

EXPERIMENTAL STUDY OF C₅/C₆ ISOMERIZATION IN LIGHT STRAIGHT RUN GASOLINE (LSRG) OVER PLATINUM MORDENITE ZEOLITE

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Abstract:

The hydroisomerization of LSRG over platinum mordenite zeolite has been used to comprehensive study about the effects of hydrogen partial pressure on catalyst activity and n-paraffins conversions. Kinetic equations for n-C₅ and n-C₆ in Light Straight Run Gasoline (LSRG) were also proposed.

Key words: *Light Straight Run Gasoline, C₅ and C₆ alkanes, platinum mordenite, kinetics*

1. Introduction

Crude oil treatment is related to the first successful excavation in 1859. 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 War II, 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 (LSRG). 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 distillation directly that includes a large amount of n-paraffin (Boiling point 27-71°C & octane number 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 tetra ethyl lead and tetra methyl lead 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.

Isomerization of light straight run gasoline leads to production of branched alkanes which are important for producing of gasoline having high octane number and low amount of aromatics and lead (Pb). Basically, two types of catalysts-the low temperature(about, 93-204°C) and high temperature (230-270°C)-are used to convert of linear alkanes to branched alkanes [1,2,3]. The first type of catalysts are very susceptible to deactivation and their utilization requires careful feed pretreatment. The second type of catalysts are Pt/H-zeolite catalysts, which can bear feed impurities. Isomerization reaction mechanism on zeolite catalyst depends on its acid center density, pores structure and operating condition [4,5,6].

Based on the earlier studies of Mills et al. [7] and Weisz and Swegler [8] a bifunctional mechanism of light alkane(C₅-C₆)isomerization can be explained according to this mechanism:

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

Dehydrogenation of n-paraffins occurs on metal center and produced olefin .Olefin is transferred from metal centers to acid sites, adsorbs one proton (H⁺) and then by rearrangement is converted to branched compound which releases proton to give iso-olefin. Iso-olefins, after penetration from acid centers to metal centers via dehydrogenation, are converted to iso-paraffins.

The aim of the present work is to investigate the effects of some parameters on the activity of platinum containing hydrogen mordenite catalyst and also establish kinetic equations for nC₅ and n-C₆ components.

2. Experimental setup

Geo-mechanical apparatus have been used to implement the reactor tests. Its flow diagram has been illustrated in figure 1.

This set-up contains a laboratory fixed-bed reactor with a condenser, a separation section and a GC analyzer. The catalyst charge (20 ml) was dried and activated directly before commencing the experiments based on the specific procedure suggested by the catalyst manufacturer.

Input feed is the mixture of C₅ and C₆ hydrocarbons which are the products of the distillation and Isomax units of a refinery in Iran. Tables 1, 2 and 3 illustrates some physical properties of this feed.

Table-1: Some physical properties of feed

Specification	Feed 1 (From LSRG)	Feed 2 (From Isom)	Feed 1,2 (Mix)
MW	-	-	85
Specific gravity, g/ml	-	-	0.674
RON	-	-	70.2
RVP, bar	1.0	0.57	0.92
Sulphur content mg/kg	400	100	<10

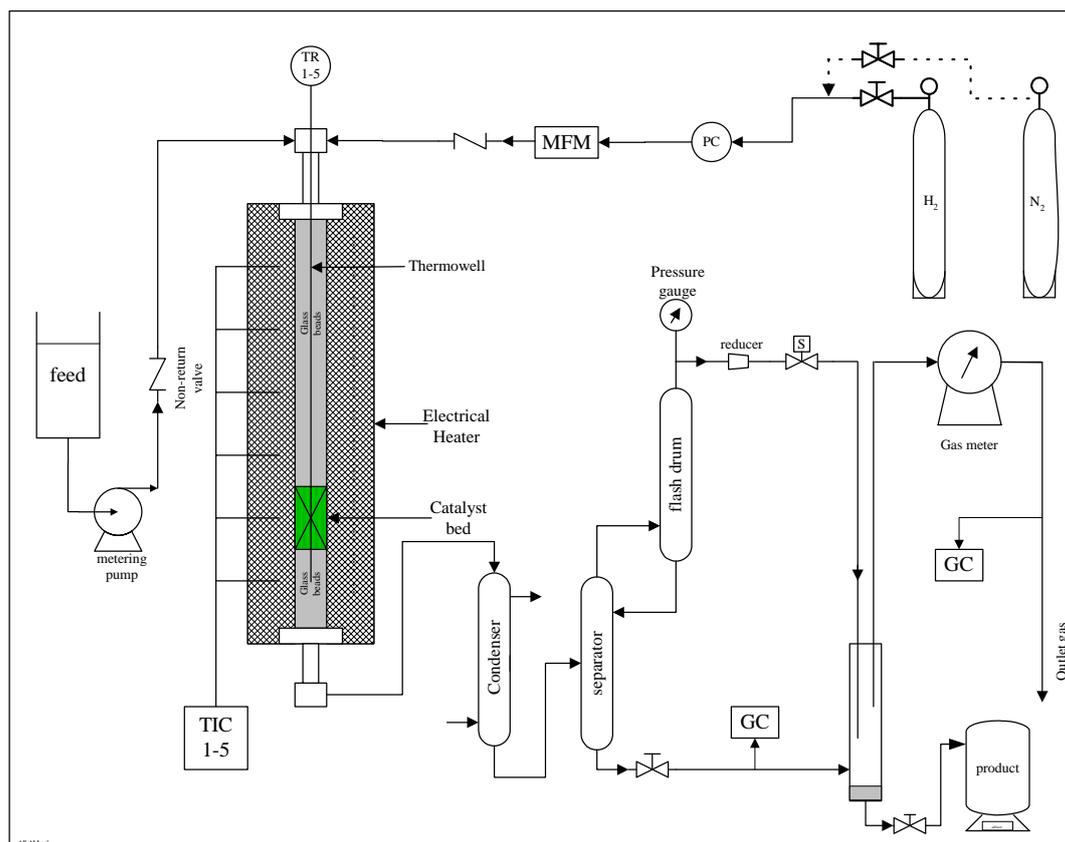


Figure-1: Schematic diagram of experimental system

Experiments were carried out under following conditions: two different temperatures, five levels of LHSV and four levels of hydrogen to hydrocarbon mole ratio(Table 4).

Table-2: Mixed feed distillation characteristics

% vol.	IBP	5	10	20	30	40	50	60	70	80	90	95	95,4
°C	38.5	45	47	49	51	54	57	61	69	78	94	110	129

Table-3: Mixed feed of distillation and Isomax units

COMPONENT	AREA%	COMPONENT	AREA%
C3	Trace	2,4-dimethylpentane	6.8
i-C4	0.1	benzene	1.4
n-C4	2.6	cyclohexane	3.1
i-C5	14.7	2-methylhexane	2.2
n-C5	19.4	2,3-dimethylpentane	0.3
2,2-dimethylbutane	0.4	3-methylhexane	2.3
2,3-dimethylbutane	3.2	2,2,4-trimethylpentane	1.5
2-methylpentane	10.0	n-C7	2.6
3-methylpentan	6.4	methylcyclohexane	3.5
n-C6	13.0	unknown	6.4
methylcyclopentane	0.1		

Table-4: Isomerization test procedure , experimental conditions

catalyst volume (ml) =20

feed MW =85

catalyst weight (g) =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]	Sample No.
1	20	260	0.66	1	48.02	13.2	B1
2	20	260	1	1	72.76	20	B2
3	20	260	1.5	0.7	76.40	30	B3
4	20	260	1.5	1	109.15	30	B4
5	20	260	1.5	1.5	163.72	30	B5
6	20	260	1.5	2	218.29	30	B6
7	20	260	2	1	145.53	40	B7
8	20	260	2.5	1	181.91	50	B8
9	20	270	0.66	1	48.02	13.2	C1
10	20	270	1	1	72.76	20	C2
11	20	270	1.5	0.7	76.40	30	C3
12	20	270	1.5	1	109.15	30	C4
13	20	270	1.5	1.5	163.72	30	C5
14	20	270	1.5	2	218.29	30	C6
15	20	270	2	1	145.53	40	C7
16	20	270	2.5	1	181.91	50	C8

3. Results and Discussion

The effect of hydrogen partial pressure on catalyst activity at two temperatures is illustrated in figures 2 and 3. At T=260°C & P=7-7.3 bar, the activity increases with relatively sharp slope for n-pentane, n-hexane and n-heptane which shows the positive effect of hydrogen on decreasing deactivation. The behavior of the curves in the mentioned pressure range shows that the activity is constant while increasing P_{H_2} . At T=270°C it seems as if the deactivation phenomenon takes place in the pressure less than P_{H_2} . Also, at this temperature and while $P_{H_2} > 8.5$, the activity decreases evidently. By increasing the temperature, the slope of the initial activity curve decreases but activity reduction is more evident in higher pressures.

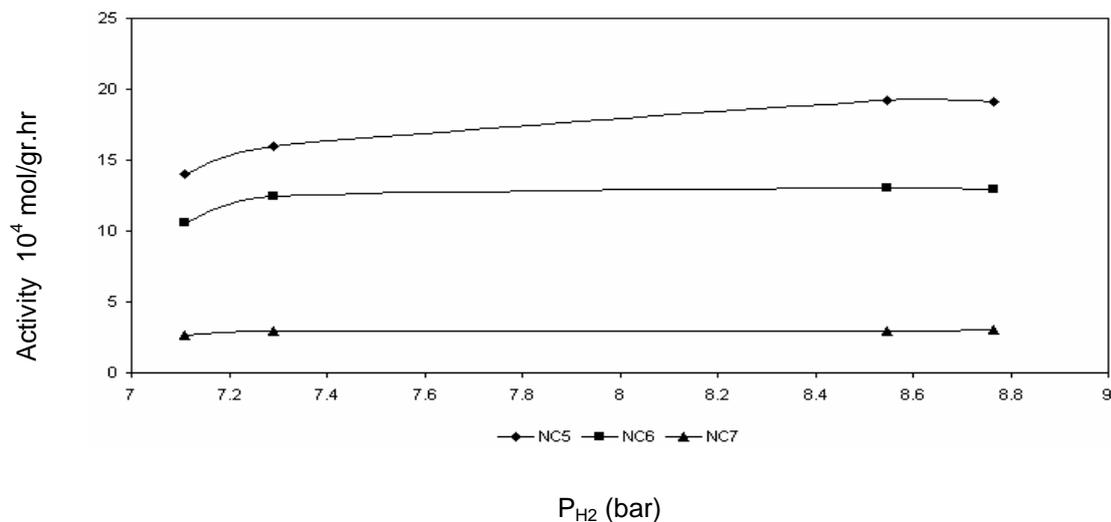


Figure-2: Effect of hydrogen partial pressure on the activity of nC₅, nC₆ and nC₇ at T=260°C, P=20bar, LHSV=1.5

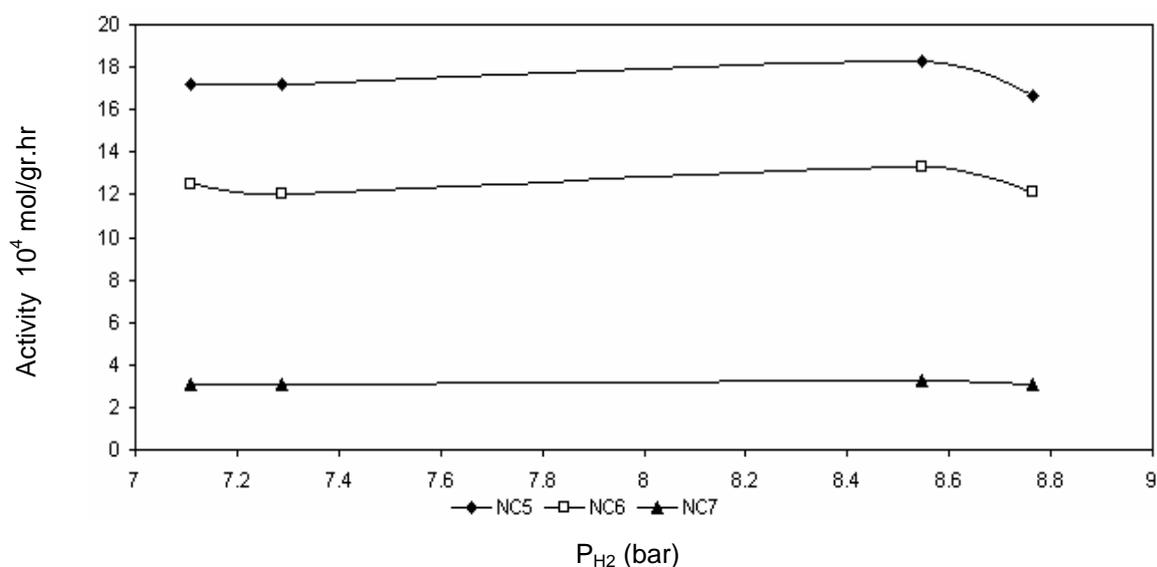


Figure-3: Effect of hydrogen partial pressure on the activity of nC₅, nC₆ and nC₇ at T=270°C, P=20bar, LHSV=1.5

The effect of hydrogen partial pressure increase on reaction conversion has been evaluated in figures 4 and 5. The curves show behaviors similar to those of the three former ones.

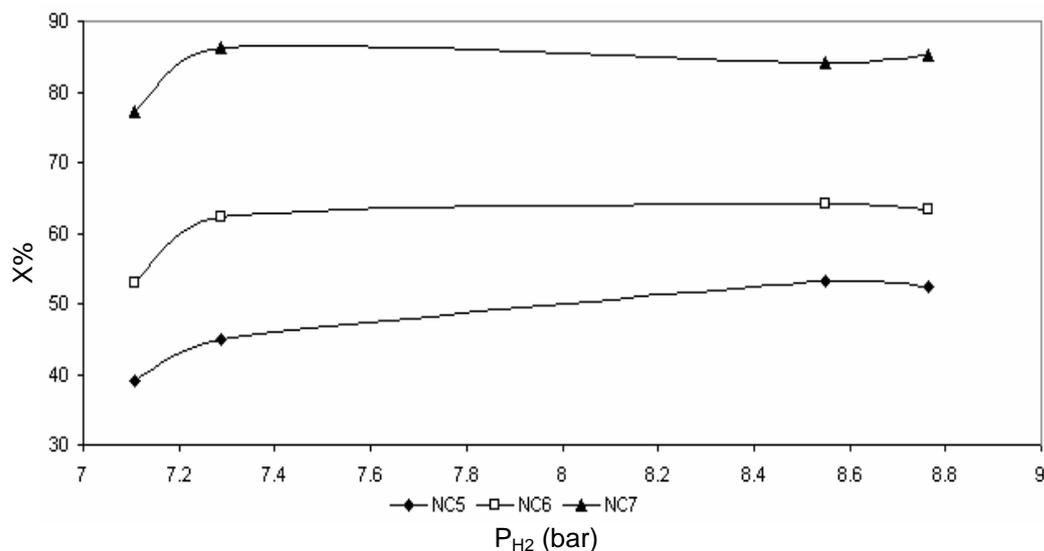


Figure-4: Effect of hydrogen partial pressure on conversion of nC_5 , nC_6 and nC_7 at $T=260^\circ\text{C}$, $P=20\text{bar}$, $LHSV=1.5$

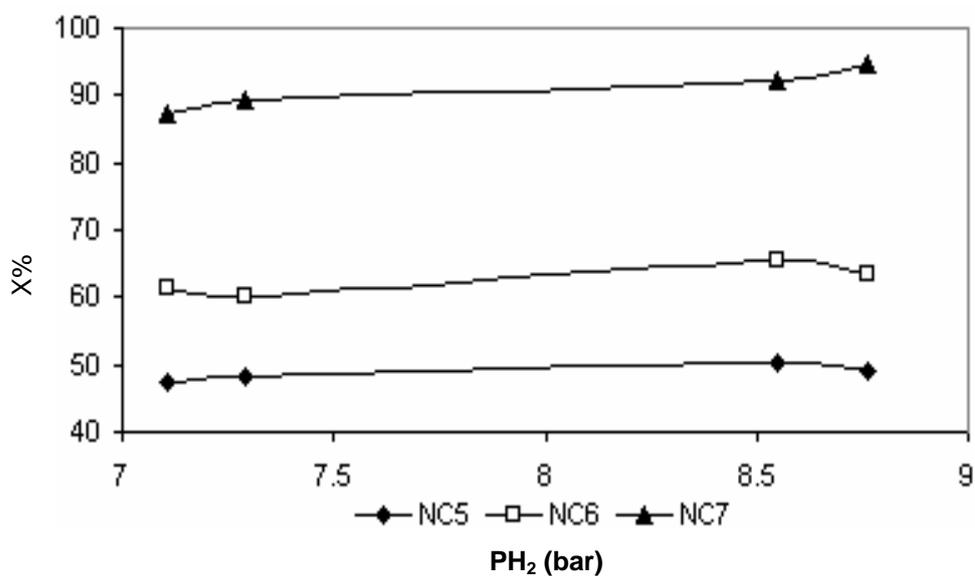


Figure-5: Effect of hydrogen partial pressure on conversion of nC_5 , nC_6 and nC_7 at $T=270^\circ\text{C}$, $P=20\text{bar}$, $LHSV=1.5$

Conversion versus W/F at two different temperatures has been illustrated figures 6 and 7. These curves show the conversion of nC_5 , nC_6 and nC_7 . All curves show that the conversion coefficient increases by increasing W/F . Conversion Variation is also proportional to temperature. The amount of conversion increases with increase of temperature. nC_7 has the maximum slope of variation while nC_5 has the minimum one which is resulted from cracking of heavier molecules.

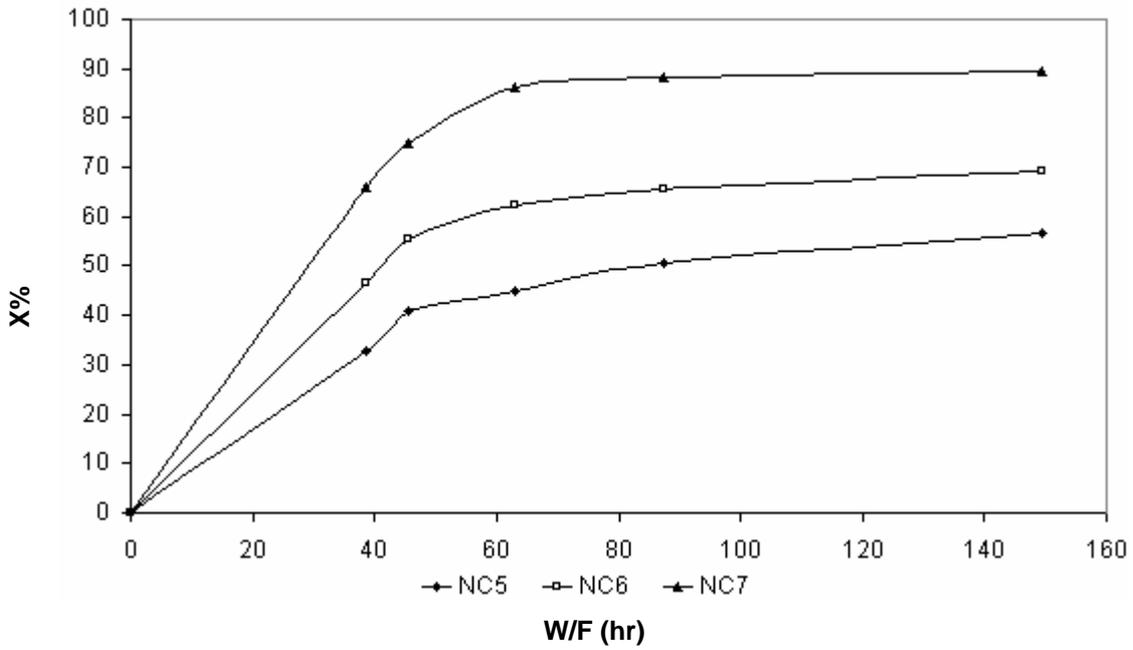


Figure-6: Conversion of nC₅, nC₆ and nC₇ vs. W/F at T=260°C, P=20bar, H₂/HC=1

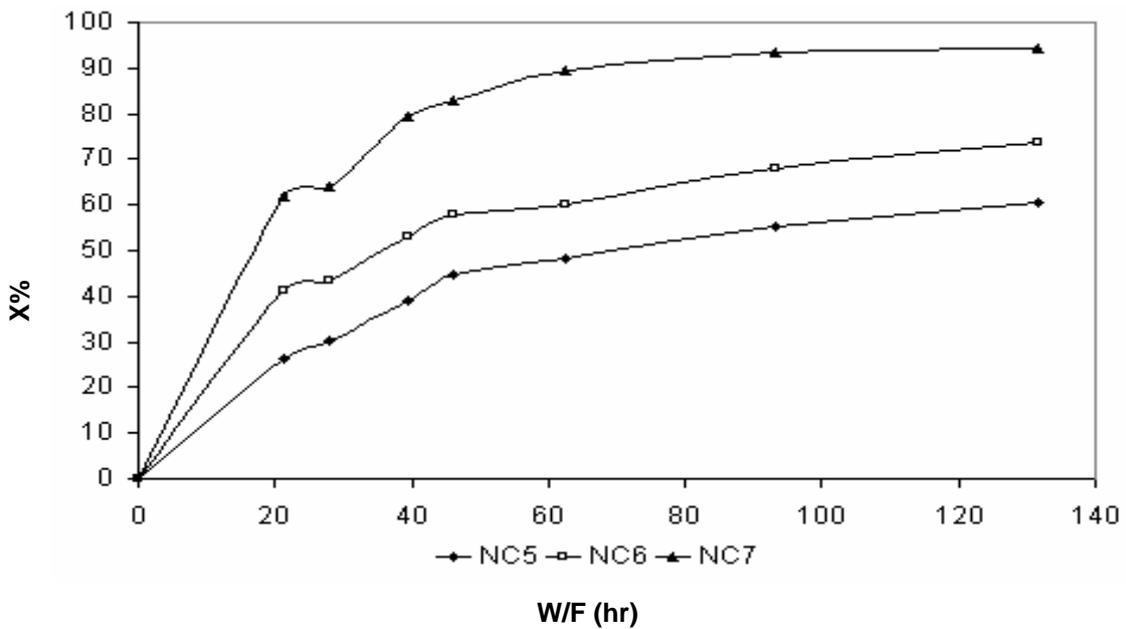


Figure-7: Conversion of nC₅, nC₆ and nC₇ vs. W/F at T=270°C, P=20bar, H₂/HC=1

For determination of kinetic parameters of rate equations for nC₅ and nC₆, at first step we must calculate the reaction rates amount, but isomerization has a complex mechanism so in practice, it is impossible to use an integral analytical method for determination of reaction rates. Thus differential analytical method has been used for this purpose. In second step rate equations are selected for nC₅ & nC₆. Then using Sequential Quadratic Programming improvement method (SQP) and also Matlab software, the kinetic parameters values are varied so that the target functions become minimum.

$$\sum_{i=1}^n (r_j^{Sim} - r_j^{exp})_i^2 \quad j: nC_5, nC_6$$

n : Test number

Following the above procedure, will result in the below equations :

@T=260 °C, P(bar)

$$r_{nc_5} = \frac{0.0851 P_{nc_5}^3}{\left[4.94 \times 10^{-3} P_{H_2} + 0.451 P_{nc_5} + 1.734 \times 10^{-4} P_{nc_6} + 1.67 \times 10^{-4} P_{nc_7}\right]^{1.03}}$$

$$r_{nc_6} = 0.12 \frac{P_{nc_6}^{1.11}}{\left[76.39 \times 10^{-3} P_{H_2}\right]^4}$$

@ T = 270 °C

$$r_{nc_5} = \frac{3.355 \times 10^{-3} P_{nc_5}^{4.71}}{\left[0.27 \times 10^{-3} P_{H_2} + 3.32 \times 10^{-4} P_{nc_5} + 0.502 P_{nc_6} + 0.0962 P_{nc_7}\right]^{2.73}}$$

$$r_{nc_6} = 0.592 P_{nc_6}^{0.981}$$

As illustrated in Tables 5, 6, 7 and 8, using the developed reaction rates we are capable to predict the reactor output with high reliability and accuracy.

Table-5 Comparison between experimental and simulation results for nC₅ rate at 270 °C

Sample no.	Exp. r_{nC_5} , T=270 °C	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 Comparison between experimental and simulation results for nC₆ rate at 270 °C

Sample no.	Exp. r_{nC_6} , T=270 °C	Sim. r_{nC_6} , T=270 °C	% 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 Comparison between experimental and simulation results for nC₅ rate at 260 °C

Sample no.	Exp. r_{nC_5} , T=260 °C	Sim. r_{nC_5} , T=260 °C	% Error
B1	0.097	0.099	2.1
B2	0.1657	0.1564	5.6
B4	0.2387	0.2641	10.6
B8	0.5952	0.5644	5.17

Table-8 Comparison between experimental and simulation results for nC₆ rate at 260 °C

Sample no.	Exp. r_{nC_6} , T=260 °C	Sim. r_{nC_6} , T=260 °C	% Error
B1	0.063	0.062	1.6
B2	0.0967	0.103	6.5
B4	0.2646	0.234	11.6
B8	1.2168	0.933	23.3

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