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ENCLOSURE (B) 1

STUDIES ON THE
DEHYDROGENATION
OF n-BUTANE

by

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SUMMARY

The purpose of this work was to obtain n-butylene by the catalytic dehydrogenation of n-butane, for the purpose of manufacturing raw gases for polymerization.

The yield of butenes was about 24 % per pass in the presence of Al_2O_3 - Cr_2O_3 catalyst. The effects of temperature and space velocity were appreciable. The activity of the catalyst decreased after one hour of use.

I - INTRODUCTIONA. HISTORY OF PROJECT

The concentration of n-butane in cracked gas is greater than that of butenes.

Dehydrogenation of n-butane is more difficult thermodynamically than the breaking of the C-C bond. Catalytic dehydrogenation is more desirable for this purpose.

Alumina-Chromium oxide which has been investigated by many authors, was used.

This work was started in April, 1938 and continued until 1942. The actual work was done in a few months. Since, in Japan, cracked gas could not be produced extensively, experiments on other catalysts were not conducted.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

Chem. Eng. Lt. Comdr., M. KUMAMOTO

II - DETAILED DESCRIPTIONA. DESCRIPTION OF TEST APPARATUS

Test apparatus for dehydrogenation is shown in Figure 1(B)1.

B. TEST PROCEDURES

This experiment was carried out with n-butane of about 94-97 % purity prepared by fractionation from cracked gas which was produced at the Mitsubishi Oil Company.

n-Butane was passed through a drying tube and, after preheating to about 300°C., through a quartz reaction tube (dia. = 16mm; length = 300mm). The reaction tube was heated electrically. The gas flow and temperature were measured.

The gas which had been passed over the catalyst was analysed by following methods: The determination of olefines and hydrogen was carried out by Hempel's method: A mercury-filled gas pipet was used for the determination of olefines by absorption. The total olefines, and butenes were determined by absorption in fuming (10 % sulphur trioxide) and 83 % sulphuric acid, respectively.

In several cases the analysis of the products of reaction was carried out by fractional distillation using a Podbielniak apparatus.

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Preparation of Catalyst - Freshly precipitated aluminium hydroxide was prepared, carefully washed, and ignited at 550°C. The alumina was mixed with CrO₃ (12% as Cr₂O₃) and dried at 120°C.

C. EXPERIMENTAL RESULTS

The pyrolytic decomposition of n-butane was investigated and the results are given in Table I(B)1.

Table I(B)1
YIELD OF BUTYLENES FROM BUTANE BY PYROLYSIS

Ex. No.		1	2	3
Conditions	Temp. (°C)	550	560	570
	Space* velocity	1080	1080	1080
Composition of Gas Produced	Total olefines (%)	15.0	18.7	12.8
	C ₄ H ₈ (%)	12.0	10.2	5.0
	H ₂ (%)	10.3	10.5	8.0
	C _n H _{2n+2} (%)	74.3	70.8	79.2

* cc/hr/cc of catalyst, assuming a catalyst volume of 30cc

The effects of temperature and space velocity in presence of Al₂O₃-Cr₂O₃ were investigated and are tabulated in Tables II(B)1 and III(B)1.

Table II(B)1
YIELD OF BUTYLENES FROM BUTANE AT VARYING TEMPERATURES
IN PRESENCE OF Al₂O₃-Cr₂O₃ CATALYST

Ex. No.		5	6	7	8	9	10
Analysis of Gas produced	Temp. (°C)	350	400	450	500	550	600
	Space velocity	1100	1100	1100	1100	1100	1100
	Total olefines (%)	4.2	7.1	10.8	14.6	25.0	28.0
	C ₄ H ₆ (%)	4.1	6.8	10.0	14.0	23.5	22.0
	H ₂ (%)	3.5	7.5	13.2	14.1	20.2	21.2
	C _n H _{2n+2} (%)	92.3	85.3	76.0	71.3	54.8	50.8

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Table III(B)₁
YIELD OF BUTYLENES FROM BUTANE AT VARYING SPACE
VELOCITY IN PRESENCE OF Al₂O₃-Cr₂O₃ CATALYST

Ex. No.		11	12	9	13	14	15
Conditions	Space* velocity	500	1000	1100	1500	1800	2000
	Temp. (°C)	550	550	550	550	550	550
Composition of Gas Produced	Total olefines (%)	28.2	25.7	25.0	21.7	19.0	12.5
	C ₄ H ₈ (%)	20.0	22.5	23.0	19.2	17.6	11.0
	H ₂ (%)	23.0	23.1	20.2	17.8	17.0	10.5
	C _n H _{2n+2} (%)	48.8	51.2	54.8	60.3	64.0	77.0

* cc/hr/cc of catalyst.

The yield of butylenes increased with increasing temperature but above 500°C. the formation of lower olefines increased. A secondary reaction may occur at higher temperatures. The optimum temperature appears to be between 500°C. and 550°C.

The effect of space velocity was also appreciable and the best space velocity at 550°C. was 1100.

The products were fractionally distilled and the results are shown in Table IV(B)₁.

Table IV(B)₁
RESULTS OF FRACTIONAL DISTILLATION BY
FODBIELNIAK APPARATUS

Ex. No.		17	18
Conditions	Temp. (°C)	520	540
	Space velocity	1100	1120
Composition of Gas Produced	H ₂ (%)	16.8	17.0
	CH ₄ (%)	1.6	2.3
	C ₂ H ₄ (%)	0.5	0.7
	C ₂ H ₆ (%)	1.0	0.4
	C ₃ H ₆ (%)	2.5	2.0
	C ₃ H ₈ (%)	7.5	6.2
	C ₄ H ₈ (%)	20.1	21.2
	C ₄ H ₁₀ (%)	50.0	50.2

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In order to investigate the activity of the catalyst during the reaction, the carbon deposited on the catalyst was determined at different times. After 4.8 hours, the charging gas could not pass through ~~the catalyst because of excessive carbon deposit.~~ The results are shown in Table V(B)1

Table V(B)1
THE YIELD OF CARBON DEPOSIT

Conditions	Temp. = 550°C.		space velocity = 1100	
Time (hr)	0.5	1.0	1.5	3.0
Yield of Carbon (%)	0.2	0.8	3.5	17.0
Total Olefines (%)	25.0	26.2	26.0	25.8
H ₂ (%)	20.2	19.4	16.2	17.8
C _n H _{2n+2} (%)	54.8	54.4	57.8	56.4

III - CONCLUSIONS

The effect of temperature and space velocity on the catalytic dehydrogenation of n-butane were found to be appreciable and the optimum conditions were determined.

The activity of Al₂O₃-Cr₂O₃ catalyst decreased after one hour of reaction. This reduction in activity may be attributed to excessive carbon deposits.

The reactivation of catalyst was not undertaken but it would be desirable to reactivate every half hour or hour.

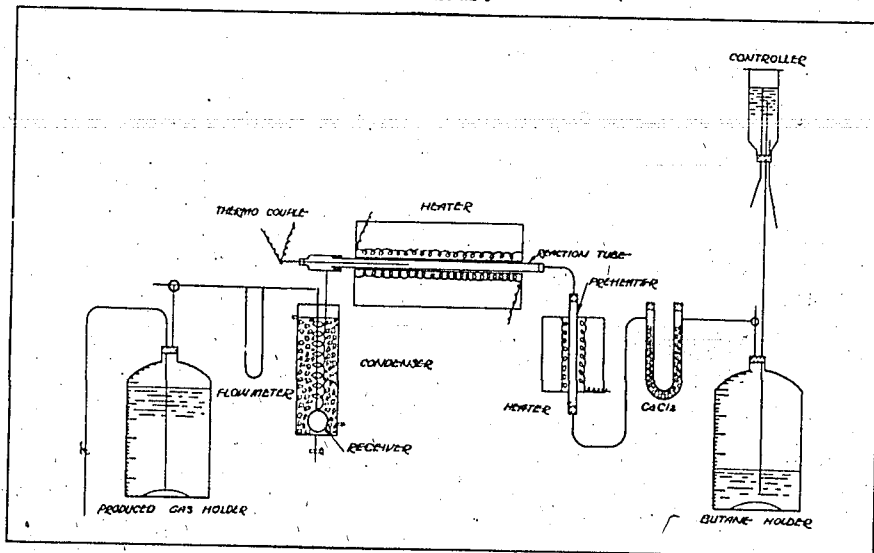


Figure 1(B)1 -
TEST APPARATUS FOR DEHYDROGENATION