

# CONVERSION OF N-HEPTANE ON Pt/Al<sub>2</sub>O<sub>3</sub> CATALYST

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( Received: Jun. 8th 1992 , Accepted: May 9th 1994 )

**ABSTRACT :** Hydrogenation reaction with *n*-heptane on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated under the steady state condition in a fixed bed reactor. The catalyst was prepared under a variety of conditions, but the one chosen was non- acidic that is not considered a hydrocracking catalyst. The main objective was to vary the selectivity of *n*- heptane as a function of reaction variables especially the partial pressure of hydrogen, because in addition to hydrogenolysis, other reactions like isomerization and cyclization also take place. Our studies on selectivity of *n*- heptane on platinum catalyst shows that in general cracking reactions preferably yield propane and *n*- butane, and at high pressures methane is also produce as a result of further cracking reactions. Products formed at low presssures (2-10atm) are: 3- methyl- hexane and 2,3- dimethyl pentane. Those produced with lower yields at higher pressures (20-40atm) were predomiantly 2- methyl hexane and 3- methyl hexane. Dominant cyclic products were 1 tr 2- dimethylcyclopentane, toluene, methylcyclohexane, and ethyl cyclopentane. Upon increasing the hydrogen partial pressure, 1 tr 2- dimethyl cyclopentane increases strongly and those of six membered rings decrease.

**KEY WORDS :** *N*- Heptane, Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst, Hydrogen, Selectivity, Hydrogenolysis.

## 1.0. INTRODUCTION :

In hydrogenolysis reactions in addition to the scission of C-C bonds there is the possibility of breaking the bonds between carbon and

heteroatoms [1].



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where *X* can be S, N, O, or a halogen atom. Hydrogenolysis occurs in many industrial processes as a side reaction (e.g. hydrocracking, reforming). Hydrocracking of hydrocarbons is accelerated via metallic catalysts like Ni, Rh and Pd. Earliest systematic investigations on the kinetics and mechanism of hydrogenolysis reactions were commenced in the 1940's [2]. These dealt mainly with the hydrogenolysis of ethane and propane and the catalysts chosen were Ni on SiO<sub>2</sub> and later Co and Fe were also utilized [3,4]. In all these studies the rate of hydrogenolysis decreased markedly with the increase in the partial pressure of hydrogen.

Later on the hydrogenolysis of larger hydrocarbons were carried out over unsupported catalysts made of group VIII elements [5]. Masumoto et al. [6] studied the reactions involving 2- methylpentane, 3- methylpentane, methylcyclopentane, 2,2- dimethylbutane, and 2,3- dimethylbutane on Ni/SiO<sub>2</sub> and Pt/SiO<sub>2</sub>. The differences observed were explained by suggesting that the C-H bonds break homogeneously upon adsorption over Ni surface, whereas they break heterogeneously over Pt. Such bond scissions occur early in adsorption and are subject of current investigations.

Platinum has a unique place among the catalysts because it leads to isomerization and cyclization reactions occur in addition to those involving cracking. It is important to realize that catalysts with acidic nature is to be avoided, because they simultaneously yield carbonium ions.

This presentation focuses on the hydrogenolysis of hydrocarbons on platinum catalyst in a fixed bed reactor under steady state conditions. Past studies involve the effects of reaction variables, especially pressure, on selectivity [7], because most reactions in the literature describe the low pressures [8]. However, most industrial processes involve higher pressures.

## 2.0. EXPERIMENTAL :

### 2.1. Materials

The catalyst PtO<sub>2</sub>, xH<sub>2</sub>O (99.9% purity) and Al<sub>2</sub>O<sub>3</sub> were purchased from Roth, AG (Karls-

ruhe, Germany). The specific surface of Al<sub>2</sub>O<sub>3</sub> was 250m<sup>2</sup>/g. Ethanol and other chemicals were from Merck, (Darmstadt, Germany).

### 2.2. Catalyst Preparation

Preparation technique has a strong influence on the catalyst's properties. In this study Pt was deposited over Al<sub>2</sub>O<sub>3</sub> surface by one of three methods [9] (all other the ratio Pt/Al<sub>2</sub>O<sub>3</sub> being 5/95, w/w).

#### 2.2.1

0.44g. PtO<sub>2</sub>, xH<sub>2</sub>O is mixed with 6.67g of Al<sub>2</sub>O<sub>3</sub> (Particle size 0.4-0.5mm) in water with constant stirring. The water is evaporated in a rotary evaporator under vacuum. The process is repeated 10-12 times to assure uniform adsorption of PtO<sub>2</sub>, xH<sub>2</sub>O on Al<sub>2</sub>O<sub>3</sub>.

#### 2.2.2

PtO<sub>2</sub>, xH<sub>2</sub>O is suspended in water/ alcohol mixture. A black porous precipitate is formed that is soluble in aqua regia. Ipatieff procedure may be used to adsorb Pt on Al<sub>2</sub>O<sub>3</sub> [10].

#### 2.2.3

Like above, except that a 5% NHCO<sub>3</sub> was added to the catalyst in order to neutralize the residual acidity. After mixing the catalyst is heated and dried in an oil bath and subsequently in an oven at 140°C.

The catalyst is then heated at 300°C. The first method proved superior and was thus, used throughout, Table 1.

Table 1: Performance of various catalysts in hydrogenolysis of *n*-heptane

%yield	Catalyst#1	Catalyst#2	Catalyst#3
	6.0	23	1.1
	%of products		
Hydrogenolysis	48.3	22.7	18.5
Isomerization	34.7	65.3	57.1
Cyclization	14.8	8.2	22.8
Aromatics	2.2	3.7	1.6

The first catalyst has the following merits:

- a) contains no residual acidity, thus behaves a monofunctional catalyst, causing hydrogenolysis only.
- b) its activity is reduced less severely during the operation.

### 2.3. Apparatus

The experiments were carried out on a semi-micro scale. The experimental set up consisted of two main parts:

- a) a pressure pump (Model No.314, Instrumentation Specialties Co., U.S.A) with capability of pumping 0.4-2ml/h hydrocarbon at pressures up to one hundred atmospheres.
- b) a reactor 7mm ID×200mm height that is bored into a piece of chrome/nickel steel having 50mm diameter, surrounded with a 1000W heater, the outside of the latter being insulated with glass wool and asbestos.

### 2.4. Method of Hydrogenolysis

Fig. 1 depicts the general design of the apparatus used in this investigation. Hydrogen is pressurized to the desired level and is first

passed through activated carbon and then over silica gel at 110°C, and finally through molecular sieve. It is then encountered with n- heptane that is injected via the pump and is vaporized by the evaporator. The mixture, after passing through a hot and short tubing, enters the upper part of the reactor where it is heated to the reaction temperature, before entering the catalytic section. Reaction products along with unreacted hydrogen is released at the atmospheric pressure via a relief valve. Sample collection is done by two different methods.

#### 2.4.1.

The hydrocarbons produced are condensed with the aid of liquid air and subsequently fractionated.

#### 2.4.2.

The products together with hydrogen are collected in glass tubes. In the case of low pressure reactions (2 atm) and those involving high ratio of hydrocarbon to hydrogen ( $n_{HC}/n_{H_2}=1/20$ ) nitrogen is added to the mixture to

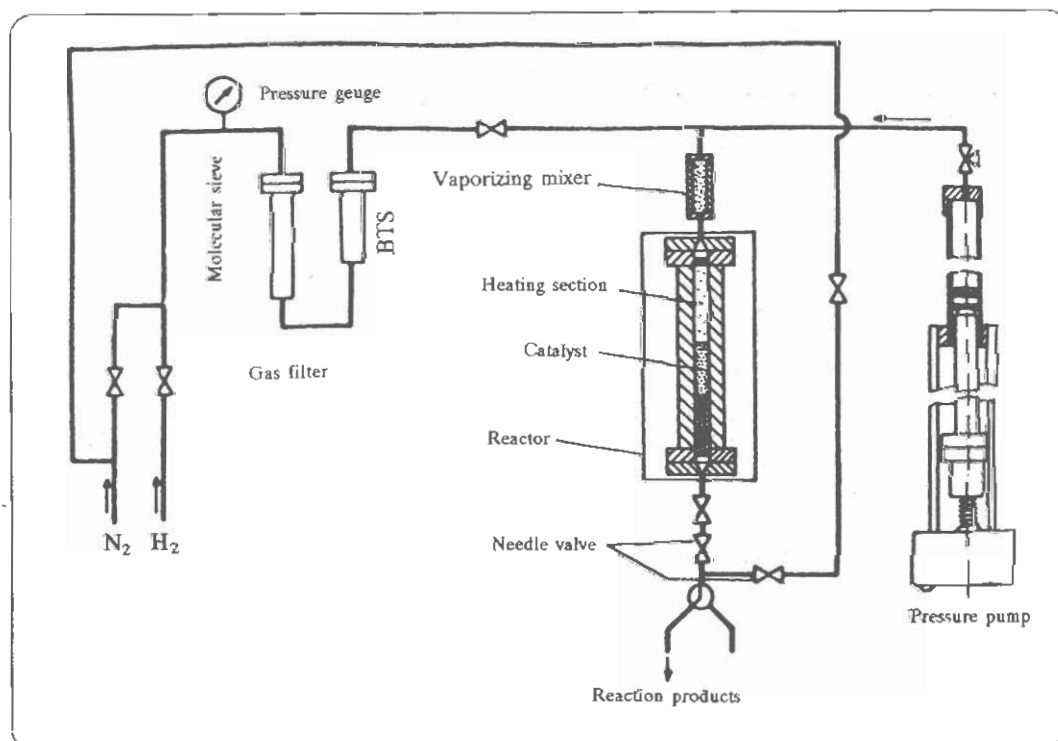


Fig. 1: Schematics of the apparatus used in hydrogenolysis of n- heptane on  $Pt/Al_2O_3$ .

lower the partial pressure of initial hydrocarbons and thus prevent their liquefaction.

### 2.5. Gas Sample Analysis

Gaseous samples consist of  $C_1$  to  $C_7$  hydrocarbons along with some hydrogen. At first analysis of the samples were carried out on a *Perkin Elmer* gas chromatograph (Model F6) using a packing column filled with  $Al_2O_3$

Reoplex. But since this column could not resolve branched hydrocarbons from naphthenes, Fig. 2, a model F20B gas chromatograph equipped with a capillary column of squalane or polypropylene glycol was used instead. In latter case, the instrument had a flame ionization detector. A typical chromatogram involving  $H_2/n$ -heptane reaction over  $Pt/Al_2O_3$  surface is shown in Fig. 3.

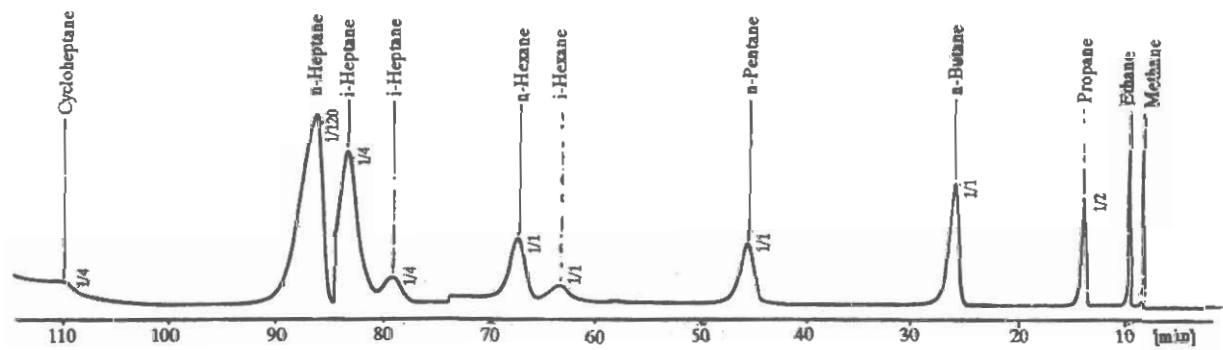


Fig. 2: Chromatogram of reaction products of *n*-heptane. Column filled with  $Al_2O_3$ /Reoplex.

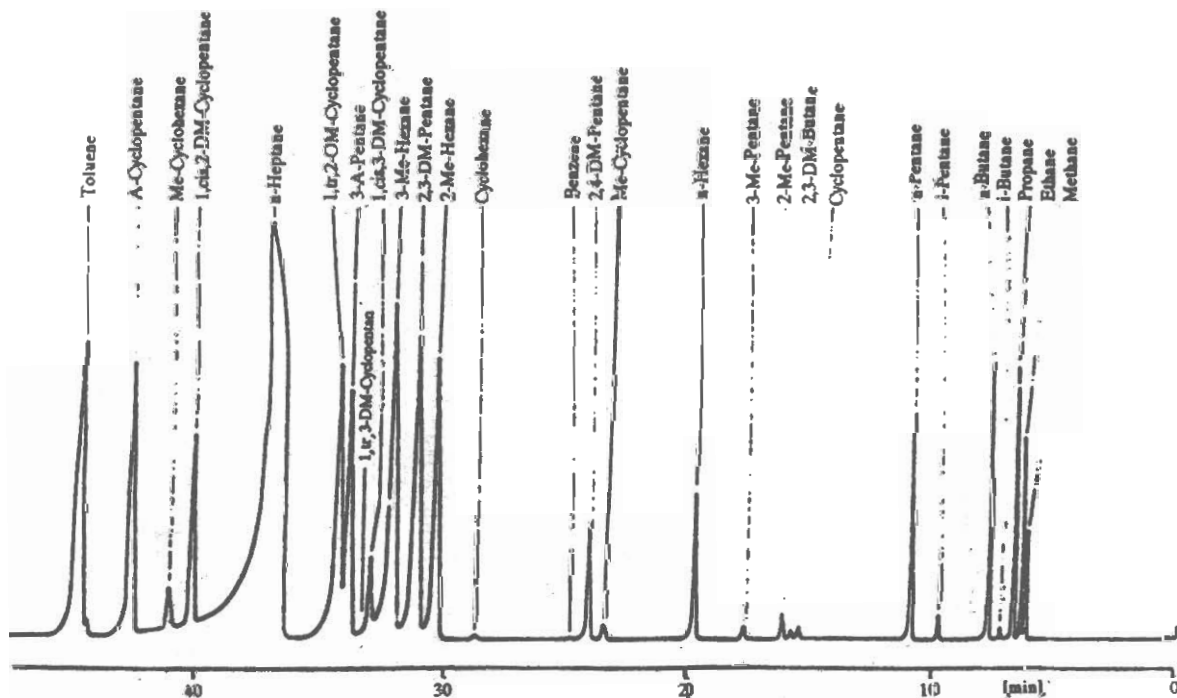


Fig.3: Chromatogram of reaction products of *n*-heptane over 5%  $Pt/Al_2O_3$ . Column filled with Squalane; 100m.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Hydrogen Pressure

Platinum is considered as a mild hydrogenolysis catalyst. Along with such effect it causes isomerization and cyclization as well. Thus, hydrogen pressure was selected as the main variable since it strongly effects the reaction rate and selectivity.

The molar ratio of n-heptane/ hydrogen were chosen as 1/400, 1/200, 1/100, 1/50 and 1/20. At a total pressure of 2 atm it was necessary to dilute the system with nitrogen in order to prevent liquefaction of heptane and heavier hydrocarbons. Other reaction conditions were kept constant, namely  $T=325^{\circ}\text{C}$ , volumetric flow rate  $0.3\text{ cm}^3\text{h}^{-1}$ , that of n- heptane =  $0.6\text{ cm}^3\text{h}^{-1}$  partial pressure of n- heptane = 0.1atm, contact time = 3.5sec.

Table 2 depicts the overall yield as well as those specifically for hydrogenolysis, isomerization, cyclization, and aromatic formation, all as a function of hydrogen partial pressure.

The results show that the overall as well as specific yields decrease with the increase in hydrogen partial pressure. Earlier studies had shown that the rate of hydrogenolysis decreases as a function of hydrogen partial pressure. The reason is that more active sites on platinum surface may be occupied with hydrogen atoms as the concentration of hydrogen in the gas increases (as evidenced from its lower heat of adsorp-

tion compared to that of n- heptane).

Consequently less sites are available for heptane. This effect on yields of various products is not the same. Namely the yield of hydrogenolysis reaction increases whereas those of the isomerization decreases. This might be due to the fact that there might be intermediate steps involved in the latter, that are prevented more extensively as a result of hydrogen adsorption on the catalyst sites. Table 3 shows the changes in hydrogenolysis products as a function of hydrogen partial pressure.

As can be seen among the products the amounts of methane and hexane increases as the partial pressure of hydrogen increases, and at 40atm hexane disappears in favor of methane. The breaking of n- heptane molecule on platinum has a limited selectivity in relation to its specific C-C bonds. If one assumes that methane is produced as a result of consecutive cracking of larger molecules the results may be explained by proposing that chemical adsorption of hydrogen on the end of the molecule is not favored at low hydrogen pressures, but is favored at higher pressures.

The distribution of  $\text{C}_2 - \text{C}_6$  molecules is less dependent on the hydrogen pressure than selectivity of methane is. Production of propane and n- butane is favored at low and medium pressures. Selectivity is related to carbonium character of the species adsorbed on Pt surface.

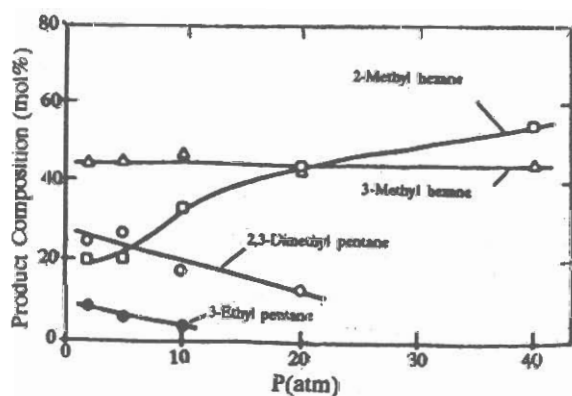
Table 2: Products yields as a function of partial pressure of hydrogen

$\text{P}_{\text{H}_2}$ (atm)		1.9	4.9	9.9	19.9	39.9
Overall yield		10.3	6.5	1.4	0.4	0.1
Hydrogenolysis	yield	2.0	1.9	0.9	0.3	0.06
	mol.ratio	19.7	30.3	59.0	75.6	71.8
Isomerization	yield	6.1	3.4	0.3	0.07	0.02
	mol.ratio	59.0	52.4	22.9	17.1	19.0
Cyclization	yield	1.5	1.0	0.3	0.03	0.01
	mol.ratio	14.5	15.0	18.0	7.3	9.2
Toluene	yield	0.7	0.2	-	-	-
	mol.ratio	6.8	2.6	-	-	-

**Table 3: Changes in product composition (mole%) as a function of hydrogen partial pressure (reaction conditions:  $P_{C_7} = 0.1 \text{ atm}$ ,  $T = 325^\circ \text{C}$ ,  $t = 3.5 \text{ s}$ ).**

$P_{H_2}(\text{atm})$	1.9	4.9	9.9	19.9	39.9
methane	16.6	22.2	32.5	40.6	68.2
ethane	12.1	10.8	8.4	5.8	4.9
propane	23.7	21.8	18.5	16.2	5.0
isobutane	0.2	0.07	-	-	-
n-butane	23.7	22.2	18.6	14.9	7.9
isopentane	0.3	0.2	-	-	-
n-pentane	12.4	11.2	9.4	9.3	5.8
cyclopentane	0.1	0.06	-	-	-
2,2 DMB	0.02	-	-	-	-
2,3 DMB	0.02	-	-	-	-
2- MP	0.5	0.3	-	-	-
3- MP	0.4	0.2	-	-	-
n-hexane	9.7	10.8	12.6	13.2	8.2
MCP	0.4	-	-	-	-
cyclohexane	0.05	0.12	-	-	-

Fig. 4 shows the strong dependence of selectivity of isomerization products with respect to partial pressure of hydrogen. At low and medium hydrogen pressures, major products consist of 3-methyl hexane, 2,3- dimethyl pentane, 2- methyl hexane, and 3- ethyl pentane.

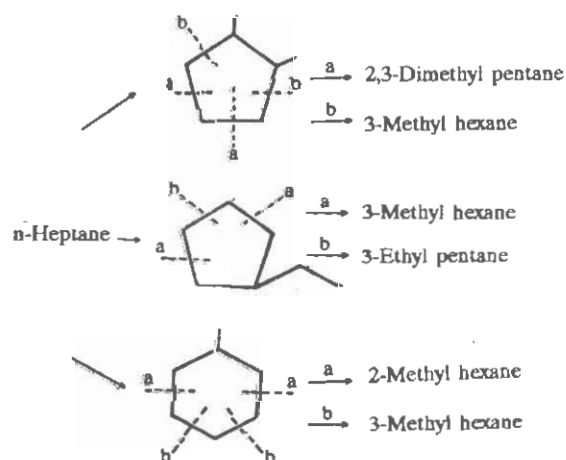


**Fig.4: Selectivity vs hydrogen partial pressure**

Since 2,3-dimethyl pentane isomer is accompanied by traces of 2,4- dimethyl pentane, it may be concluded that the catalytic action of catalyst "I" does not involve a carbonium ion in the

transition state. If there were sufficient acidic centers involved the amount of 2,4- and 2,3-dimethyl pentane would have been equal.

With the increase in the hydrogen pressure the amount of 2,3- dimethyl pentane and that of 3- ethyl pentane decreases whereas that of 2- methyl hexane increases extensively and the amount of 3- methyl hexane remains unchanged. The distribution of these isomers, especially at low and medium pressures (2-10 atm) may be explained via 5 membered intermediates:



Whether 1,2- dimethyl cyclopentane, ethyl cyclopentane, and methyl cyclohexane appear simultaneously or one of them dominantly appear as the intermediate, depends strongly on the hydrogen partial pressure. Product distribution indicates that at low and medium pressures 1,2- dimethyl cyclopentane may be a more suitable intermediate. Upon increase in hydrogen partial pressure the isomerization product distribution becomes unwieldy and approaches the reactions involving aliphatic intermediates.

### 3.2. Product Selectivity

As can be discerned from Fig. 5, nearly 60% of the cyclic products at low pressures (2 atm) consist of cyclopentane derivatives and the rest 40% is made of toluene and methyl cyclohexane. With the increase in hydrogen partial pressure the equilibrium between toluene and methyl cyclohexane is shifted in favor of methyl cyclohexane, in such a way that practically no toluene is formed at 5 atm. At high pressures the formation of 5 membered rings are favored over six membered ones. Products formed at low hydrogen pressures are: toluene, 1-tr, 2- dimethyl cyclopentane, ethyl cyclopentane, methyl cyclohexane, and 1-cis, 2- dimethyl cyclopentane along with traces of 1- cis, 3- and 1-tr, 3- dimethyl cyclopentane. With the increase in pressure the amount of 1-tr, dimethyl cyclopentane increases continuously, so that at

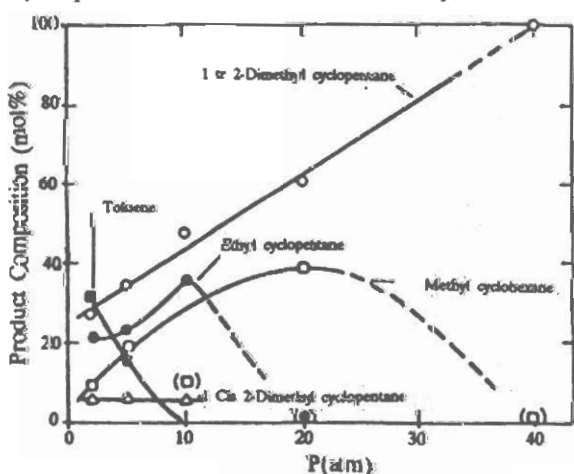
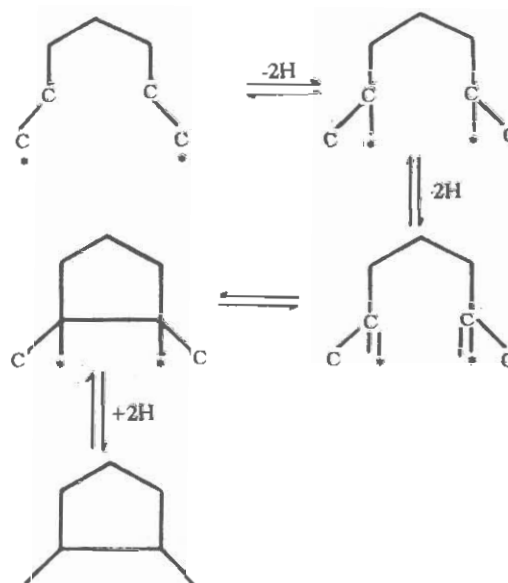


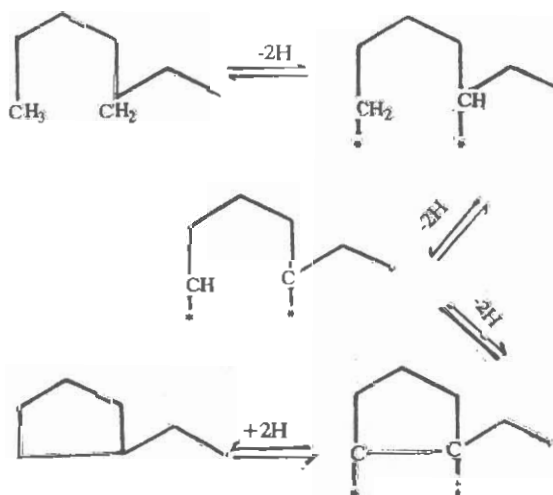
Fig. 5: Selectivity of cyclic products vs hydrogen partial pressure.

40 atm it is practically the only product found. The amount of ethyl cyclopentane at 20 atm and that of methyl cyclohexane at 40 atm are so low that they can not be traced chromatographically. At 40 atm methylcyclohexane makes up about 4% and 1-tr, 2- dimethyl cyclopentane forms 96% of the product mixture.

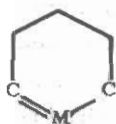
The following mechanism may be envisioned for cyclomerization of heptane via chemisorption on active centers.



And for the formation of ethyl cyclopentane:



A recent article on the cyclization of pentane on Pt and Pd, reports that a 1,1,5- adsorption on a metal atom seems a satisfactory explanation [11].



Thus, cyclization of n- heptane might be explained in a similar fashion.

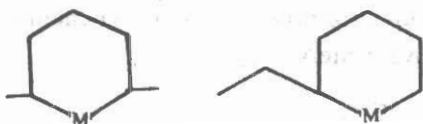


Table 4 shows the results for the reactions carried out at 325° and 375°C, where it is seen that the overall yield is increased from 10.3% to 25.3%.

As can be seen the yield of various product groups remain unchanged but the number of branched and cyclic compounds increases. At 375°C the amount of 2- methyl hexane as 28.8%

compared to 20% at 325°C. This increase is at the cost of reduction in the amount of 2,3- dimethyl pentane and 3- methyl hexane. This shift may be explained on the basis of displacement of methyl group at 375°C. Since ethyl cyclopentane varies from 30.8% at 325°C to 44% at 375°C, it may be concluded that at 325°C the adsorbed species is 1,2- dimethyl cyclopentane and 375°C it is ethyl cyclopentane.

### 3.3. The effect of contact time

The effect of contact time on the selectivity of n-heptane on 5% Pt/Al<sub>2</sub>O<sub>3</sub> was studied. Contact time is determined by dividing the empty space of catalyst in the reaction by the volumetric flow rate of the input gas into the reactor. In this study the contact time was varied between 0.88 to 5.88 s. and the reaction conditions were:

$$n_{C_7} / n_{H_2} = 1/20, P_{C_7} = 0.1 \text{ atm}, P_{H_2} = 1.9 \text{ atm} \\ P = 2 \text{ atm}, T = 325^\circ \text{C}$$

Table 4: Reaction of n- heptane on 5% Pt/Al<sub>2</sub>O<sub>3</sub> at 2 atm and 375°C

Overall yield (mol%):	25.3	Hydrogenolysis	products(mol%)
Hydrogenolysis:	4.8 (19.0)	methane	20.3
Isomerization:	14.2 (56.0)	ethane	12.9
Cyclization:	4.8 (19.1)	propane	23.6
Toluene:	1.5 (5.9)	isobutane	1.1
		n-butane	22.4
		isopentane	1.5
		n-pentane	9.4
		cyclopentane	0.9
		2-methylpentane	1.1
		3-methylpentane	0.8
		n-hexane	4.8
		methyl cyclohexane	0.7
		cyclohexane	0.5
Cyclic	products(mole%)	isomerization	products(mol%)
1,1-DMCP	1.1	2,2-DMP	0.4
1,cis-3DMCP	5.7	2,4-DMP	1.8
1,tr 3-DMCP	5.3	2,3-DMP	9.5
1,tr 2-DMCP	26.0	2-MH <sub>x</sub>	28.8
1,cis 2-DMCP	6.8	3-MH <sub>x</sub>	51.6
MCH <sub>x</sub>	11.0	3-EP	7.8
ECP	44.0		



Fig. 6 shows the yield of the various groups as well as the total yield and Fig.7 depicts the selectivity of the groups vs the contact time. As can be seen the individual as well as the total yields increase with the contact time. It is also apparent that increasing the contact time leads into the increase in isomerization and hydrogenolysis while it decreases the formation of cyclic components.

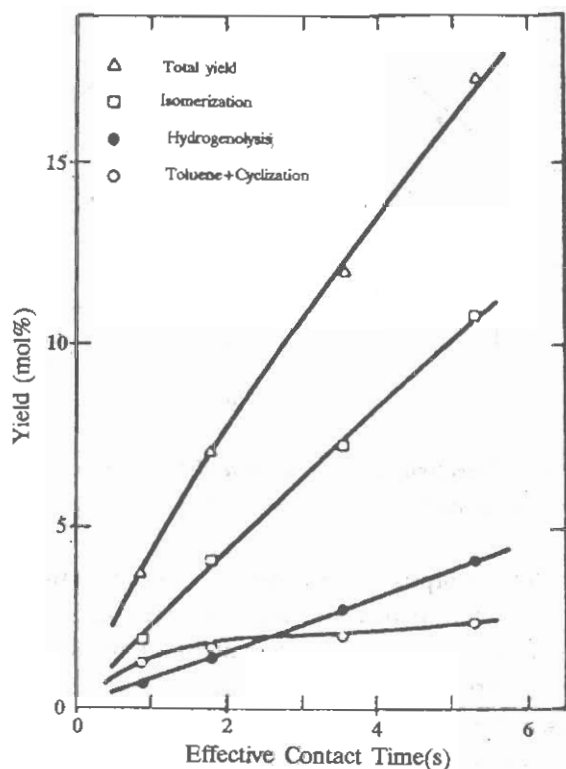


Fig.6: Yields of various components formed over  $Pt/Al_2O_3$  as a function of contact time ( $n_{C_7}/n_{H_2} = 1/20$ ,  $P=2atm$ ,  $T=325^\circ C$ )

Thus, it may be concluded that at least part of the cyclic components acting as intermediates are initially desorbed and re-adsorbed chemically afterwards. The changes in hydrogenolysis products with respect to contact time seem to be miniscule, Table 5.

Figs.8 and 9 show the ratio of isomerization and cyclization products as a function of contact time. It is seen that the composition of isomerization products vary only slightly while the amount of 2,3- dimethyl pentane increases and that of 2-methyl hexane decreases. The composi-

tion of cyclic products vary considerably. As

Table 5: Composition of hydrogenolysis (mol%) as a function of effective contact time ( $P_{C_7}=0.1atm$ ,  $P=5atm$ ,  $T=325^\circ C$ )

Compound	t(s)	0.88	1.76	3.51	5.26
methane		16.6	16.2	16.1	15.2
ethane		11.3	11.2	12.4	11.7
propane		24.3	24.2	24.1	27.7
isobutane		0.1	0.1	0.2	0.2
n-butane		24.4	24.0	23.9	22.4
isopentane		0.3	0.3	0.4	0.4
n-pentane		12.5	12.3	12.2	11.5
cyclopentane		0.2	0.2	0.1	0.1
2-methylpentane		0.2	0.4	0.6	0.8
3-methylpentane		0.2	0.2	0.5	0.7
n-hexane		9.8	9.5	9.1	9.0
methylcyclopentane		0.1	0.1	0.3	0.2
cyclohexane		-	-	0.1	0.1

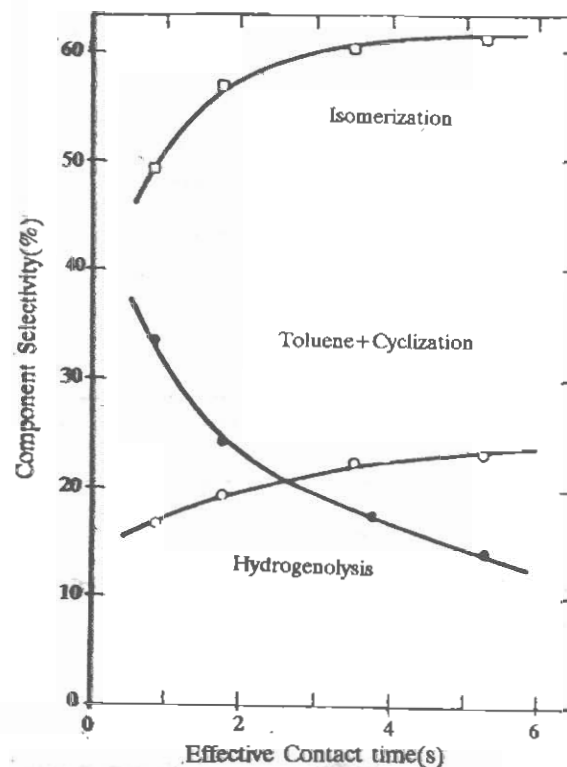


Fig.7 : Selectivity of various components for the reaction of n- heptane over  $Pt/Al_2O_3$  as a function of effective contact time (conditions as in Fig.6).

mentioned earlier, these might be explained via selectivity of a secondary reaction involving cyclic products. In particular Fig.8 shows that the amounts of cyclopentane derivatives, tr 1,2-dimethyl cyclopentane and ethyl cyclopentane are reduced whereas those of toluene and methyl cyclohexane increase. tr 1,2- dimethyl cyclopentane and ethyl cyclopentane are considered the primary products of cyclization, since they form more than 66% of the total products. As cited in the literature, six membered ring compounds are more stable and harder to open than the five membered rings. With the increase in contact time more of the five membered ring compounds are transformed into branched heptanes and hence selectivity of the five membered rings are reduced. Consequently the proportion of six membered ring compounds increases.

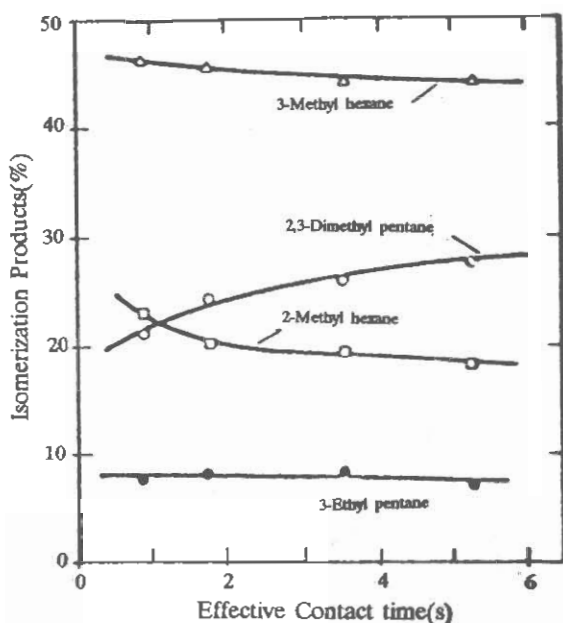


Fig.8 : Isomerization selectivity as a function of effective contact time ( $P=2\text{atm}$ ,  $T=325^\circ\text{C}$ ,  $5\% \text{Pt}/\text{Al}_2\text{O}_3$ )

#### 4.0. CONCLUSIONS :

The observations reported may be summarized as follows: with the increase in hydrogen partial pressure the rate of n-pentane reaction with hydrogen over  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst decreases. Among the three concurrent reactions (hydro-

genolysis, isomerization, and cyclization) the yield of isomerization reaction is severely decreased at pressures above 10atm.

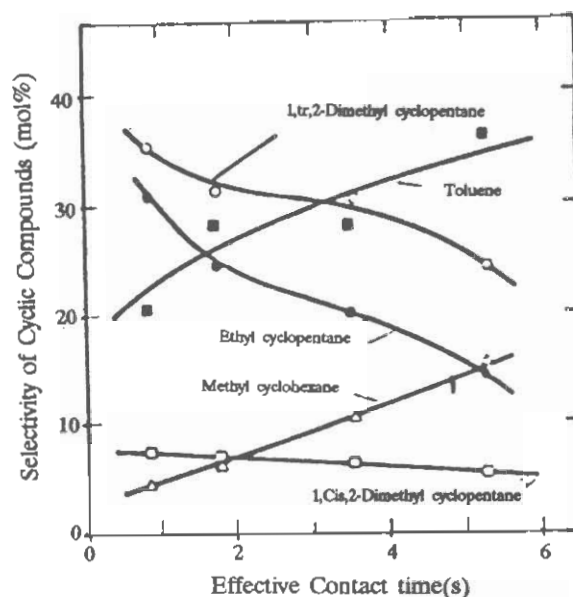


Fig.9 : Selectivity of ring compounds as a function of effective contact time (conditions as before)

The composition of isomerization products shows that at low and medium pressures the reaction proceeds via adsorption of cyclic five membered species and at higher pressures via alkyl displacement as a consequence of hydrogen atoms being adsorbed on the active centers of the catalyst.

With the increase in contact time the overall yield as well as the yield of hydrogenolysis and isomerization products increase extensively whereas, that of the cyclic components remain effectively unchanged, indicating the occurrence of a readsorption and consequent cleavage. Experiments indicate that cyclic components, especially 1tr, 2- dimethyl cyclopentane act as intermediates in the formation of isomers.

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