

Material Balance And Reaction Kinetics Modeling For Penex Isomerization Process In Daura Refinery

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Abstract. Penex Deisohexanizer isomerization of light straight run naphtha is a significant process for petroleum refining and proved to be effective technology to produce gasoline components with a high octane number. Modeling of the chemical kinetic reactions is an important tool because it is a better tool for optimization of the experimental data into parameters used for industrial reactors. The present study deals on the isomerization process in Daura refinery. Material balance calculations were done mathematically on the unit for the kinetics prediction purpose. A kinetic mathematical model was derived for the prediction rate constants K_1 and K_2 and activation energy E_a at operating temperatures range 120-180°C. According to the model, the results show that with increasing of temperature leads to increased K_1 directly, where the K_2 values proportional inversely. The activation energy results show that $E_{a1(nC6)} < E_{a1(C5)} < E_{a1(CH)}$, and for $E_{a2(iC5)} < E_{a2(2,2-DMB)} < E_{a2(2,3-DMB)} < E_{a2(MCP)}$.

1 Introduction

The Penex Deisohexanizer (DIH) isomerization is a process operated using the catalytic reaction of n-pentanes, n-hexanes, and mixtures thereof to produce isomeric hydrocarbons. The reactions take place in a hydrocatalytic fixed bed reactor to promote conversion and minimize hydrocracking [1]. The process of light naphtha can produce isomeric hydrocarbons with higher octane number, in addition, that the typical Penex unit product can blend into gasoline pool, and the non-converted low octane components (nC₆, CH and MP's) from the deisohexanizer column (DIH) can be recycled to the reactor section for further upgrading [2].

The major elements of Penex (DIH) isomerization processes are reactors operated using chlorinated-alumina (Pt/Al₂O₃-Cl) as catalyst [3, 4]. This catalyst is proven to be active at lower temperatures (120-180°C) in which equilibrium favorable to produce iso-paraffins. [5]. The scheme of Penex (DIH) process is illustrated in Fig. 1. [6]

The most important process variables in Penex isomerization unit are the reactor temperatures. The higher temperatures than equilibrium lead to increase the amount of hydrocracking and increase the carbon formation on the catalyst.

A typical UOP Penex unit is provided with two reactors in series. All of the benzene rings in the LSRN feed are hydrogenated in the first reactor and some conversion of cyclohexane (CH) and methyl cyclopentane (MCP) to hexanes also occurs, as does some hydrocracking of C₇ components to C₃ and C₄.

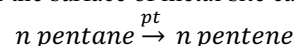
The hydrogenation of benzene rings, naphthene conversion to hexane, and C₇ hydrocracking are exothermic reactions and, for a typical feedstock, contribute more to the temperature rise in the reactor than exothermic reaction of paraffin isomerization.

The concentrations and outlet temperature will be influenced by the catalyst and by the mass of C₆ cyclic and C₇ components in the feed.

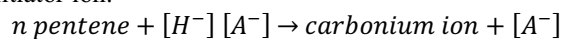
2 Penex Unit Reaction Mechanism

2.1 nC₅ Reaction Mechanism [7]

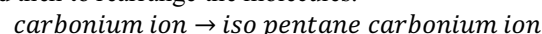
The Isomerization reaction of normal paraffins to isoparaffins is slightly exothermic and thermodynamically favorable at a temperature range 120-180°C. The kinetics of the reaction proceed in series through an olefin as an intermediate product formed by dehydrogenation of n-paraffins through an adsorption mechanism on the surface of metal site catalyst.



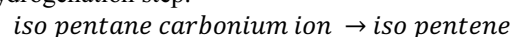
Because of low equilibrium conversion of paraffin isomerization, n-olefins can be converted to carbonium ion with the aid of injection of strong chloride acid as initiator ion.



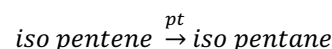
This initiator ion allows equilibrium forward to removes n-olefin from the first hydrogenation reaction, and then to rearrange the molecules.



The high catalytic acidity causes a hydrogenation reaction to proceed at a higher reaction rate. Then, the carbonium ion converted iso-paraffin to iso-olefin by dehydrogenation step.



In the last reaction, the iso-olefin is hydrogenated again to form iso-paraffin in the presence of surface of the catalyst.



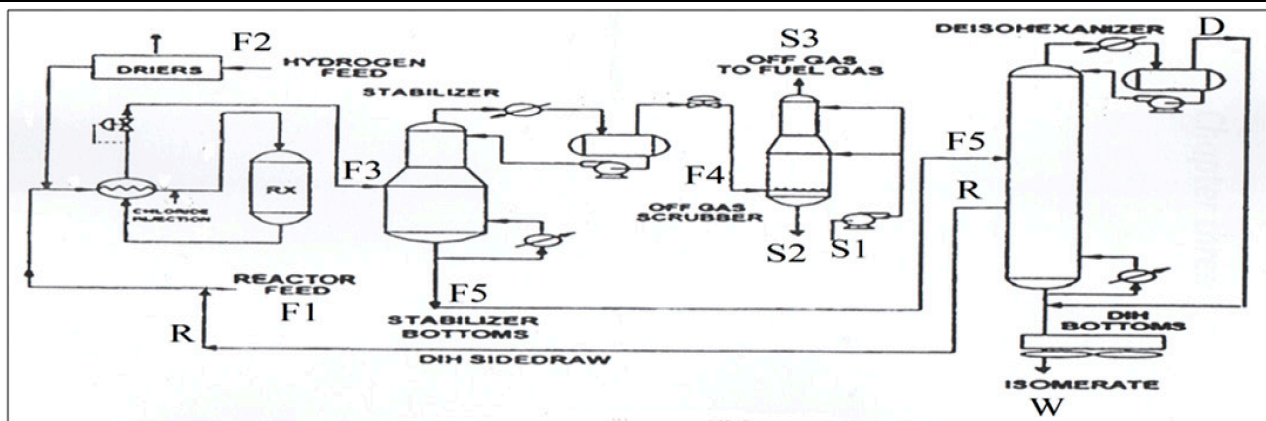
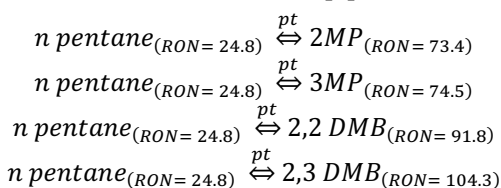


Fig. 1 Block Diagram of Penex (DIH) Isomerization Unit

Generally, the final steps of (n-C₆) isomerization proceed similarly, thus (n-C₆) several iso-products like 2-MP, 3-MP, 2,2-DMB, and 2,3-DMB is can be produced.

2.2 nC6 Reaction Mechanism [8]



The relationship between equilibrium conversion vs. isomerization reaction temperatures of (C₅ and C₆) paraffins are shown in Fig. 2 and 3, respectively [5].

2.3 Other Reactions [9]

There are several reactions occurring inside and outside of the reactors.

2.3.1 Inside Reactors:

a) Naphthene ring of methyl cyclopentane (MCP) and cyclohexane (CH) present in the Penex feed will hydrogenate to n-paraffins, and then to iso-paraffins. The increasing in reactor temperature leads to increase Naphthene ring opening reactions.

b) As the temperature increased, the naphthenes shift forwards to (MCP) production.

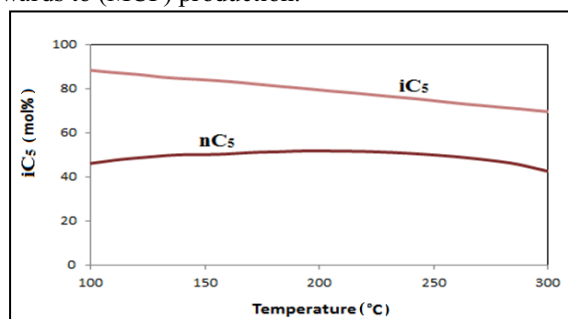


Fig. 2: C₅ Paraffin Equilibrium Curves [5].

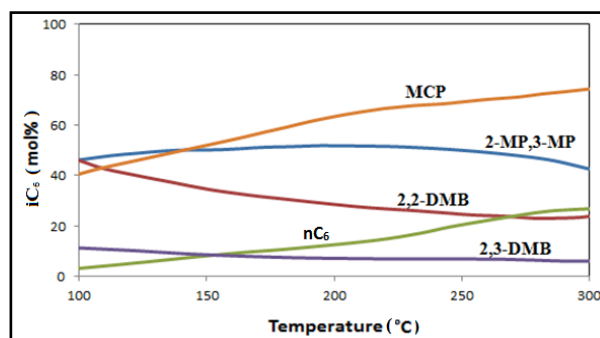
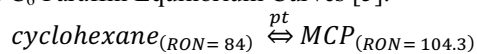
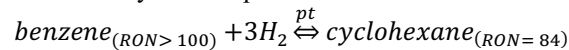


Fig 3: C₆ Paraffin Equilibrium Curves [5].



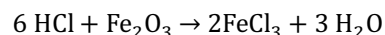
c) Very quickly hydrogenation reaction of the benzene ring in the presence of a catalyst (Pt/Al₂O₃-Cl) proceed at very low temperature.



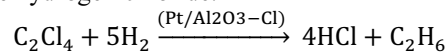
d) Hydrocracking of Penex feed according to types of feed quality. For example, C₇ molecules tend to hydrocrack easily than smaller ones, paraffins of C₅ and C₆ hydrocrack to some extent. The severity of hydrocracking tends to reduce yield and increase product temperature.

2.3.2 Outside Reactors :

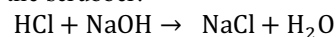
a) Hydrogen chloride is injected annually at period of maintenance time, to limit corrosion problems in units, the reaction run until removed any rust present in the unit.



b) Perchloroethylene (C₂Cl₄) is injected before reactors at approximately the temperature of (110°C) or higher. The present hydrogen will react with this promoter in the presence of a catalyst (Pt/Al₂O₃-Cl) to produce hydrogen chloride.



c) Neutralization of hydrogen chloride formed in above reaction using caustic soda (NaOH) to form salt and water in the scrubber.



3 Material Balance

As shown by Fig. 1, there are three streams entering to the reactor of Penex unit, the feed (LSRN), makeup gas (H_2) and recycle (from Deisohexanizer) and outlet stream exit as a product from the reactor. The product stream (F3) exits from the reactor, enters to stabilizer column. In this process, overhead light gases (CH_4, C_2H_6, C_3H_8 , and $i-C_4H_{10}$) and some of nC_5 and iC_5 which is removed and exit from the top of column, in addition to H_2 and HCl , which then enter to scrubber.

The outlet product from the top of stabilizer column enters to the scrubber column where $NaOH$ solution

injected into the scrubber. From the bottom of the stabilizer, the product stream contains ($nC_5, iC_5, nC_6, 2-MP, 3-MP, 2,2-DMB, 2,3-DMB, MCP$ and CH) which goes to Deisohexanizer (DIH) column. The outlet product from the bottom of stabilizer enters to the DIH column. There are two streams exit from DIH column, top stream (D) and bottom stream (W).

The mass balance calculations on the unit assuming feed rate of Penex unit =10, 000 BPD is presented in Table (1) and (2) respectively.

Table 1: Material Balance Calculations on the Reactor and Stabilizer Unit Assuming Feed Rate =10,000 BPD

	Comp.	Mwt	Density (Kg/m ³)	Reactor (kg/hr)				Stabilizer (kg/hr)		
				F1 in	F2 in	R in	F3 out	F3 in	F4 out	F5 out
1	nC ₅	72	626	11276.16	0	199.731	5278.9	5278.9	18.47	5260.43
2	iC ₅	72	616	5688.17	0	135.817	12020.96	12020.96	281.52	11739.44
3	nC ₆	86	655	14808.4	0	17440.5	17736.79	17736.79	0	17736.79
4	2-MP	86	653	4899.84	0	24902.4	29802.27	29802.27	0	29802.27
5	3-MP	86	664	3915.52	0	21467.1	25382.58	25382.58	0	25382.58
6	2,2-DMB	86	674	139.37	0	719.031	12145.51	12145.51	0	12145.51
7	2,3-DMB	86	695	1572.30	0	6559.16	11356.35	11356.35	0	11356.35
8	MCP	84	749	39.199	0	23.968	501.12	501.12	0	501.12
9	BZ	78	876	483.451	0	8444.62	0	0	0	0
100	CH	84	778	731.71	0	199.731	8738.38	8738.38	0	8738.38
11	H ₂	2	0.0899	0	208.52	0	170.55	170.55	170.55	0
12	CH ₄	16	0.668	0	227.39	0	227.39	227.39	227.39	0
13	C ₂ H ₆	30	1.264	0	343.92	0	343.92	343.92	343.92	0
14	C ₃ H ₈	44	1.882	0	392.32	0	392.38	392.38	392.38	0
15	i-C ₄	58	2.5326	0	230.77	0	230.77	230.77	230.77	0
16	C ₂ Cl ₄	166	1622	0	0	0	0	0	0	0
17	HCl	36.5	1.63	0	0	0	11.43	11.43	11.43	0
18	NaOH	40	2130	0	0	0	0	0	0	0
19	NaCl	58.5	2165	0	0	0	0	0	0	0
20	H ₂ O	18	1000	0	5.15	0	0	0	0	0
	Total			43554.12	1408.07	79892.3	123838.18	123838.18	1676.44	43554.12

Table 2: Mass Balance Calculations on the Scrubber and Deisohexanizer Unit Assuming Feed Rate =10,000 BPD

	Comp.	Mwt	Density (Kg/m ³)	Scrubber (kg/hr)			Deisohexanizer (kg/hr)			
				F4 in	S1 out	S2 out	F5 in	R out	W out	D out
1	nC ₅	72	626	18.47	18.47	0	5260.43	199.731	0	5060.70
2	iC ₅	72	616	281.52	281.52	0	11739.44	135.817	0	11603.62
3	nC ₆	86	655	0	0	0	17736.79	17440.5	48.14	248.15
4	2-MP	86	653	0	0	0	29802.27	24902.4	6.95	4892.92
5	3-MP	86	664	0	0	0	25382.58	21467.1	20.00	3895.48
6	2,2-DMB	86	674	0	0	0	12145.51	719.031	0	11426.48
7	2,3-DMB	86	695	0	0	0	11356.35	6559.16	1.61	4795.58
8	MCP	84	749	0	0	0	501.12	23.968	823.67	0
9	BZ	78	876	0	0	0	0	8444.62	0	0
100	CH	84	778	0	0	0	8738.38	199.731	52.75	0
11	H ₂	2	0.0899	170.55	170.55	0	0	0	0	0
12	CH ₄	16	0.668	227.39	227.39	0	0	0	0	0
13	C ₂ H ₆	30	1.264	343.92	343.92	0	0	0	0	0
14	C ₃ H ₈	44	1.882	392.38	392.38	0	0	0	0	0
15	i-C ₄	58	2.5326	230.77	230.77	0	0	0	0	0
16	C ₂ Cl ₄	166	1622	0	0	0	0	0	0	0
17	HCl	36.5	1.63	11.43		0	0	0	0	0
18	NaOH	40	2130	0	0	2.5	0	0	0	0
19	NaCl	58.5	2165	0	0	18.32	0	0	0	0
20	H ₂ O	18	1000	0	0	140.91	0	0	0	0
	Ttotal			1676.44	1665	161.73	43554.12	79892.3	122662.9	42798.85

The concentration of reactants in the isomerization reactions (nC_5 , nC_6 and CH) in the inlet stream to the reactor is calculated from the mass balance, these concentrations are used to calculate K_1 (rate constant for the formation of intermediate olefin). The results are shown in Table (3).

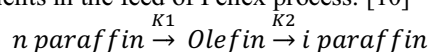
Whereas the mole fraction of the produced isomers outlet from reactor (iC_5 , 2,2-DMB, 2,3-DMB and MCP) are calculated from the mass balance, these mole fractions are used to calculate K_2 (rate constant for the formation of isomers).

Table 3 Concentration of Reacted Components.

Component	F_{A0} (Kmole)	V (m ³)	$C_{A0}=F_{A0}/V$ (K mole/m ³)
nC_5	156.613	18.013	8.694
nC_6	172.191	22.608	7.161
CH	104.03	11.23	9.26

4 Development Model

In the typical isomerization process, several reactions are taken place: paraffin isomerization; naphthene hydrogenation; naphthene isomerization, benzene saturation, hydrocracking; and naphthene alkylation. Table (4) list the reactions and equilibrium conversion suggest for isomerization of normal paraffinic components in the feed of Penex process. [10]



The model developed in this study are taken following assumptions: 1st order reactions at steady state, isothermal conditions, gas phase reaction, constant physical properties, and neglected gradient in pressure drop, temperature and concentration respectively.

Mass balance has been developed over the cross section of the segment of the catalyst bed, as illustrated in Fig. 3.

$$C_{A0} = C_A + C_N + C_{ISO} \quad (8)$$

$$C_A = C_{A0} \exp(-K_1 t) \quad (9)$$

$$C_N = \frac{K_1 C_{A0}}{K_2 - K_1} [\exp(-K_1 t) - \exp(-K_2 t)] \quad (10)$$

$$C_{ISO} = C_{A0} \left[1 - \exp(-K_1 t) - \frac{K_1}{K_2 - K_1} [\exp(-K_1 t) - \exp(-K_2 t)] \right] \quad (11)$$

Table 4 A Typical Reactions for LSRN Isomerization

Reactions	Conv. %	Equ. No.
$nC_5 \rightleftharpoons iC_5$	54	(1)
$nC_6 \rightleftharpoons 2,2\text{-DMB}$	35	(2)
$nC_6 \rightleftharpoons 2,3\text{-DMB}$	10	(3)
$BZ+3H_2 \rightleftharpoons CH$	100	(4)
$CH \rightleftharpoons MCP$	59	(5)
$2\text{-MP} \rightarrow 3\text{-MP}$		(6)
$3\text{-MP} \rightarrow 2,2\text{-DMB} + 2,3\text{-DMB}$		(7)

The design equation for volume of tubular reactor:

$$V = F_{A0} \frac{\int dx}{-K_1 C_{A0}} \quad (12)$$

And reactant concentration of C_A in gas phase:

$$C_A = C_{A0} \frac{(1-x)T_0}{(1-\varepsilon x)T} \quad (13)$$

Where ε is refer to voidage in reactor bed.

Putting equation (13) into (12) and re-arrange, to get the reaction rate constant K_1 as shown in equation (14). From Arrhenius equation (15), the activation energy (E_{a1}) and frequency factor (K_0) can be calculated by plot ($\ln K_1$) vs. ($1/T$), as illustrated in Fig. 4.

$$K_1 = \frac{F_{A0}}{V C_{A0}} \left[\ln \frac{1}{1-x} (1+\varepsilon) - \varepsilon x \right] \frac{T}{T_0} \quad (14)$$

$$\ln K_1 = \ln K_0 - \frac{E_a}{RT} \quad (15)$$

5 Results And Discussion

The model shown by equation (14) can be used to calculate isomerization reaction rate constant K_1 , using data given from Penex unit in the Daura Refinery: Volume of catalyst in each reactor = 35.66 m³, Hold up = 75 %, $\varepsilon = 0.393$, and $T_0 = 50^\circ\text{C}$.

Table (5) represents the results of K_1 at temperatures range of 120-180 °C. It was shown that calculated reaction constants of (K_1) values increased with increasing temperature and reach maximum value at a temperature (180°C).

Applying equation (15) and plot ($\ln K_1$) vs ($1/T$) for components listed in Table (6) are shown in Fig. 5.

The activation energy (E_{a1}) and Frequency factor (K_{01}) are calculated from these plots and tabulated in Table (7). The results show that $E_{a1(nC6^*)} < E_{a1(nC6^{**})} < E_{a1(C5)} < E_{a1(CH)}$.

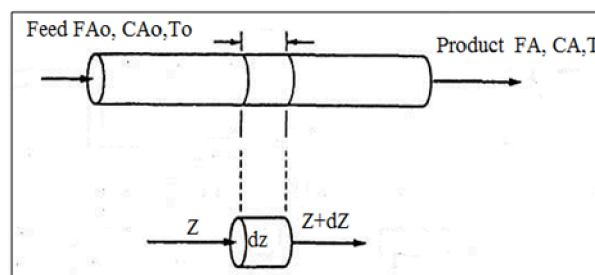


Fig. 3: Segment of Tubular Catalyst Bed Reactor.

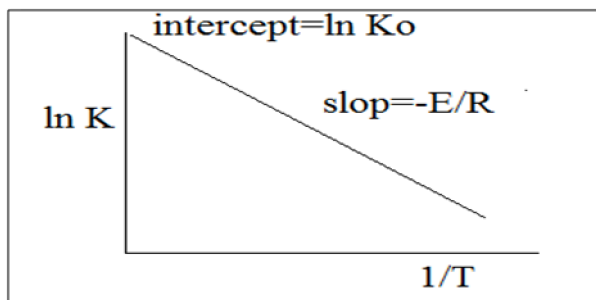


Fig. 4: The Relationship Between (ln K₁) vs. (1/T)

Table 5: Results of K₁.

T(°C)	T(K)	K ₁ (h ⁻¹)			
		nC ₅	nC ₆ *	nC ₆ **	CH
120	393	0.398	0.241	0.056	0.289
135	408	0.413	0.250	0.058	0.300
150	423	0.429	0.260	0.060	0.311
165	438	0.444	0.269	0.062	0.322
180	453	0.459	0.278	0.065	0.333

Where nC₆* for nC₆ ↔ 2,2-DMB at x=0.35, and nC₆** for nC₆ ↔ 2,3-DMB at x=0.1

Table 6: lnK₁ and 1/T Values.

1/T	ln K ₁			
	nC ₅	nC ₆ *	nC ₆ **	CH
0.0025	-0.9202	-1.4164	-2.8759	-1.2429
0.0025	-0.8828	-1.3789	-2.8385	-1.2055
0.0024	-0.8467	-1.3428	-2.8024	-1.1694
0.0023	-0.8118	-1.3080	-2.7675	-1.1345

Equation (11) can be used to calculate the rate constant K₂ for reaction on olefin to iso-paraffin. The required data were taken from Daura Refinery; as LHSV =1.5, residence time t =1/ LHSV = 0.667 h. The values of K₂ are shown in Table (8), which was shown that K₂ values decreasing with increasing temperature, which means that product isomerate concentrations were increased as a result of temperature sensitivity of isomerization reactions.

Applying equation (15) and plot (lnK₂) vs (1/T) for components listed in Table (9) are shown in Fig. 6. The values of the activation energy (Ea₂) and Frequency factor (K_{o2}) are calculated from these plots and tabulated in Table (10). The results show Ea₂ (iC₅) < Ea₂(2,2-DMB) < Ea₂(2,3-DMB) < Ea₂(MCP).

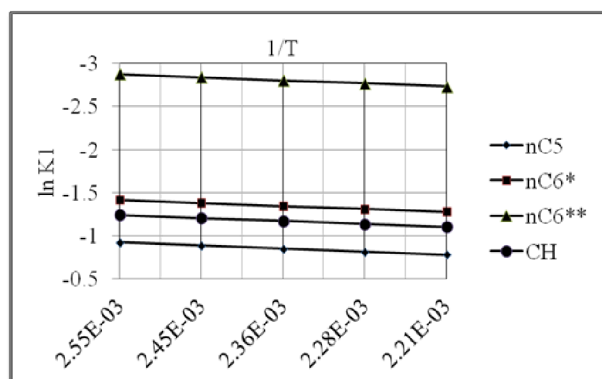


Fig. 5: Plot (ln K₁) vs. (1/T)

Table 7: Activation Energy and K_{o1} Results.

Component	Ea ₁ (KJ/mole)	K _{o1}
nC ₅	2738.822	0.460
nC ₆ *	1525.743	0.263
nC ₆ **	1835.182	0.061
CH	2880.394	0.334

Table 8: Results of K₂.

T(°C)	T(K)	K ₂ (h ⁻¹)			
		iC ₅	2,2-DMB	2,3-DMB	MCP
120	393	0.1547	0.2566	1.2062	0.0147
135	408	0.1480	0.2477	1.1512	0.0124
150	423	0.1430	0.2389	1.0998	0.0113
165	438	0.1384	0.2308	1.0529	0.0099
180	453	0.1346	0.2232	1.0099	0.0097

Table 9: lnK₂ and 1/T Values

1/T	ln K ₂			
	iC ₅	2,2-DMB	2,3-DMB	MCP
0.0025	-0.8106	-0.5907	0.0814	-1.8327
0.0025	-0.8298	-0.6062	0.0612	-1.9066
0.0024	-0.8446	-0.6218	0.0413	-1.9469
0.0023	-0.8588	-0.6368	0.0224	-2.0044
0.0022	-0.8711	-0.6513	0.0043	-2.0132

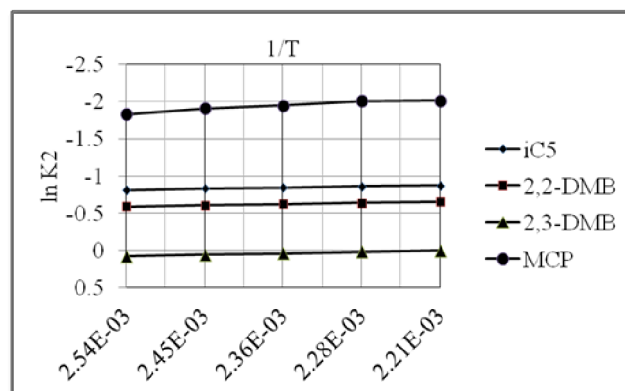


Fig. 6: Plot (ln K₂) vs. (1/T)

Table 10: Activation Energy and K_{o2} Results.

Component	Ea ₂ (KJ/mole)	K _{o2}
iC ₅	1.503	0.281
2,2-DMB	1.519	0.349
2,3-DMB	1.931	0.602
MCP	4.632	0.038

6 Conclusions

1. The increasing temperature leads to increased K_1 according to reactor model (proportional directly).
2. The K_2 values decreased when the temperature increased for the isomerate (proportional inversely) which indicates the increasing in the isomerate concentration.
3. The activation energy results show that $E_{a1(nC_6)} < E_{a1(C_5)} < E_{a1(CH)}$, and for $E_{a2(iC_5)} < E_{a2(2,2-DMB)} < E_{a2(2,3-DMB)} < E_{a2(MCP)}$, which means the reaction of lower activation energy have higher reaction rate.

Abbreviations

dz	Integration Step for the Reactor Length
2,2-DMB	2,2-Dimethylbutane
2,3-DMB	2,3-Dimethylbutane
2-MP	2-Methylpentane
3-MP	3-Methylpentane
BZ	Benzene
nC_6^*	Concentration for $nC_6 \leftrightarrow 2,2-DMB$ at $x=0.35$,
nC_6^{**}	Concentration for $nC_6 \leftrightarrow 2,3-DMB$ at $x=0.1$
CA	Concentration of n-paraffin present at time t
CAo	Concentration of inlet LSRN stream (mole/m ³)
Ciso	Concentration of i-paraffin.
CN	Concentration of n-olefin
CH	Cyclohexane
D	Top stream of DIH shown in Fig. 1
DIH	Deisohexanizer (DIH)
E_{a1}	Activation energy for n paraffin $\xrightarrow{K_1}$ Olefin
E_{a2}	Activation energy for Olefin $\xrightarrow{K_2}$ i paraffin
F1	Reactor feed shown in Fig. 1
F2	Hydrogen feed shown in Fig. 1
F3	Stabilizer feed shown in Fig. 1
F4	Scrubber feed shown in Fig. 1
F5	DIH feed shown in Fig. 1
FAo	Mole rate of inlet component LSRN
Fiso	Mole rate of isomerate product
HC	Hydrocarbon
i-C ₄	Iso-butane
iC ₅	Iso-pentane
iC ₆	iso-hexane
K1	Rate Constant for Paraffins (hr ⁻¹)
K2	Rrate Constant for Olefins (hr ⁻¹)
Ko	Frequency Factor
LHSV	Liquid Hourly Space Velocity
LSRN	Light straight run naphtha
MCP	Methyl cyclopentane
nC_5	Normal pentane
nC_6	Normal hexane
Pt	Platinum
Pt/ZrO ₂	Sulfated zirconia

SO ₄	
Pt/Al ₂ O ₃ -Cl	Chlorinated alumina
R	DIH sidedraw shown in Fig. 1
R	Gas Constant (8.314 J/K.. mole)
RON	Research Octane Number
t	Residence time (hr)
S1	NaOH solution feed to scrubber shown in Fig. 1
S2	Bottom of scrubber shown in Fig. 1
S3	Off gas outlet from the scrubber shown in Fig. 1
T	Temperature (K)
To	Initial temperature (K)
V	Volume of reactor (m ³)
W	Bottom stream of DIH shown in Fig. 1
x	reaction conversion
Zt	Length of reactor (Cm)
ϵ	Voidage

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