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ENCLOSURE (B) 5

ISOMERIZATION OF n-HEXANE

by

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AND ILLUSTRATIONS

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SUMMARY

As a fundamental work pertaining to the isomerization of gasoline, the isomerization of n-hexane was tried.

To obtain isomerizates containing 20% of isomeric paraffin hydrocarbons from n-hexane using Mo-compounds as the catalyst, high temperatures and pressures, such as 400°C and 200kg/cm<sup>2</sup>, are required.

Isomeric hexanes were obtained from n-hexane at 110°C in 16-18% yield and 62.5-64.5% selectivity using anhydrous aluminium chloride catalyst which was regenerated by hydrogen chloride.

Some decomposition of product occurred and the yield of liquid per initial content of n-hexane was about 50%.

Hydrogen pressure was effective in suppressing the decomposition, and the results of some experiments under pressure are as shown in Table I(B)5.

TABLE I(B)5

Initial hydrogen pressure (atm.)	Reaction temperature (°C)	Yield of isomer (%)	Selectivity (%)
40	120	67.5	97.4
40	160	72.3	93.4

At temperatures above 200°C, decompositions occurred in spite of the application of hydrogen pressure.

I. INTRODUCTION

A. There are many reports on the isomerization of C<sub>5</sub>-C<sub>8</sub> normal paraffin hydrocarbons. Aluminium chloride was reported to be the most effective isomerizing agent when compared with molybdenum trisulphide, zinc chloride, etc.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT:

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II. DETAILED DESCRIPTIONA. DESCRIPTION OF TEST APPARATUS1. The Reaction Under Pressure

A shaking autoclave having a capacity of one litre was used.

2. Flow Method Under Atmospheric Pressure

A silica tube, 1,500mm in length, 20mm in diameter and slightly inclined, was placed in an electric furnace and from its upper side the raw materials were charged.

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TABLE II(B)5

EFFECT OF MO-COMPOUNDS IN ISOMERIZATION OF n-HEXANE

No.	Catalyst	Catalyst used (wt. raw material)	Reaction temp. (°C)	Pressure (kg/cm <sup>2</sup> )	Liq.-yield (%)	Isomerizate (% raw material)	Octane rating C6-fract.
24	MCL	25	400	00	76.5	14.5	31.5
27	MS	7.5	300	15	80.0	3.2	30.8
33	MCL	25	400	30	76.7	9.2	31.1

Note: Raw Material - Octane rating C6-fract. of 33.2.  
MCL - ammonium thiomolybdate on active charcoal.  
MS - molybdenum trisulfide.

TABLE III(B)5

ISOMERIZATION WITH  $AlCl_3$  AT ATMOSPHERIC PRESSURE

No.	$AlCl_3$ used, (wt. % of raw mat.)	HCl used, (wt. % of raw mat.)	Reaction temp., (°C)	Gas produced, (wt. %)	Yield of liquid, (wt. %)	Isomeric hexane, (%)	Selectivity of isomerization (%)	Octane rating
Raw material								33.2
71	25	63	85	20.5	66.0	7.8	38.0	40.4
72	25	88	85	25.0	69.0	8.2	31.0	
73	25	86	90	34.0	60.0	10.4	46.0	
74	25	105	90	30.0	61.5	10.8	48.5	
75	25	93	95	24.0	56.0			49.5
76	25	75	95	23.0	62.5	10.4	33.3	
77	25	73	95	28.0	56.0	7.0	42.9	
78	25	75	100	23.5	56.0	8.9	33.3	
79	25	75	100	30.0	57.5	8.8	40.5	42.3
80	25	73	105	32.0	54.0	11.2	54.8	
81	25	95	105	33.5	50.5	10.9	60.0	
82	25	72	110	29.5	57.5	18.6	64.5	
83	25	72	110	38.0	48.0	15.7	62.5	
84	25	63	115	40.0	46.0	17.7	69.2	
85	25	73	115	37.0	48.0	13.1	44.1	
86	25	55	120	38.0	48.0	12.7	54.3	
87	25	65	120	37.5	48.0	12.2	63.2	

TABLE IV(B)5.  
ISOMERIZATION WITH  $AlCl_3$  UNDER PRESSURE

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No.	AlCl <sub>3</sub> used, (wt. % of raw mat.)	Reaction temp. (°C)	Duration (hr)	H <sub>2</sub> initial pressure (atm.)	Yield of liquid, (wt. %)	Yield of l- <i>n</i> -C <sub>6</sub> (%)	n-C <sub>6</sub> reacted (%)	Selectivity of isom. (%)	Composition of products				
									C <sub>6</sub> and below	l-C <sub>6</sub>	l- <i>n</i> -C <sub>6</sub> higher		
91	10	120	6	00	80	12.8	90	32.0	12	14	16	48	8
92	10	120	6	20	61	18.3	80	37.5	11	27	30	18	12
93	10	120	6	40	72	33.8	91	51.6	8	30	47	7	6
94	10	120	6	60	83	59.8	69	98.5	1	0	68	29	0
95	10	80	6	10	93	44.6	56	85.7	1	6	48	32	1
96	10	160	6	40	83	59.0	77	92.3	1	4	71	14	1
97	10	200	6	40	60	24.6	88	46.5	13	23	41	10	11
98	10	120	3	40	87	32.2	80	75.0	8	9	60	17	3
99	10	120	9	40	90	67.5	77	87.4	0	2	75	18	0
100	10	200	3	40	49								
101	10	200	9	40	60	30.6	91	56.1	13	25	51	78	2
102	10	160	6	40	85	72.3	91	93.4	4	2	85	4	0

Selectivity =  $\frac{l-C_6 \text{ Produced}}{n-C_6 \text{ Reacted}} \times 100$

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TABLE V(B)5  
 REPRESENTATIVE RESULTS OF ISOMERIZATION OF n-HEXANE

	Number		
	78	95	99
Pressure (atms.)	1	40	40
Reaction temperature (°C)	100	80	120
Yield of liquid (%)	56	93	90
C <sub>4</sub> and lower (%)	12	1	0
C <sub>5</sub> (%)	15	6	2
2.2-Dimethylbutane (%)	0	7	0
2.3-Dimethylbutane (%)	5	18	12
2-Methylpentane (%)	2	6	15
3-Methylpentane (%)	8	27	48
Total i-Hexane (%)	15	58	75
n-Hexane (%)	52	32	18
C <sub>7</sub> and higher (%)	3	1	0

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B. TEST PROCEDURES1. Method Under Pressure

n-Hexane and catalysts were charged and air was replaced by hydrogen chloride or hydrogen. They were then heated under the given conditions.

2. Flow Method

Catalysts were placed in the reaction tube and heated by means of an electric furnace. As soon as the reaction tube reached the desired temperature, n-hexane was introduced at the rate of 1 cc/min. The products were withdrawn from the lower side of the tube.

3. Analysis of the Products

To determine the amount of isomeric paraffin hydrocarbons, the precise fractional distillation was adopted using the standard Podbielniak apparatus.

C. EXPERIMENTAL RESULTS1. Isomerization in the Presence of Mo-compounds

The results shown in Table II(B)5 indicate that Mo-compounds were of little effect since the octane ratings of the products were not increased in spite of the fact that fractional distillation data show that some branched isomers were produced. The lowering of the octane rating of product could be caused by the formation of higher hydrocarbons.

2. Isomerization With AlCl<sub>3</sub> at Atmospheric Pressure

As shown in Table III(B)5, n-hexane was isomerized to isomeric hexanes with yields of 7-18%, and the octane rating increased from 7-16 numbers. However, the liquid yield was low, since decomposition accompanied the reaction.

3. Isomerization With AlCl<sub>3</sub> Under Pressure

As shown in Table IV(B)5, hydrogen pressure was necessary not only to suppress the decomposition but to promote isomerization.

Some representative results are tabulated in Table V(B)5.

III. CONCLUSIONS

## A. The best conditions for the isomerization of n-hexane were as follows:

Catalyst .....	AlCl <sub>3</sub> and HCl
Hydrogen pressure .....	about 50 atms
Reaction temperature .....	120-140°C
Amount of catalyst .....	10% by weight based on raw material
Duration of reaction .....	3-5 hrs

## B. Under the above conditions the results are as follows:

Yield of isomeric hexanes .....	60-70%
Selectivity of isomerization .....	93-97%

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C. Because of the mild conditions and plentiful supply of catalyst, the use of aluminum chloride in the isomerization of low grade paraffine gasoline offers promise for commercial application. However, additional experimentation is required.