmospheric and high pressure are due to hydrogen effect on residence time of Olefin intermediates in catalyst holes.

Rapid deactivation that takes places on catalyst under atmospheric pressure and the limitation effect of hydrogen on residence time of olefin intermediates in catalyst holes can be affected these differences. The catalyst that has more acid centers is more exposed to the initial deactivation. Hydrogen has positive effect on the stability of these catalysts.

Iglesia and his colleagues explained that hydrogen absorbs to Platinum and produces iso-alkane by transferring hydride ion to isomerated carbonium ion^[11,12].

Fujimoto and his co-workers believed that hydrogen (as H^+ , H^-) transfers from metal surface to zeolite and H^+ reduces acid centers in zeolite and H^- produces isomeric production after reaction with Carbonium ion^[13].

High pressure hydrogen occupies holes and active sites of catalyst and decreases the carbonium ion and intermediate elements concentration on the

catalyst surface that leads to the lack of availability of intermediate Olefins to the surface and proper dehydrogenation that decreases catalyst activity. So, hydrogen pressure should be stabilized in a defined amount to reach the optimum operation condition^[14].

Since the transition element concentration is affected by temperature (the concentration reduces in lower temperature), all attempts are taken to produce the catalysts that have capability to give isomers in a good amount at low temperature^[15, 16].

The amount of distribution in isomerization products of n-paraffin depend on^[14]:

- 1) Length of normal paraffin chain
- 2) Concentration of acid site of catalyst
- 3) The ratio of Pt per catalyst acidic site

Generally, the products are the result of isomerization and hydro-cracking.

Production of C1, C2 is very low and no olefin will produce. It implies that all olefins that are produced in the presence of Pt are converted to paraffin.

Selectivity in conversion of n-heptane is as follows:

Multi branches isomers < cracking products < one-branch isomers

In addition, as pressure increases, increasing in isomerization yield in high acid sites (Si/Al<18) to low acid sites (Si/Al>18) changes quickly. One-branch distribution ratio is 1 (2M.Hexane/3M.Hexane \cong 1) and with pressure increasing this ratio doesn't change.

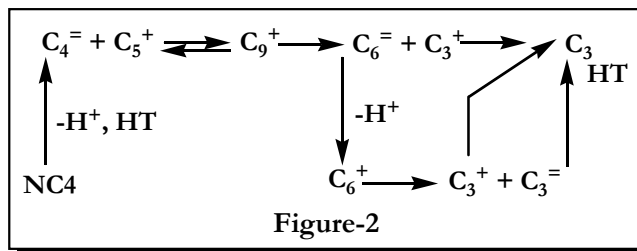
Two-branches isomers that have third kind of carbon are preferred. (i.e. 2.4 and 2.3 D.M. pentane produces and then 2, 2 and 3, 3-D.M. pentane will produce)

The products of NC6 are, respectively, 70% Isobutane, 15% Propane, 12% Pentane that indicates two stage-reaction of NC4.

NC4 has converted to its products through dimerization, isomerization and cracking processes.

For instance Propane producing stages from NC4 have been shown in figure 2.

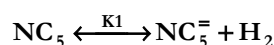
The products from NC4 are methyl pentane, dimethyl butane and C3-C5. The amount of isomerization is 1.5-2.5 as many as of cracking (i.e. C3-C5 production) and with increasing Al atoms the amount



of C3 and C5 increases. NC4 cracking gives propane but C4 and C5 cracking do not give C3. The major products of NC6 are Olefins (pentene, butane, propane) that result from cracking products and the ratio of isomeric products to cracking products is low.

For instance the mechanism of n-Pentane isomerization is illustrated as follows^[17, 18]:

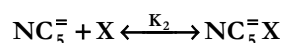
1. NC5 dehydrogenation with Pt



Assuming that it reaches equilibrium with high velocity:

$$K_1 = \frac{P_{\text{NC}_5^-} \cdot P_{\text{H}_2}}{P_{\text{NC}_5}}$$

2. NC5⁻ adsorption in acid sites

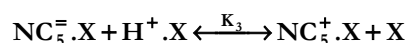


Assuming high velocity and subsequently at equilibrium:

$$K_2 = \frac{C_{\text{NC}_5^- \cdot \text{X}}}{P_{\text{NC}_5^-} \cdot C_{\text{V}}}$$

X is active site on catalyst.

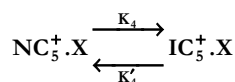
3. Producing Carbonium ion by NC5⁻·X



At equilibrium state:

$$K_3 = \frac{C_{\text{NC}_5^+ \cdot \text{X}} \cdot C_{\text{V}}}{C_{\text{NC}_5^- \cdot \text{X}} \cdot C_{\text{H}^+ \cdot \text{X}}}$$

4. Rearrangement step of NC5⁺



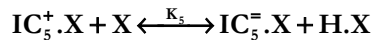
As a limiting step of reaction:

$$r = K_4 \cdot C_{\text{NC}_5^+ \cdot \text{X}} - K_4' \cdot C_{\text{IC}_3^+ \cdot \text{X}}$$

$$r = K_4 \left(C_{\text{NC}_5^+ \cdot \text{X}} - \frac{C_{\text{IC}_3^+ \cdot \text{X}}}{K_5} \right)$$

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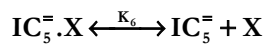
5. Releasing hydrogen



With high velocity to reach equilibrium state:

$$K_5 = \frac{C_{iC_5^-.X} \cdot C_{H.X}}{C_V \cdot C_{iC_5^+.X}}$$

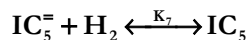
6. Desorption of iC_5^- from acid site



It reaches equilibrium state:

$$K_6 = \frac{P_{iC_5^-} \cdot C_V}{C_{iC_5^-.X}}$$

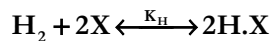
7. Hydrogenation step in the presence of Pt



It reaches equilibrium state:

$$K_7 = \frac{P_{iC_5}}{P_{iC_5^-} \cdot P_{H_2}}$$

Besides, if hydrogen is adsorbed to gas phase:



$$K_H = \frac{C_{H.X}^2}{C_V \cdot P_{H_2}}$$

Final equation will be achieved by combination of these equations and assuming rearrangement step as a limiting step of the reaction:

$$r = \frac{A \cdot C_V}{P_{H_2}^{1/2}} \left(P_{NC_5} - \frac{P_{iC_5}}{K} \right)$$

$$A = K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot K_H$$

$$K = K_1 \cdot K_2 \cdot K_3 \cdot K_5 \cdot K_6 \cdot K_7 \cdot K_S$$

$$C_V = \frac{C_m}{1 + aP_{H_2}^{1/2} + b \frac{P_{NC_5}}{P_{H_2}} + c \frac{P_{NC_5}}{P_{H_2}^{1/2}} + d \frac{P_{iC_5}}{P_{H_2}^{1/2}} + eP_{iC_5}}$$

Denominator is:

The effect of empty hole on the catalyst surface:

1

Hydrogen adsorption step: $a = K_1$

NC_5 adsorption step: $b = K_1 \cdot K_2$

Carbonium ion production step: $c = K_1 \cdot K_2 \cdot K_3 \cdot K_H$

Carbonium ion conversion step:

$$d = \frac{K_H}{K_5 \cdot K_6 \cdot K_7}$$

iC_5^- desorption step: $e = K_6$

One-dimensional-pseudo homogeneous, tubular flow model continuity equation

For the simplest model of the classification, which is one-dimensional pseudo homogeneous tubular flow model, continuity equation simplifies as follows:

$$\frac{d(uC_A)}{dx} + \rho_B(-r_A) = 0$$

Replacing conversion coefficient (f_A) in the reaction:

$$uC_A = qC_A / \pi r^2 = F_A / \pi r^2 = F_{A0}(1 - f_A) / \pi r^2$$

$$d(uC_A) = -\left(F_{A0} / \pi r^2 \right) df_A \frac{df_A}{dx} - \frac{\pi r^2 \ell_B (-r_A)}{F_{A0}} = 0$$

The best form of continuity equation (or mass balance) is that can calculate the amount of required catalyst for conversion percentage (f_A).

$$W = f_B V = f_B \pi r^2 x$$

$$dx = dw / f_B \pi r^2$$

$$\frac{dw}{df_A} = \frac{F_{A0}}{(-r_A)} = 0$$

$$W = F_{A0} \int \frac{df_A}{(-r_A)}$$

Rate Equation for One-dimensional, Pseudo Homogeneous Tubular Flow

This equation is the same as the rate equation related to plug reactor equation, and their difference is just in the unit ($-r_A$).

In above equation the unit ($-r_A$) is equal to $(\text{mol(A)})(\text{KgCat.})^{-1}(\text{S})^{-1}$ and in the equation related to plug reactor is $(\text{mol(A)})\text{m}^{-3} \cdot \text{S}^{-1}$.

Selecting proper laboratory reactor for kinetic study

Laboratory reactors are used to investigate industrial catalysts and determining optimum operating condition in industrial production units.

Also, in industry, laboratory reactors are used for catalysts test and their modeling proceeding or de-

scription of kinetic of reaction in catalytic processes that in both the operation beforehand in industrial unites is required^[19].

The objectives of Kinetic study in laboratory are as follows:

- 1) Quality control test to achieve appropriate alternative for existing process
- 2) Different catalysts test for improving existing industrial process
- 3) Different catalysts test for a new developing process
- 4) Developing a kinetic model to achieve optimum condition for existing process
- 5) Developing a kinetic model to design a new catalysts process foundation

In this article, fifth objective has followed up for kinetic study and tests implementation to follow up 3rd, 4th objectives in two other articles will be presented.

Several kinds of reactors exist for using specific object; however, the significance of non-gradient reactors is increasing quickly.

Although, this condition cannot implement completely but these reactors are used for catalytic reaction under uniform temperature and concentration to simplify mathematical analysis and kinetic description of components and actual results can be used.

These reactors can solve most problems in scale up. Tubular reactors are used for determination of catalyst lifetime that is slowly deactivated. Bigger tubular reactors use for laboratory and pilot scale measuring accuracy of laboratory non-gradient reactor operation.

Tubular reactors are the best laboratory models for isomerization reaction in fixed bed reactors. Concentration Gradient can be decreased by smaller catalyst size. By using longer and less diameter tube, temperature gradient and concentration gradient are also decreasing.

EXPERIMENTAL

Apparatus

After determining the kind of reactor and selecting proper model for investigating the kinetic of reaction, several tests are designed by using proper laboratory equipments to carry out the isomerization reaction.

Geomechanical apparatus is used to implement reactor tests. Its flow diagram illustrates in figure 3. This set-up contains a laboratory fixed-bed reactor with a condenser as well as separation section and GC analyzer. Feedstock and H₂ can be introduced to the reaction section and N₂ can be purged to all

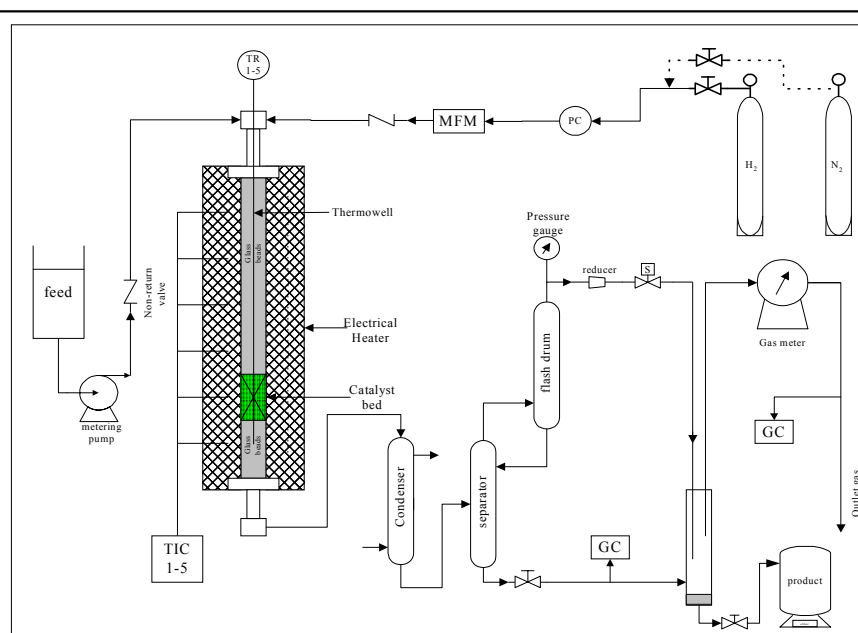


Figure 3

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parts of aforementioned set-up.

Procedure

20 ml grading catalyst (Zeolite type) place in reactor. Reactor tests begin after drying and pretreatment of the catalyst based on the specific procedure of catalyst producer.

The tests are designed at two different temperatures. Feed flow rate has been changed in a specific schedule to obtain a reasonable conclusion. Same tests in a random shape have been done to check the repeatability of the test results.

Input feed is the mixture of C5 and C6 hydrocarbons coming out from distillation unit and isomax

TABLE 1

Specification	Feed 1 (From LSRG)	Feed 2 (From Isom)	Feed 1,2 (Mix)
MW	-	-	85
SPGr	-	-	0.674
RON	-	-	70.2
RVP	14.7 (Psi)	8.38	13.52
Sulphur (Cont.)	400	100	<10

TABLE 2: Mixed feed boiling point range

IBP	38.5 °C
5.0	45
10.0	47
20.0	49
30.0	51
40.0	54
50.0	57
60.0	61
70.0	69
80.0	78
90.0	94
95.0	110
95.4	129

in one of the refineries in Iran that has following characteristics:

The specification of the tests and their results are as follows:

DISCUSSION

In previous section, designing and implementation of tests have been described. As it is consid-

TABLE 3: Mixed feed of distillation and isomax unites

COMPONENT	AREA%
C3	Trace
IC4	0.1
NC4	2.6
IC5	14.7
NC5	19.4
2,2 D.M.Butane	0.4
2,3 D.M.Butane	3.2
2 M.Pentane	10.0
3 M.Pentane	6.4
NC6	13.0
M. Cyclopentane	0.1
2,4 D.M.Pentane	6.8
Benzene	1.4
Cyclohexane	3.1
2 M.Hexane	2.2
2,3 D.M.Pentane	0.3
3 M.Hexane	2.3
2,2,4 T.M.Pentane	1.5
NC7	2.6
M Cyclohexane	3.5
Un known	6.4

ered, several tests are repeated in the same condition to evaluate the precision of the results. The tests were done under P=20bar and at T=260°C, 270°C

The effect of partial pressure of Hydrogen on catalyst activity at two temperatures is shown in diagrams 1, 2. At T=260°C and P=7-7.3, for compo-

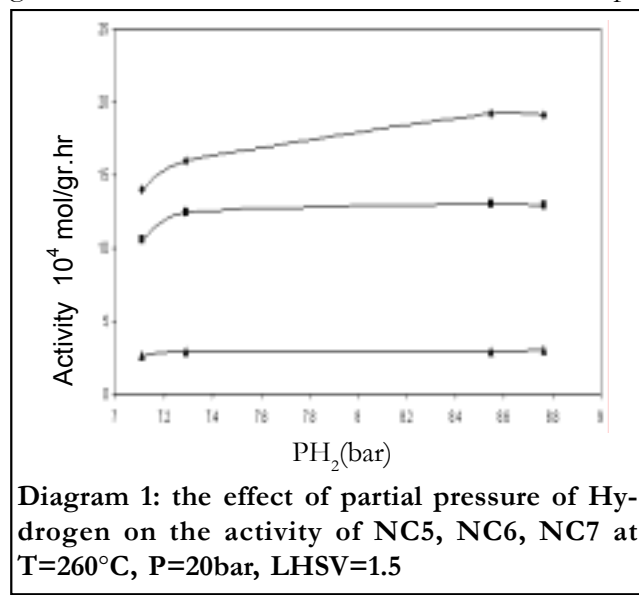
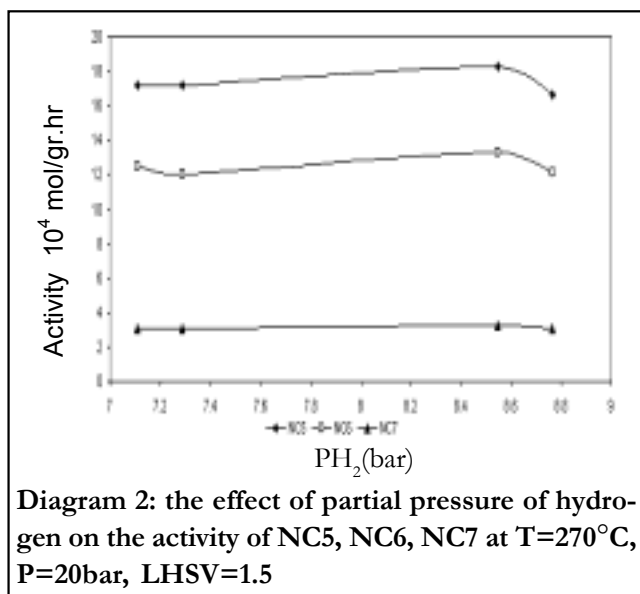


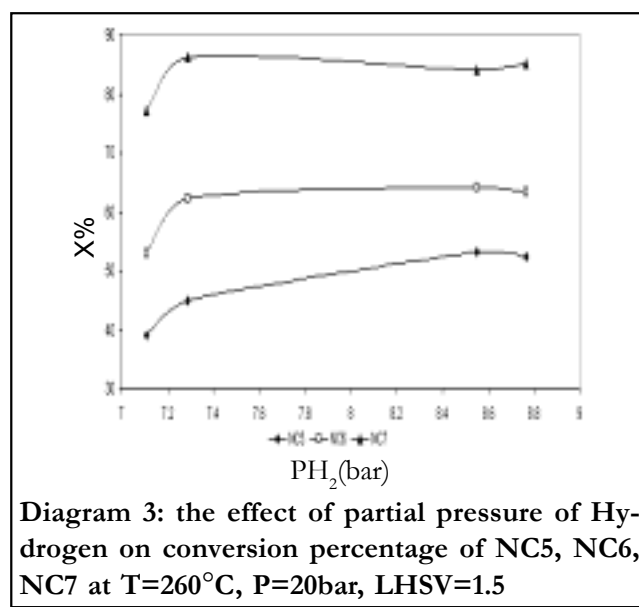
Diagram 1: the effect of partial pressure of Hydrogen on the activity of NC5, NC6, NC7 at T=260°C, P=20bar, LHSV=1.5

TABLE 4: Isomerization test procedure
 catalyst volume (ml)=20 Feed MW =85
 catalyst weight (gr) =16 Feed density (g/ml) =0.674
 Ambient temp. (°C) =27 Ambient press. (mbar) =906

Test No.	Press. [bar]	Temp. [°C]	LHSV [h ⁻¹]	H ₂ /HC [mol/mol]	H ₂ flow [ml/min]	Feed flow [ml/hr]	Feed flow [ml / 6 min]	Sample No.
1	20	260	0.66	1	48.02	13.2	1.32	B1
2	20	260	1	1	72.76	20	2	B2
3	20	260	1.5	0.7	76.40	30	3	B3
4	20	260	1.5	1	109.15	30	3	B4
5	20	260	1.5	1.5	163.72	30	3	B5
6	20	260	1.5	2	218.29	30	3	B6
7	20	260	2	1	145.53	40	4	B7
8	20	260	2.5	1	181.91	50	5	B8
9	20	270	0.66	1	48.02	13.2	1.32	C1
10	20	270	1	1	72.76	20	2	C2
11	20	270	1.5	0.7	76.40	30	3	C3
12	20	270	1.5	1	109.15	30	3	C4
13	20	270	1.5	1.5	163.72	30	3	C5
14	20	270	1.5	2	218.29	30	3	C6
15	20	270	2	1	145.53	40	4	C7
16	20	270	2.5	1	181.91	50	5	C8



nents n-pentane, n-hexane, n-heptane, the activity increases with relatively higher slop that implies the positive effect of hydrogen on decreasing deactivation. The curves character in the mentioned range shows that the activity is constant with increasing PH₂. At T=270°C, it seems that, perhaps, deactivation phenomenon takes place in the pressure less than PH₂. Also, at this temperature and PH₂>8.5, the



activity decreasing is evident. Then, by increasing temperature, the slop of initial activity changes has been decreased but activity decreasing is more evident in higher pressure.

The effect of increasing hydrogen partial pressure on conversion coefficient of reaction is evaluated in diagram-3, 4. The curves character is the same

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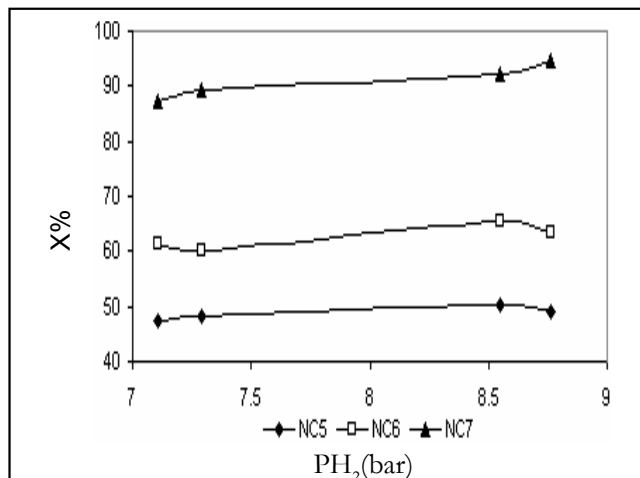


Diagram 4: the effect of partial pressure of Hydrogen on conversion percentage of NC5, NC6, NC7 at $T=270^{\circ}\text{C}$, $P=20\text{bar}$, $LHSV=1.5$

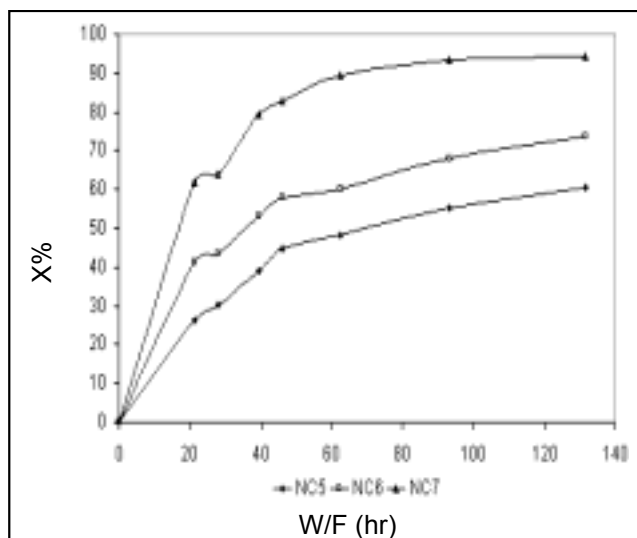


Diagram-6: conversion percentage of NC5, NC6, NC7 vs. W/F at $T=270^{\circ}\text{C}$, $P=20\text{bar}$, $H_2/HC=1$

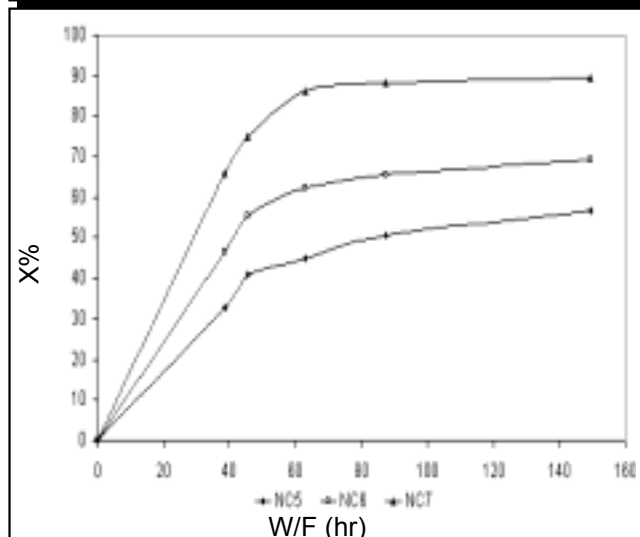


Diagram 5: conversion percentage of NC5, NC6, NC7 vs. W/F at $T=260^{\circ}\text{C}$, $P=20\text{bar}$, $H_2/HC=1$

as three previous curves.

Conversion coefficient versus W/F at two temperatures is described in diagram-5, 6. These curves have taken into consideration for NC5, NC6 and NC7. All curves show that the conversion coefficient increases by increasing W/F. These changes are proportional to the temperature and the amount of conversion increases as temperature increases. The slope of changes is the most for NC7 and the least of all for NC5 that is caused by cracking of heavier molecules.

Rate equation versus P_i can be obtained by calculating the slope of curves at different points, cal-

culating partial pressure for NC5, NC6, NC7 and the amounts of W/F.

According to the results and complexity of mechanism of reaction, the reaction rate equation can not be determined by determining curve equation. Since, after curve fitting, some equations with low correlation coefficient resulted, the other methods are used to obtain rate equations.

9- Kinetic Equations based on experimental results

In previous sections, the equation of reaction rate for modeling one-dimensional, pseudo homogeneous tubular flow obtained by using mass balance and continuity equation. In isomerization process that the reaction carried out in fixed bed catalyst reactor, the above equation can be used with considering suitable condition and omitting heat gradient and concentration gradient.

There are two methods to use this equation. The first is determination the rate of reaction by using integral method. In this method, a defined mechanism and its related rate equation that obtained from differential rate equation integration in differential reactor condition will be tested.

The second method is differential analysis. Integral analysis method is considered as a direct and rapid approach to prove simpler rate equations. But, for more complicated rate equations, the equation obtained from integration has little application. In these cases, using differential method in which the

reaction rate can be, directly, obtained from related curve differentiation, is more appropriate. In this method, at first, the curve $X_{A,out}$ versus $W/FA0$ is drawn, then the possible best curve passes through origin and $X_{A,out}$, $W/FA0$. To determine reaction rate for each X_A , it is enough to determine the tangent slope with the curve at that point. Consequently, the results including reaction rate for related concentration will be obtained that in the next stage by guess a rate equation, should its parameters be determined in a way that corresponds on the test results.

However, the complexity of reaction mechanism is so that it takes away the analysis power by using simple methods from researcher. Therefore, for next investigation it has been decided to write more notable reactions and regarding to initial and final amounts of components to achieve stoichiometry coefficient of each compounds by try and error method.

In practice, it is impossible to use integral analysis method because of complex isomerization mechanism of such a feed.

Thus, the differential analytical method is used. For this purpose, at first, rate equation for NC_5 and NC_6 is supposed according to existing references.

Then, by target function definition for each component (NC_5 , NC_6) and using sequential Quadratic Programming improvement method (SQP) and Matlab software, the kinetic parameters amounts

TABLE 5

Exp.No.	Exp. $r_{nC_5}, T=270$	Sim. $r_{nC_5}, T=270$ °C	% Error
C1	0.1392	0.135	1.6
C2	0.1836	0.169	7.95
C4	0.2182	0.272	24.66
C7	0.5327	0.408	23.41

TABLE 6

Exp.No.	Exp. $R_{nC_6}, T=270$	Sim. $R_{nC_6}, T=270$	% Error
C1	0.1582	0.15	5.18
C2	0.2044	0.203	0.7
C4	0.189	0.24	26.3
C7	0.4496	0.351	22.22

TABLE 7

Exp.No.	Exp. $r_{nC_5}, T=260$	Sim. $r_{nC_5}, T=260$	% Error
B1	0.097	0.099	2.1
B2	0.1657	0.1564	5.6
B4	0.2387	0.2641	10.6
B7	0.5952	0.5644	5.17

TABLE 8

Exp.No.	Exp. $R_{nC_6}, T=260$	Sim. $R_{nC_6}, T=260$	% Error
B1	0.063	0.062	1.6
B2	0.0967	0.103	6.5
B4	0.2646	0.234	11.6
B7	1.2168	0.933	23.3

changed so that the target function reach to the possible minimum.

$$\sum_{i=1}^n (r_j^{\text{Sim}} - r_j^{\text{Exp}})^2$$

j: nC_5, nC_6

n: Test number

@ $T=260^\circ\text{C}$, P(bar)

$$r_{nC_5} = \frac{0.0851P_{nC_5}^3}{\left[4.94 \times 10^{-3} P_{H_2} + 0.451 P_{nC_5} + 1.734 \times 10^{-4} P_{nC_6} + 1.67 \times 10^{-4} P_{nC_7}\right]^{0.03}}$$

$$r_{nC_6} = 0.12 \frac{P_{nC_6}^{1.11}}{\left[76.39 \times 10^{-3} P_{H_2}\right]^4}$$

@ $T=270^\circ\text{C}$

$$r_{nC_5} = \frac{3.355 \times 10^{-3} P_{nC_5}^{4.71}}{\left[0.27 \times 10^{-3} P_{H_2} + 3.32 \times 10^{-4} P_{nC_5} + 0.502 P_{nC_6} + 0.0962 P_{nC_7}\right]^{2.73}}$$

$$r_{nC_6} = 0.592 P_{nC_6}^{0.981}$$

The tests that are used at $T=260^\circ\text{C}$: B1, B2, B4, B8.

The tests that are used at $T=270^\circ\text{C}$: C1, C2, C4, C7.

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