ENCLOSURE (B) 6

STUDIES ON THE ISOMERIZATION OF n-BUTANE

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Normal butane was isomerized in liquid phase, using $AlCl_3$ catalyst and HCl as a promoter, and a maximum yield of 66% isobutane was obtained. Best conditions for the reaction were as follows:

Contact time	2 hrs
Amount of $AlCl_3$	118 wt%
Amount of HCl	25 wt%
Temperature	110°C
Pressure	15-20 kg/cm^2
Support	Japan acid clay

I. INTRODUCTION

Isomerization of n-butane to isobutane with aluminum chloride catalyst has been well known since 1937. In 1940 it was desired to investigate the production of isobutane from the normal butane contained in refinery waste gases.

Laboratory work on this subject was carried on from Sept., 1940 to April, 1941, and pilot plant work from Dec., 1942 to March, 1944. The laboratory test results checked those reported in the literature and are reported herewith. (Ind. Eng. Chem., vol. 26, 461 (1936); Rec. d. Trav. Chem., vol. 59, 793 (1940) etc.)

Although a pilot plant was considered in 1941, it was not constructed until after the author had inspected the Nederlandsche Kolonial Petroleum Maastchappii unit at PALEMBANG in the autumn of 1942. Reports of pilot plant tests were all destroyed, but it is recalled that the results were practically identical with the laboratory tests, except for HCl corrosion, especially in the hydrogen chloride gas compressor.

A. Laboratory tests

The laboratory tests were carried out in a horizontal shaking steel autoclave of 600cc total volume. This apparatus was equipped with external electric heaters and a thermocouple in the center of the hollow shaft extending through the autoclave.

Anhydrous $AlCl_3$ was first charged to the autoclave, then normal butane, cooled by dry ice-alcohol solution, and finally crystals of HCl produced by cooling with liquid air. The autoclave was closed, and brought up to the desired temperature. After the desired reaction time, gas was released to a gas meter. The gas was analyzed by Podbielniak and Hempel methods. Experimental data secured are summarized in the following tables.

Table I(B)6 shows effect of reaction time on yield. In this table the rate of isomerization is defined as the yield of i-butane as wt% of n-butane charged. Selectivity is defined as the wt% of the normal butane which is converted. (i.e. n-butane charged less n-butane unconverted). It is concluded from these data that the required reaction time is 90 minutes or over.

Table II(B)6 shows the effect of reaction temperature. It is concluded that the optimum temperature range is 110-115°C.

Tables III(B)6 and IV(B)6 show the effect of HCl addition on life of the $AlCl_3$ catalyst. In Table III(B)6 catalyst life in absence of HCl is

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Table I(B)6

EFFECT OF REACTION TIME

Test No.	Time (min)	Temp.°C (max)	Press. (kg/cm²) max	Produced gas (l)	Gas Analysis (% by Volume)					Degree of Isomerization(%)	Selectivity (%)
					H_2-C_2H_6	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
101	30'	110(110)	14.7	33.2	5.3	20.6	22.3	5.7	46.1	23.8	45.7
102	60'	110(110)	16.5	32.8	5.8	17.9	34.0	1.6	35.7	33.5	64.0
15	90'	110(112)	17.3	36.6		17.6	60.6		21.8	62.7	81.0
16-1	120'	110(111)	16.2	39.0		23.8	59.3		17.4	65.7	81.5
14	180'	110(110)	16.5	35.7		16.0	60.5		23.5	61.0	80.2
9	240'	110(110)	16.0	35.0		10.9	65.6		23.4	65.2	87.2

Conditions

n-C_4H_{10} ..... 150cc (89.4% purity)
$AlCl_3$ ..... 100 gm
HCl ..... 2.5 gm (crystal state)

Table II(B)6

EFFECT OF REACTION TEMPERATURE

Test No.	Reaction Temp.°C	Press. kg/cm²(max)	Produced gas (l)	Gas Analysis (% by Volume)					Degree of Isomerization(%)	Selectivity (%)
				H_2-C_2H_6	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
123	105(105)	10.2	34.6		15.4	30.2	4.0	50.6	34.3	77.0
16-1	110(111)	16.2	39.0		23.8	59.3	0	17.4	65.7	81.5
121	115(117)	17.2	35.2		14.6	51.1	2	26.8	59.5	86.4
124	130(1[illegible])	15.5	35.5		57.5	10.5		32.5	10.1	15.0

Conditions

n-C_4H_{10} ..... 150cc (84.4% purity)
$AlCl_3$ ..... 100 gm
HCl ..... 2.5 gm (crystal state)
Reaction time ..... 120 min

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Table III(B)6

CATALYST LIFE WITHOUT HCl

Test No.	Time of Using Same Catalyst (hrs)	Pressure (kg/cm^2) max	Produced gas (l)	Gas Analysis (% by Volume)					Degree of Isomerization	Selectivity
				$C_2H_6-H_2$	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
18-1	0	12.9	35.5	1.9	14.3	43.5		40.3	45.5	98.8
18-2	4	11.6	33.0	2.4	13.9	42.7	3.6	37.4	44.7	73.5
18-4	6	12.3	36.0	0	29.5	23.5		47.0	34.2	98.0
18-6	10	12.5	35.5	3.0	26.7	19.5	2.3	48.5	44.5	98.2
18-16	30	7.8	36.5	3.0	8.1	4.8	3.2	81.0	5.0	87.0
18-20	38	7.5	35.0	2.0	3.0	8.8	5.8	80.4	10.8	100

Conditions

n-C_4H_{10} ..... 150cc (89.4% purity)
$AlCl_3$ ..... 100 gm
HCl ..... not used
Reaction time ..... 120 min
Reaction temp. ..... 110°C

Table IV(B)6

CATALYST LIFE WITH ADDITION OF HCl

Test No.	Time of Using Same Catalyst (hrs)	Pressure (kg/cm^2) max	Produced gas (l)	Gas Analysis (% by Volume)					Rate of Isomerization	Selectivity
				$H_2-C_2H_6$	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
17-1	0	15.8	31.3		11.6	66.1		22.3	58.4	71.5
17-2	2	14.5	34.3		13.5	63.5		23.2	61.4	79.2
17-3	4	14.3	31.8		16.9	59.0		24.1	51.8	66.3
17-4	6	14.3	37.2		11.2	53.3		35.5	56.4	89.1
17-	8	15.1	34.8		16.5	55.0		28.5	54.5	75.7
17-	10	15.0	33.8		19.2	47.0		33.7	45.0	66.2
17-	14	12.5	34.1		13.1	44.2		42.7	45.0	73.2
17-18	18	14.5	32.2		16.9	44.8	4.7	53.5	43.3	63.0
17-22	22	14.2	31.3		9.3	44.7		45.0	39.9	66.3
17-26	28	12.3	34.5		13.3	43.5		43.3	42.8	73.2
17-32	42	12.1	33.5		25.6	39.3	3.3	31.8	43.5	72.6
17-	48	13.5	34.3		18.7	39.1	3.2	39.0	44.2	71.8
17-	56	14.5	34.6		23.4	34.2	3.2	39.2	38.7	68.2

Conditions

Same as Table III(B)6 with 2.5 gm HCl added

seen to decline rapidly after 10 hours. In Table IV(B)6, with all conditions the same except for addition of 2.5 g m of HCl every two hours, the catalyst life exceeds 56 hours.

B. Pilot plant tests. See Figure 1(B)6.

A flow sheet of the reaction section of the pilot plant constructed to investigate isomerization of n-butane and also the processing of spent butanes from the alkylation pilot plant at OFUNA, is given by Plate I(B)6 Spent hydrocarbon gases from the alkylation pilot unit were compressed, liquefied and pumped into the gas separation unit, where pentane and heavier propanes and isobutane fractions were removed.

The normal butane was washed with 98% sulphuric acid to remove water and sent together with HCl gas into the reaction chambers, filled with anhydrous aluminum chloride supported on acid clay or bauxite and heated to about 110°C.

Since 1942 only three complete tests were made on this unit and all data were destroyed. The important problems in operating this plant were as follows:

1. Dehydration of HCl was necessary to prevent corrosion. Drying of the HCl gas was very difficult. Washing with 98% H_2SO_4 and passing through layers of $AlCl_3$ crystals or Zn-metal was not satisfactory and corrosion of cast iron and other metals in the compressor piston, piston rings, etc. was severe. Also there was difficulty with stuck valves due to sludge deposition. It was also necessary completely to remove Cl_2 from HCl to prevent an explosion with excess H_2 in the compressor. The purification of hydrochloric acid was finally accomplished by washing the HCl gas with a saturated solution of stannous chloride.

2. The life of the catalyst was five days. In order to reduce the consumption of $AlCl_3$, the recovery of the catalyst would be necessary in a large scale plant. This was not done on a pilot plant scale.

II. CONCLUSIONS

It was concluded from these experiments that the liquid phase isomerization of n-butane was practical for a larger scale application. Pilot plant difficulties were mainly centered on corrosion in the HCl compression and handling system. To the writer's knowledge, no commercial application has been made of this process in Japan.

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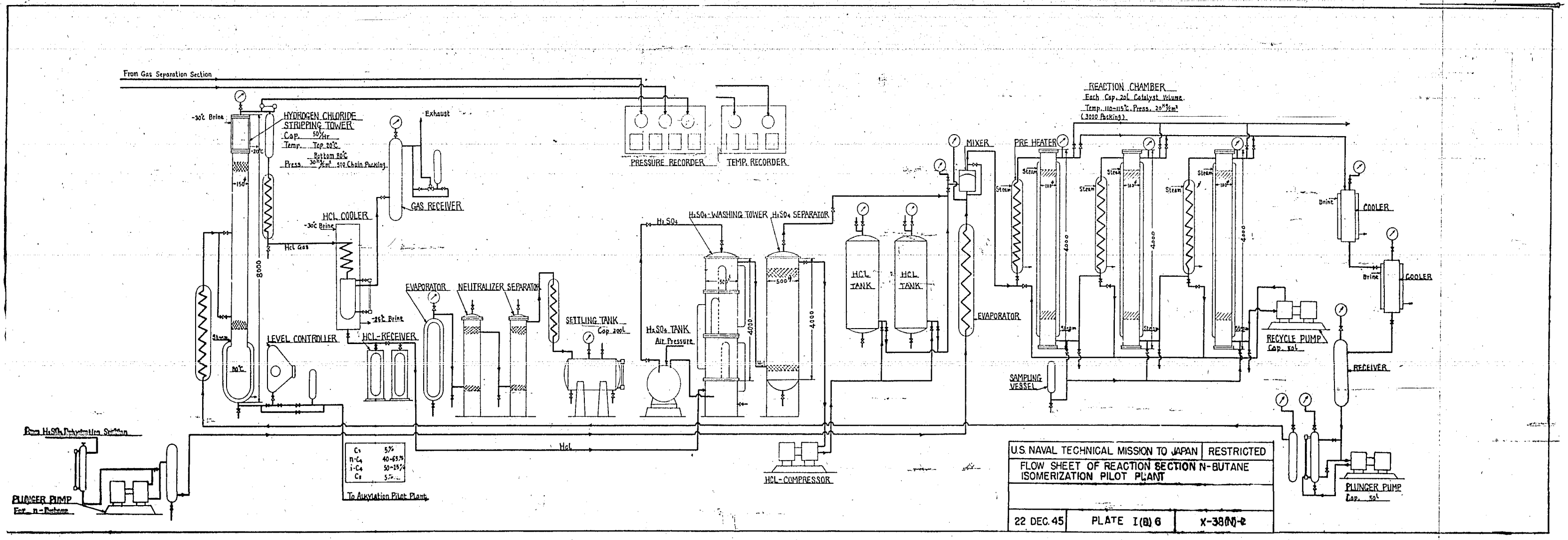
Figure 1(B)6
ISOMERIZATION PLANT OF CASCADE


From Gas Separation Section
-30°C Brine
HYDROGEN CHLORIDE STRIPPING TOWER
Cap. 50%/Hr
Temp. Top 20°C
Bottom 80°C
Press. 30 Kg/cm² sq Chain Packing
Exhaust
GAS RECEIVER
PRESSURE RECORDER
TEMP. RECORDER
HCL COOLER
-30°C Brine
Hcl Gas
-25°C Brine
LEVEL CONTROLLER
HCL-RECEIVER
EVAPORATOR
NEUTRALIZER SEPARATOR
SETTLING TANK
Cap. 20ℓ
H₂SO₄
H₂SO₄-WASHING TOWER
H₂SO₄ SEPARATOR
H₂SO₄ TANK
Air Pressure
HCL TANK
HCL TANK
MIXER
EVAPORATOR
REACTION CHAMBER
Each Cap. 20ℓ Catalyst Volume
Temp. 110-115°C, Press. 20 Kg/cm²
(3000 Packing)
PRE HEATER
Steam
Brine
COOLER
COOLER
RECYCLE PUMP
Cap. 50ℓ
SAMPLING VESSEL
RECEIVER
PLUNGER PUMP
Cap. 50ℓ
From H₂SO₄ Polymerization Section
PLUNGER PUMP
For n-Butane
Hcl
C₃ 5%
n-C₄ 40-65%
i-C₄ 50-15%
C₅ 5%
To Alkylation Pilot Plant
HCL-COMPRESSOR
U.S. NAVAL TECHNICAL MISSION TO JAPAN | RESTRICTED
FLOW SHEET OF REACTION SECTION N-BUTANE ISOMERIZATION PILOT PLANT
22 DEC. 45 | PLATE I(B) 6 | X-38(N)-2