ENCLOSURE (B) 10

# STUDIES ON THE SYNTHESIS OF ISOOCTANE FROM ACETYLENE

by

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## LIST OF TABLES
## AND ILLUSTRATIONS

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## SUMMARY

Isooctane was synthesized from acetylene through the course of acetylene acetaldehyde, aldol, crotonaldehyde, butanol, butene, isobutene, isooctene and isooctane. For each step the conditions for obtaining maximum yields were studied on a laboratory scale.

## I. INTRODUCTION

### A. History of Research

Usually isooctane has been synthesized from butenes in the cracked gas of petroleum. The poor production of petroleum and the small capacity of the cracking plants in our country obliged us to seek other sources and procedures for synthesizing isooctane in response to the demands of the air force. Since there was comparatively abundant electric power and coal, a course of isooctane synthesis as mentioned above was invented in 1937. The problem for chemists was to isomerize n-butene to isobutene, since the other reactions were known and some of them had been carried out commercially, though on a small scale. When the possibility of the above isomerization reaction was ascertained, it was decided that the plan be carried into execution by Chosen Nitrogen Fertilizer Co. at KONAN in Korea, on the scale of 30,000 Kl. per year of isooctane, and the research was stressed. At first this research was made at the Tokuyama Fuel Depot and then continued at the 1st Fuel Depot at YOKOHAMA (OFUNA). Though this research had been continued from 1937 to 1945 and many improvements were offered, only a part of these have been practiced commercially, since the plan for the erection of new factories did not materialize. This report is a summary of the studies of each reaction.

### B. Key Research Personnel Working on Project

Chem. Eng. Capt. Dr. FUJIO

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## II. DETAILED DESCRIPTION

### A. On the Synthesis of Acetaldehyde from Acetylene

Although acetaldehyde has been synthesized commercially from acetylene using a dilute sulphuric acid solution of mercuric sulphate as the catalyst, the exact conditons of the reaction used by each factory were not known.

#### 1. Procedure

The experiments were made on a laboratory scale. A known volume of acetylene was dissolved in a known volume. The catalyst solution in a thermostat and then the acetaldehyde formed was separated by steam distillation and was determined by the neutral sodium sulphite method.

#### 2. Results

The results are summarized in Tables 1 - 7(B) 10 and Figures 1 - 6(B) 10. From the data the following conclusions are derived.

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## Table I(B)10
## EFFECT OF REACTION TEMPERATURE

| | Experiment No. | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Temp. of Cat. Sol (°C) | 25 | 30 | 35 | 40 | 45 | 55 |
| Wt. of $CH_3COH$ produced (gm) | 1.489 | 1.533 | 1.576 | 1.555 | 1.620 | 1.248 |
| Yield of $CH_3COH$ to Theor. (%) | 76.8 | 79.1 | 81.6 | 80.9 | 83.6 | 65.7 |
| Time of Absorption of $C_2H_2$ (hr-min) | 6-8' | 4-52' | 2-28' | 2-48' | 3-25' | 6-22' |

Composition of Cat. Sol ................ 4 gm of $HgSO_4$ in 100cc of 25% $H_2SO_4$
Vol. of Cat. Sol. taken ................................................ 26cc
Vol. of $C_2H_2$ absorbed ................................................ 1 lit.

Above data are plotted in Figure 1(B)10

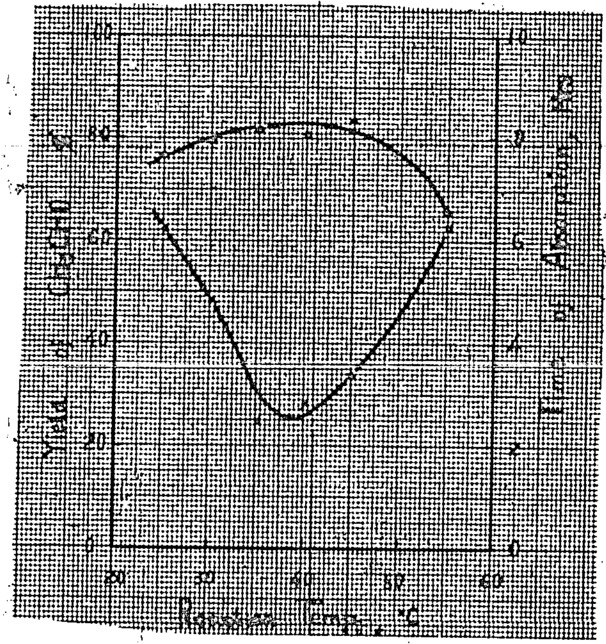


Figure 1(B)10
REACTION TEMPERATURE, °C

*ENCLOSURE (B)10*

Table II(B)10
EFFECT OF CONC. OF $H_2SO_4$

| | Experiment No. | | | | |
|---|---|---|---|---|---|
| | 7 | 8 | 9 | 10 | 11 |
| Conc. of $H_2SO_4$ (% by wt.) | 15.3 | 20.1 | 24.8 | 30.9 | 35.5 |
| Wt. of $CH_3COH$ produced (gm) | 1.445 | 1.467 | 1.555 | 1.533 | 1.401 |
| Yield of $CH_3COH$ to theoretical (%) | 75.2 | 76.4 | 80.9 | 79.8 | 72.9 |
| Time of absorbtion of $C_2H_2$ (hr-min.) | 5-30' | 3-58' | 2-48' | 3-9' | 4-15' |

Comp. of Cat. Sol ........................... 4 gm of $HgSO_4$ in 100cc of 25% $H_2SO_4$
Vol. of Cat. Sol. taken ........................................................ 26cc
Vol. of $C_2H_2$ absorbed ........................................................ 1 lit.
Temp. of Cat. Sol ........................................................ 40°C

Above data are plotted in Figure 2(B)10

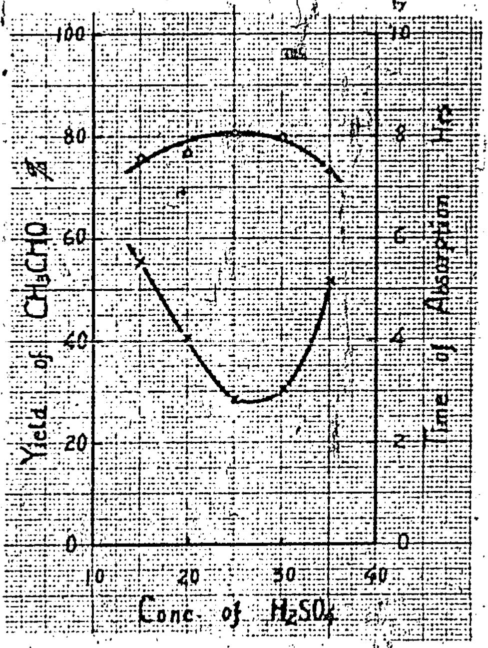


Figure 2(B)10
EFFECT OF CONCENTRATION OF $H_2SO_4$

ENCLOSURE (B)10

### Table III(B)10
### EFFECT OF CONCENTRATION OF $HgSO_4$ IN CAT. SOL.

| | Experiment No. | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| $HgSO_4$ in 100cc of cat. sol. (gm) | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Wt. of $CH_3COH$ produced (gm) | 1.445 | 1.511 | 1.576 | 1.555 | 1.489 | 1.489 | 1.467 |
| Yield of $CH_3COH$ to theoretical (%) | 74.8 | 78.2 | 81.6 | 80.2 | 77.0 | 76.9 | 75.9 |
| Time of Absorption of $C_2H_2$ (hr-min.) | 5-0' | 3-36' | 2-28' | 2-50' | 3-4' | 4-5' | 4-52' |

Conc. of $H_2SO_4$ .......... 25%
Vol. of cat. sol. taken .......... 26cc
Vol. of $C_2H_2$ absorbed .......... 1 lit.
React. temp .......... 40°C

Above data are plotted in Figure 3(B)10

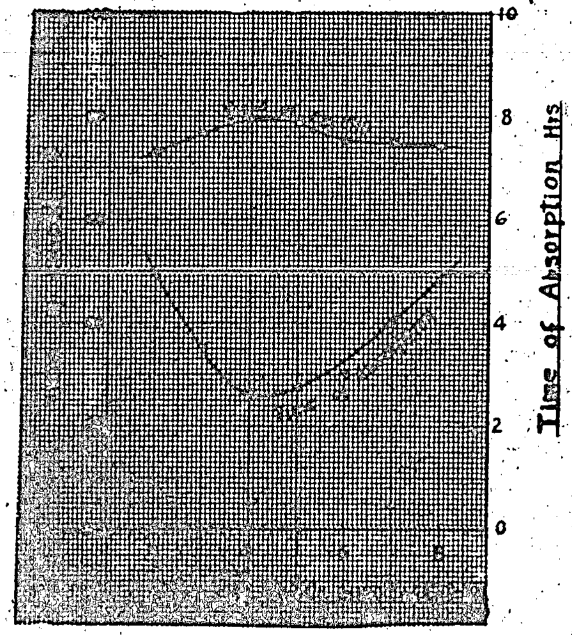


Figure 3(B)10

EFFECT OF CONCENTRATION OF $HgSO_4$ IN CATALYTIC SOLUTION

ENCLOSURE (B)10

### Table IV(B)10
### EFFECT OF VOLUME OF $C_2H_2$ ABSORBED

| | Experiment No. | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Vol. of $C_2H_2$ absorbed (lit.) | 0.5 | 0.75 | 1.0 | 1.25 | 1.40 |
| $CH_3COH$ produced (gm) | 0.788 | 1.149 | 1.555 | 1.883 | 2.080 |
| Yield of $CH_3COH$ to theor. (%) | 82.6 | 85.1 | 80.9 | 78.4 | 77.3 |
| Time of absorption (hr-min.) | 1-9' | 2-8' | 2-48' | 4-34' | 6-56' |

Comp. of cat. sol .............................. 4 gm of $HgSO_4$ in 100cc of 25% $H_2SO_4$
Vol. of cat. sol. taken .............................. 26cc
React. temp .............................. 40°C

Above data are plotted in Figure 4(B)10

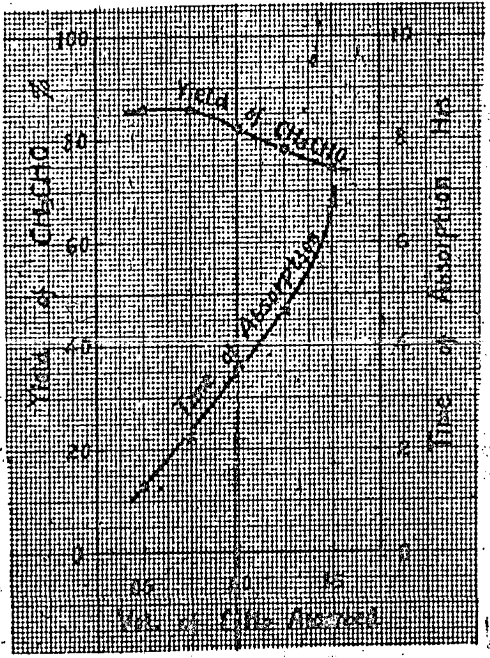


Figure 4(B)10
EFFECT OF VOLUME OF $C_2H_2$ ABSORBED

ENCLOSURE (B)10

Table V(B)10

EFFECT OF ADDITION OF $CH_3COOH$

| | Experiment No. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Wt. of $CH_3COOH$ in 100cc of cat. sol. (gm) | 0.2 | 0.6 | 1.0 | 1.4 |
| Wt. of $CH_3COH$ produced (gm) | 1.712 | 1.712 | 1.784 | 1.617 |
| Yield of $CH_3COH$ to theoretical (%) | 88.1 | 88.1 | 91.7 | 81.4 |
| Time of absorption of $C_2H_2$ (hr-min.) | 1-50' | 1-42' | 1-48' | 2-0' |

Comp. of cat. sol ........................ 4 gm of $HgSO_4$ in 100cc of 25% $H_2SO_4$
Vol. of cat. sol. taken ........................................................ 26cc
React. temp ........................................................................ 40°C
Vol. of $C_2H_2$ absorbed ..................................................... 1 lit.

Above data are plotted in Figure 5(B)10

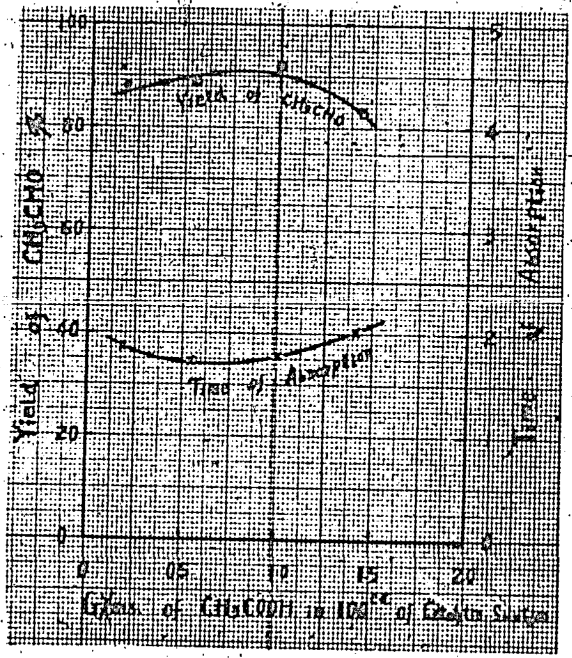


Figure 5(B)10

EFFECT OF ADDITION OF $CH_3COOH$

ENCLOSURE (B)10

Table VI(B)10
EFFECT OF ADDITION OF $Fe_2(SO_4)_3$

| | Experiment No. | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Wt. of $Fe_2(SO_4)_3$ in 100cc of cat. sol. (gm) | 0.65 | 1.33 | 2.00 | 2.66 | 3.25 |
| Wt. of $CH_3COH$ produced (gm) | 1.570 | 1.594 | 1.594 | 1.617 | 1.570 |
| Yield of $CH_3COH$ to theoretical (%) | 81.1 | 82.3 | 82.3 | 83.5 | 81.1 |
| Time of absorption of $C_2H_2$ (hr-min.) | 2-51' | 3-56' | 4-0' | 4-53' | 4-25' |

Comp. of cat. sol ........................ 4 gm of $HgSO_4$ in 100cc of 25% $H_2SO_4$
Vol. of cat. sol. taken ................................................ 26cc
React. temp ................................................................ 40°C
Vol. of $C_2H_2$ absorbed ............................................. 1 lit.

Above data are plotted in Figure 6(B)10

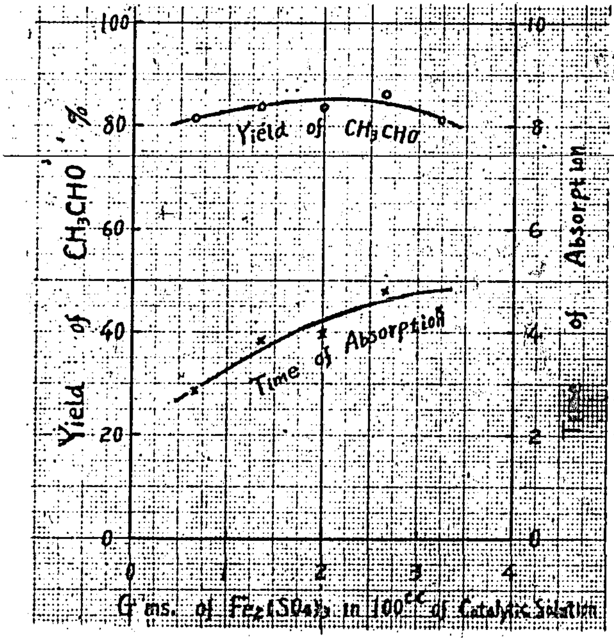
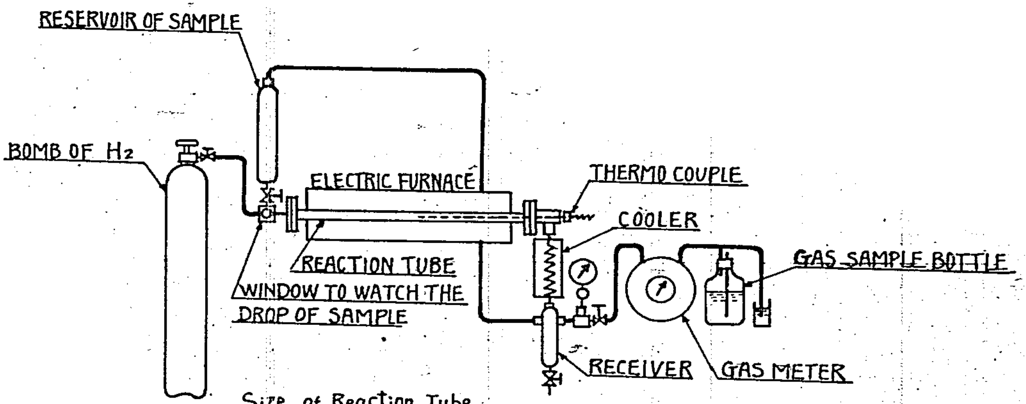


Figure 6(B)10
EFFECT OF ADDITION OF $Fe_2(SO_4)_3$

ENCLOSURE (B)10



Size of Reaction Tube

| | |
|---|---|
| Inn. Dia. | 25 mm. φ |
| Length | 1000 m.m |
| Vol. of Cat. | 50 c.c. |

Figure 7(B)10

HIGH PRESSURE HYDROGENATION APPARATUS
FOR CROTONALDEHYDE TO BUTANOL

Table VII(B)10
EFFECT OF ADDITION $Fe_2(SO_4)_3$ TOGETHER WITH $CH_3COOH$

| | Experiment No. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Vol. of $C_2H_2$ absorbed (lit.) | 0.5 | 0.75 | 1.0 | 1.3 |
| Wt. of $CH_3COH$ produced (gm) | 0.591 | 1.403 | 1.855 | 1.903 |
| Yield of $CH_3COH$ to theoretical (%) | 97.9 | 96.0 | 95.2 | 76.1 |
| $Fe_2(SO_4)_3$ reduced (%) | 27.7 | 33.3 | 38.8 | 44.4 |
| Time of absorp. of $C_2H_2$ (hr-min.) | 0-50' | 1-0' | 1-42' | 4-48' |

Comp. of cat. sol ....................... 1 gm of $CH_3COOH$ and 2 gm of $Fe_2(SO_4)_3$ in 100cc of 25% $H_2SO_4$
Vol. of cat. sol. taken ................................................ 26cc
React. temp ............................................................ 40°C

3. Conclusions

a. The best concentration of sulphuric acid is 25%.

b. The best concentration of mercuric sulphate is 4 - 5 gm per 100cc of diluted sulphuric acid.

c. As an additive reagent, acetic acid (1 gm per 100cc of catalyst) increases the velocity of absorption of acetylene by the catalyst and increases the yield of acetaldehyde.

d. Ferric sulphate (2 gm per 100cc of catalyst) inhibits the reduction of mercuric sulphate to metallic mercury. This concentration was selected on the basis of known commercial practice.

e. The optimum reaction temperature is 40°C.

f. To obtain a high yield of acetaldehyde, it is necessary to separate the produced acetaldehyde from the catalyst solution as soon as possible.

g. In the continuous operation it is desirable that the separation of acetaldehyde be done after absorbing 30 - 40 times of acetylene by volume of the catalyst solution.

h. The maximum yield is 98% of the theoretical when the reaction has been conducted as mentioned above.

B. On the Synthesis of Crotonaldehyde from Acetaldehyde

Acetaldehyde condenses to aldol in the presence of alkaline solutions, and aldol is dehydrated by distillation to crotonaldehyde.

## ENCLOSURE (B)10

### 1. The Experimental Procedure was as Follows

The reaction flask was equipped with a motor-driven effective agita~~tor, a thermometer for measuring the temperature of the content of~~ the flask, a burette for introducing the alkali solution into the flask, and a reflux condenser cooled with ice water to avoid the loss of acetaldehyde. It was placed in a low temperature bath, and freshly distilled pure acetaldehyde was condensed by adding caustic soda solution under strong agitation. After the reaction ceased, the agitator, the burette and the condenser were substituted by two plugs and an efficient distilling column, the top of which was cooled by ice. The contents of the flask were distilled after the caustic soda was neutralized with dilute sulphuric acid. At first unreacted acetaldehyde was distilled out into an ice cooled receiver, and after all the acetaldehyde had been distilled the temperature of the content of the flask rose to 150°C and a mixture of crotonaldehyde and water, formed by the dehydration of aldol, was distilled. The distillate, which was gathered in another receiver, separates into two layers on standing. The upper layer is crotonaldehyde saturated with water and the lower layer is water saturated with crotonaldehyde. The yield of crotonaldehyde was calculated from the solubility curves and the weights of the layers. The rate of the condensation was calculated from the weight of acetaldehyde used and recovered.

### 2. Experimental Results

The experimental results are shown in Tables VIII(B)10 and IX(B)10.

### 3. Conclusions

From these experiments the following conclusions were made:

a. The quantity of caustic soda required for the beginning of the condensation reaction varies on each sample. It appears that the reaction begins after the neutralization of acetic acid formed by contact of the acetaldehyde with air. A freshly distilled sample requires less caustic soda to start the reaction than an old one. For 1 kg of a freshly distilled sample 20cc of 10% caustic soda is sufficient to accomplish the reaction.

b. Since the condensation reaction occurs suddenly, the addition of the alkali solution after the neutralization of the free acid must be done carefully, otherwise the contents of the flask boil and a yellow colored aldehyde resin is formed.

c. The concentration of caustic soda has no serious effect on the initiation and the rate of the reaction. From the standpoint of safety the use of a less concentrated solution is better. In practical operation it is suitable to use caustic soda of less than 5% concentration.

d. The velocity of the addition of caustic soda will be determined in accordance with the cooling capacity.

e. Whenever about 75% of the acetaldehyde used has reacted, the progress of the reaction becomes slow and then stops. It appears that this point represents an equilibrium state.

*ENCLOSURE (B)10*

## Table VIII(B)10
## EFFECT OF VOLUME OF CAUSTIC SODA ADDED

| | Experiment No. | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Vol. of NaOH sol. added (cc) | 6 | 8 | 10 | 12 | 16 | 20 | 25 |
| Time required for addition (min.) | 6 | 8 | 35 | 37 | 47 | 45 | 50 |
| $CH_3COH$ reacted (%) | 8.0 | 38.0 | 68.5 | 72.0 | 74.4 | 76.0 | 75.6 |
| Wt. of Crotonaldehyde obtained (gm) | 9.5 | 118.4 | 230.6 | 242.9 | 253.9 | 268.3 | 256.6 |
| Yield of crotonaldehyde to theoretical (%) | 29.5 | 78.3 | 82.1 | 84.8 | 85.5 | 86.8 | 85.3 |
| Residue and loss. (%) | 19.0 | 7.9 | 6.6 | 7.3 | 8.3 | 10.8 | 5.2 |

Wt. of acetaldehyde used (gm) .................................................. 500
Conc. of NaOH sol ................................................................ 10% by Wt.
Reaction temp ...................................................................... 10 - 20°C

## Table IX(B)10
## EFFECT OF CONCENTRATION OF CAUSTIC SODA SOLUTION ADDED

| | Experiment No. | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Conc. of NaOH sol. (%) | 5 | 10 | 15 | 5 | 10 | 15 |
| Vol of NaOH sol. added (cc) | 40 | 20 | 13.3 | 50 | 25 | 16.6 |
| Time required for addition (min.) | 75 | 45 | 35 | 85 | 50 | 40 |
| $CH_3COH$ reacted (%) | 70.4 | 76.0 | 69.0 | 77.3 | 75.6 | 63.0 |
| Wt. of crotonaldehyde obtained (gm) | 238.0 | 262.3 | 237.4 | 271.2 | 256.6 | 216.5 |
| Yield of crotonaldehyde to theoretical (%) | 85.0 | 88.0 | 87.2 | 88.3 | 85.3 | 86.4 |
| Residue and loss (%) | 9.1 | 10.8 | 9.0 | 7.0 | 8.2 | 11.1 |

Wt. of acetaldehyde used (gm) .................................................. 500
Reaction temp (°C) ................................................................ 10 - 20

f. Though the reaction occurs from 0°C to 20°C, the temperature of the reaction must be below 10°C to avoid the resinification and boiling of acetaldehyde.

g. In these experiments 85 - 88% of the acetaldehyde used was converted to crotonaldehyde, and most of the remainder formed residual resins.

h. To diminish the resinification loss the distillation of crotonaldehyde must be done as quickly as possible.

i. Crotonaldehyde forms an azeotropic mixture with water boiling at 85°C which consists of 24.6% of water and 75.4% of crotonaldehyde by weight. In distilling a mixture of crotonaldehyde and water, the azeotronic mixture is distilled but on standing the distillate separates into two layers. The ratio of the upper and lower layers at 20°C is 3.9 to 1 by weight and 4.4 to 1 by volume. The specific gravity of the layers are 0.870 and 0.986 at 20°C, respectively.

## C. On the Hydrogenation of Crotonaldehyde to Butanol

### 1. Hydrogenation at Ordinary Pressures

In the hydrogenation of crotonaldehyde, butanol is produced through butylaldehyde as an intermediate. In the preliminary test of the catalyst it was known that, though nickel catalyst has a strong activity, it shows a tendency to crack aldehydes. On the contrary, copper catalyst has little cracking action but requires a high temperature to accomplish the hydrogenation of aldehydes. Consequently, the mixed catalysts of nickel and copper were studied.

Freshly distilled anhydrous crotonaldehyde was hydrogenated at atmospheric pressure by Sabatier's method. Through a glass tube packed with tablets of the catalyst and heated in an electric furnace a known volume of hydrogen and crotonaldehyde vapour were passed in a steady flow. The products were passed through a cooler and collected in a receiver. The temperature was measured at the centre of the catalyst layer.

The analysis of the products was made by precise distillation and separating the fraction in three parts: below 105°C, 105 - 120°C and the residue.

The fraction below 105°C is a mixture of the azeotropic mixture of butyl aldehyde, crotonaldehyde, and butanol, with water which was formed from the catalyst and the dehydrating action of the catalyst on butanol. The fraction of 105° - 120°C is practically pure butanol, the purity of which was confirmed by physical constants. The experimental data are summarized in Table X(B)10.

### 2. Hydrogenation under Pressure

To accelerate the reaction, tests were made under pressure. The apparatus used is shown in Figure 7(B)10, and the other conditions were same as in the case at ordinary pressures.

The bromine method for crotonaldehyde and the hydroxylamine method for total aldehydes were used. The experimental data are summarized in Table XI(B)10. From the above experiments the following conclusions are derived.

a. For hydrogenation at ordinary pressures:

(1) The optimum temperature for the mixed catalyst of ~~nickel and copper on diatomaceous earth is 100 - 180°C,~~ and the product contains 80 - 85% of butenol and 10 - 15% of butylaldehyde.

(2) When six times the theoretical amount of hydrogen to crotonaldehyde are used, butanol and butylaldehyde in the product are 91% and 0 - 5%, respectively.

(3) The rate of hydrogenation increases with the decrease of the velocity of crotonaldehyde at constant hydrogen ratio. When crotonaldehyde of 0.4 of the catalyst volume per hour is passed through the catalyst, butanol and butyl aldehyde in the product are 93% and 4.5% respectively.

b. For hydrogenation at 10 atmospheric pressure:

(1) As the catalyst carrier, magnesia is better than Japanese acid clay.

(2) As the raw materials of the catalyst, nitrates and sulphates of copper and nickel give nearly the same results.

(3) The catalyst consisting of 3 parts of copper, 1 part of nickel, and 8 parts of magnesia and reduced at 300°C gives a product which consists of 92% of butanol and 5 - 6% of butylaldehyde.

(4) With increases in space velocity the content of butanol in the products decreases, and causes the cracking of aldehyde by the local heating of the catalyst.

(5) In comparing the mixed catalyst of U. O. P. type with copper and nickel catalyst, the former has a strong tendency to crack aldehyde, and 10 - 13% of butylaldehyde remains in the product.

(6) Crotonaldehyde saturated with water is more difficult to hydrogenate than an anhydrous sample and the separation of the product is more troublesome due to the formation of an azeotropic mixture.

(7) However, the effect of pressure on the yield and composition of reaction product is small as judged from these experiments.

(8) Because of the difficulty of perfect hydrogenation of crotonaldehyde, it is necessary to fractionate butanol from the product.

3. On the Relation between the Type of Reaction Tube and the Durability of the Catalyst

Even in laboratory scale experiments, crotonaldehyde has a tendency to crack at high space velocity due to local heating of the catalyst. To obtain high yields of butanol and long life of the catalyst in commercial plants, it is essential that the design must avoid such local heating of the catalyst layer.

ENCLOSURE (B)10

## Table X(B)10
## EXPERIMENTAL DATA OF HYDROGENATION OF CROTONALDEHYDE AT ATMOSPHERIC PRESSURE

| Catalyst | React. Temp. °C | Time of Exp. hr. | Wt. of Crotonaldehyde Used(gm) | Vel. of Crotonaldehyde gms. per gm of Cat. | Vel. of $H_2$ in l. per $H_2$ | Consumption of $H_2$ in l. | Ratio of $H_2$ used to Theoretical | Wt. of product in gms. | % of Fract. below 105°C | % of Fract. of 105 - 120°C | % of Loss and Residue | $d^{20}_{4}$ of Fract. of 105 - 120°C | $n^{20}_{D}$ of Fract. of 105 - 120°C | % of CO in Waste $H_2$ | % of $CH_4$ in Waste $H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu 3, Ni 1, Diatm. Earth 4 Reduced at 180°C | 160 | 5 | 59 | 0.78 | 29 | 31.2 | 4 | 54.0 | 17.4 | 78.0 | 4.6 | 0.828 | 1.3940 | | |
| | 180 | 6 | 73 | 0.81 | 29 | 40.7 | 4 | 65.0 | 13.4 | 85.0 | 1.6 | 0.823 | 1.3940 | | |
| | 210 | 6 | 66 | 0.73 | 29 | 44.5 | 4 | 64.0 | 13.4 | 86.5 | 0.1 | 0.822 | 1.3918 | 1.1 | 2.5 |
| | 230 | 4 | 44 | 0.73 | 29 | 23.7 | 4 | 42.3 | 17.0 | 81.0 | 2.0 | 0.824 | 1.3200 | 3.0 | 4.2 |
| | 250 | 4 | 44 | 0.73 | 29 | 24.6 | 4 | 42.0 | 16.4 | 74.5 | 9.1 | | | 10.3 | 9.7 |
| Cu 2, Ni 2, Diatm. Earth 4 Reduced at 180°C | 130 | 4 | 46 | 0.77 | 29 | 25.0 | 4 | 42.0 | 14.4 | 82.0 | 3.6 | 0.815 | 1.3973 | | |
| | 160 | 4 | 50 | 0.83 | 29 | 27.9 | 4 | 46.0 | 11.3 | 85.0 | 3.7 | 0.843 | 1.3970 | | |
| | 180 | 3 | 36.5 | 0.81 | 29 | 20.8 | 4 | 35.0 | 12.6 | 83.5 | 3.9 | 0.823 | 1.3928 | 0.7 | |
| | 200 | 4 | 47.0 | 0.79 | 29 | 24.8 | 4 | 44.0 | 16.2 | 82.0 | 1.8 | 0.829 | 1.3930 | 2.4 | 3.6 |
| Ni 1, Diatm. Earth 4 Reduced at 300°C | 100 | 4 | 44.0 | 0.73 | 28 | 25.2 | 4 | 43.0 | 26.1 | 72.0 | 1.9 | | | | |
| | 130 | 4 | 46.0 | 0.77 | 28 | 25.5 | 4 | 44.0 | 15.2 | 82.5 | 2.3 | | | | |
| | 160 | 4 | 44.0 | 0.73 | 28 | 24.9 | 4 | 43.0 | 13.6 | 86.0 | 0.4 | | | | |
| | 180 | 4 | 44.0 | 0.73 | 28 | 24.0 | 4 | 43.0 | 13.7 | 84.5 | 1.8 | | | 3.5 | 6.1 |
| | 200 | 4 | 43.0 | 0.72 | 28 | | | 10.0 | 9.0 | | | | | 15.7 | 19.1 |
| Cu 1, Ni 3, Diatm. Earth 4 Reduced at 180°C | 100 | | | | 29 | | | | 27.4 | 71.0 | | | | | |
| | 130 | | | | 29 | | | | 22.8 | 75.5 | | | | | |
| | 160 | | | | 29 | | | | 16.7 | 82.0 | | | | | |
| | 180 | | | | 29 | | | | 15.1 | 81.5 | | | | 3.6 | 5.8 |
| | 200 | | | | 29 | | | | | | | | | 12.1 | 10.2 |
| Cu 3, Ni 1, Diatm. Earth 4 Reduced at 300°C | 180 | 5 | 85.0 | 1.13 | 32.0 | 39.5 | 3 | 80.0 | 38.7 | 60.0 | 1.3 | | | | |
| | 180 | 6 | 73.0 | 0.81 | 30.0 | 40.7 | 4 | 65.0 | 13.4 | 85.0 | 1.6 | 0.8232 | 1.3940 | - | |
| | 180 | 4 | 47.0 | 0.78 | 35.0 | 26.3 | 5 | 44.0 | 4.9 | 91.5 | 3.6 | | | | |
| | 180 | 4 | 48.0 | 0.80 | 42.0 | 29.1 | 6 | 44.0 | | 91.0 | 9.0 | | | | |
| Cu 1, Ni 1, Diatm. Earth 2 Reduced at 180°C | 180 | 3 | 36.5 | 0.81 | 28 | 20.8 | 4.0 | 35.0 | 12.6 | 83.5 | 3.9 | 0.8227 | 1.3928 | | |
| | 180 | 4 | 32.0 | 0.53 | 28 | 18.3 | 5.5 | 32.0 | 5.4 | 90.9 | 3.7 | 0.8244 | 1.3905 | | |
| | 180 | 7 | 42.0 | 0.40 | 28 | 25.8 | 7.0 | 42.0 | 4.5 | 93.0 | 2.5 | 0.8244 | 1.3920 | | |

## Table XI(B)10
## EXPERIMENTAL DATA OF HYDROGENATION OF CROTONALDEHYDE UNDER PRESSURE

| Composition of Catalyst | Temp. of Reduct. of Catalyst °C | React. Temp. °C | Vel. of Liq. Croton. per Vol. of Cat. per hr. | Time of Exp. hrs. | Wt. of Croton-aldehyde gms. | Vel. of Hydrogen L. per hr. | Vol. of Hydrogen L. | Wt. of Product gms. | % of Fract. in Product below 105°C | % of Fract. 115 - 120°C in Product | % of Loss and Residue | Vol. of Waste Hydrogen L. | % of CO in Waste Hydrogen | % of $CH_4$ in Waste Hydrogen | % of Crotonaldehyde in Product | Note |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu 3<br>Ni 1 | 140 | 140 | 0.40 | 7 | 120.3 | 19.4 | 135.8 | 121.2 | 19.8 | 77.3 | 2.9 | 61.5 | 0.7 | 3.2 | 0 | Wt. of Cat. Used was 20 gms. Press. of Hydrogen was 10 atms. gauge. Anhydrous Crotonaldehyde was Used. |
| Cu 3<br>Ni 1<br>MgO 8 | 180 | 180 | 0.47 | 7 | 112.0 | 24.7 | 172.8 | 60.0 | 17.5 | 70.0 | 12.5 | 124.0 | 4.2 | 7.1 | 0 | |
| | 160 | 160 | 0.47 | 7 | 112.5 | 28.6 | 200.0 | 70.5 | 17.0 | 66.0 | 17.0 | 128.0 | | | 0 | |
| | 140 | 140 | 0.46 | 7 | 109.0 | 19.0 | 133.4 | 91.9 | 17.1 | 79.6 | 3.3 | 69.2 | 8.5 | 4.0 | 0 | |
| | 140 | 120 | 0.64 | 5.7 | 123.5 | 18.6 | 104.4 | 113.5 | 68.0 | 21.0 | 9.0 | 50.7 | 1.2 | 4.2 | 36.6 | |
| Cu 3<br>Ni 1<br>Clay 16 | 140 | 130 | 0.46 | 7 | 111.0 | 18.5 | 129.7 | 90.0 | 26.0 | 59.0 | 12.0 | 65.8 | 3.6 | 6.5 | 1.0 | |
| Cu 3<br>Ni 1<br>MgO 8 | 180 | 160 | 0.32 | 6 | 93.0 | 23.6 | 141.3 | 83.0 | 6.0 | 91.5 | 2.5 | 89.5 | 3.1 | 4.5 | 0 | |
| | 180 | 140 | 0.36 | 7 | 122.0 | 24.6 | 172.2 | 114.0 | 5.0 | 92.0 | 3.0 | 100.5 | 2.2 | 2.5 | 0 | |
| | 180 | 140 | 0.49 | 7 | 123.5 | 24.0 | 168.2 | 116.5 | 7.2 | 89.7 | 8.1 | 93.3 | 1.6 | 2.0 | 5.7 | |
| Ni 65<br>Diatm.<br>Earth 30<br>Graphite<br>5 a.o.p.<br>type | 180 | 100 | 0.22 | 6 | 85.0 | 26.3 | 157.5 | 81.0 | 12.4 | 79.0 | 8.6 | 116.0 | 1.2 | 4.9 | 0.04 | |
| | 180 | 110 | 0.32 | 6 | 93.0 | 28.8 | 172.8 | 91.5 | 9.2 | 83.0 | 7.8 | 120.0 | 0.8 | 2.0 | 0.03 | |
| | 180 | 160 | 0.31 | 6 | 89.5 | 18.0 | 108.0 | 17.0 | 90.0 | 0.0 | 10.0 | 106.0 | 1.1 | 53.1 | 0 | |
| | 180 | 120 | 0.34 | 6 | 98.5 | 28.0 | 168.0 | 80.0 | 13.1 | 83.0 | 3.9 | 111.0 | 0.1 | 3.9 | 0 | |
| | 180 | 130 | 0.43 | 5 | 104.0 | 33.3 | 166.7 | 91.0 | 10.5 | 84.0 | 5.5 | 111.5 | 1.7 | 6.2 | 0 | |
| | | | | | | | | | * | ** | # | | | | ## | Croton. Sat. with Water was Used. The others, Same as Above |
| Cu 3<br>Ni 1<br>MgO 8 | 180 | 160 | 0.38 | 6 | 106.5 | 31.4 | 188.0 | 105.5 | 83.6 | 5.4 | 8.2 | 127.0 | 1.6 | 1.0 | No | |
| | 180 | 160 | 0.55 | 4 | 106.0 | 42.5 | 169.5 | 94.5 | 83.1 | 4.8 | 10.4 | 119.5 | 5.7 | 6.9 | Slightly | |
| | 180 | 160 | 0.80 | 3 | 115.5 | 57.0 | 170.5 | 94.5 | 76.8 | 10.9 | 11.6 | 119.0 | 7.4 | 10.0 | Slightly | |
| | 180 | 140 | 0.40 | 6 | 115.5 | 33.2 | 197.0 | 127.0 | 96.8 | 10.5 | 11.1 | 127.0 | 0.5 | 0.5 | Slightly | |
| | 180 | 140 | 0.63 | 4 | 120.0 | 47.0 | 189.0 | 125.0 | 64.1 | 20.0 | 11.6 | 120.0 | 1.5 | 2.1 | Faint | |
| | 180 | 140 | 0.77 | 3 | 111.0 | 62.0 | 186.5 | 123.0 | 50.8 | 28.1 | 7.3 | 120.5 | 1.1 | 1.2 | Slightly | |

When hydrous crotonaldehyde was used the analysis was made chemically; the analysis by fractionation was meanless for the formation of azeotropic mixture.

*% of Butanol in Product
**% of Aldehydes in Product

#% of Water in Product
##Odor of Croton. in Product

Two types of catalyst tubes were tested with regard to the distribution of temperature of the catalyst layer and the durability of the catalyst. The crotonaldehyde used was the upper layer of the azeo~~tropic mixture, the purity of which is 90% by weight.~~

a. Apparatus and procedure.

A mixed catalyst of nickel, copper, and diatomaceous earth in the ratio of 1:3:8, respectively, was used after reduction at 200°C in the reaction tube. The apparatus used is shown in Figure 8(B)10. Crotonaldehyde in a measuring cylinder (3) was introduced with a small bellows pump (4) into an evaporator (2) which was heated by steam. Hydrogen which was sent through a gas meter (1) was mixed with the vapor of crotonaldehyde at (2). The mixture of hydrogen and the vapor of crotonaldehyde was preheated by a preheater (5) and passed through the catalyst table (6), the temperature of which was controlled by boiling water at a pressure corresponding to the reaction temperature. The reaction product was cooled with a water cooler (7) and was gathered in a receiver (8). Waste hydrogen escapes through a gas meter (9). The heat of the reaction was conducted from the catalyst layer to water and steam evaporated at (11) was condensed at (5) and (2), returned to a boiler (10) provided with an electric heater (12). The temperature of the catalyst layer was measured with two thermocouples which were moved along the catalyst layer. Two catalyst tubes were used one of which (No.1) is 25mm in diameter and 1400mm in length and has a capacity of 0.7 liters; the other (No.2) is a multitublar reaction vessel with nineteen tubes of 15mm in diameter and 200mm in length having a total capacity of 0.8 litre. The reaction product was separated into three fractions by precise distillation.

b. Experimental results.

The condition of the experiments using No. 1 reaction tube were as follows:

(1) The quantity of hydrogen used was eight moles per mole of crotonaldehyde.

(2) The temperature of boiling water was 150 - 160°C.

(3) The velocity of crotonaldehyde was 0.25 litre (liquid) per one litre of the catalyst per hour.

After elapsed times of 2, 12, 100, 150, and 200 hours the temperature distribution of the catalyst layer was measured and the results of distillation of the product are shown in Table XII(B)10.

With the time lapse, the point of maximum temperature moved from the top to the bottom of the reaction tube, and the content of butanol in the product decreased. The analytical data of the waste gas after six hours shows the cracking of aldehyde.

$CO_2$ ...... 0.0

$CO$ ... 9.0

$C_2H_{2n-2}$ ... 10.7

$O_2$ ...... 0.4

$H_2$ ... 78.4

$N_2$ ........ 1.1

$C_nH_{2n}$ ... 0.8

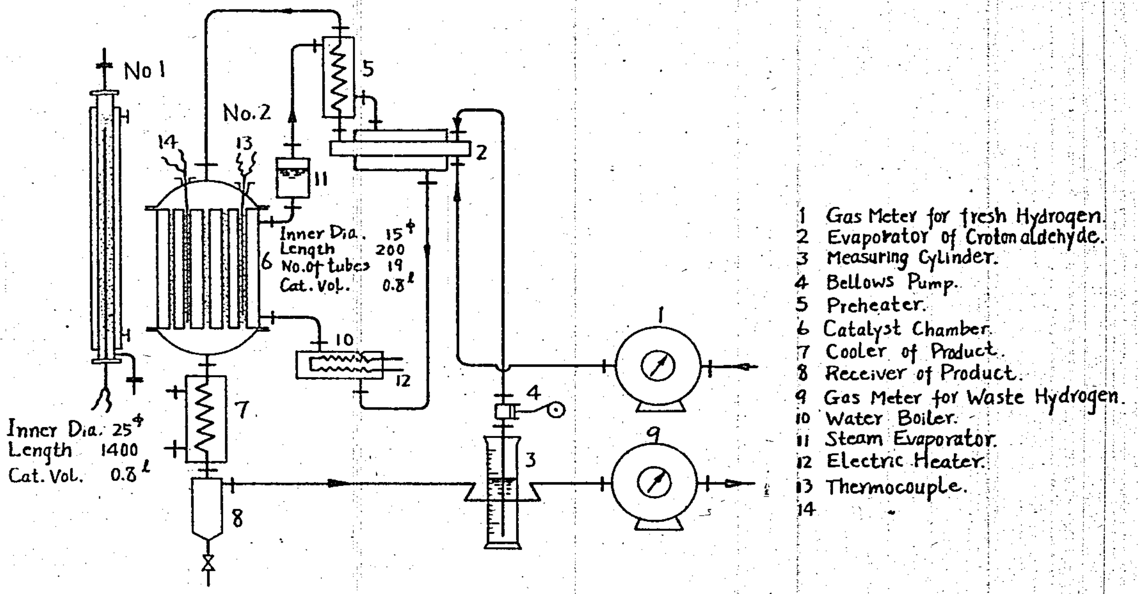


Figure 8(B)10

DIAGRAM OF HYDROGENATION APPARATUS OF CROTONALDEHYDE UNDER ORDINARY PRESSURE

ENCLOSURE (B)10

### Table XII(B)10
### TEMPERATURE DISTRIBUTION ALONG THE REACTION TUBE AND DISTILLATION DATA OF HYDROGENATED PRODUCT

| | | Time from Starting (hrs) | | | | |
|---|---|---|---|---|---|---|
| | | 2 | 12 | 100 | 150 | 200 |
| Distance from inlet of reaction tube (cm) | 20 | 230 | 180 | 164 | 150 | 141 |
| | 40 | 225 | 160 | 169 | 155 | 142 |
| | 60 | 200 | 150 | 166 | 166 | 144 |
| | 80 | 190 | 145 | 160 | 172 | 150 |
| | 100 | 172 | 140 | 151 | 172 | 154 |
| | 140 | 172 | 139 | 150 | 160 | 154 |
| Temp. of hot water (°C) | | 160 | 150 | 164 | 163 | 164 |
| Butyl aldehyde in liq. fract. (%) | | 0.3 | 8.5 | 35.8 | 38.6 | 47.0 |
| Crotonaldehyde fract. (%) | | 1.6 | 5.1 | 2.2 | 0.1 | 1.9 |
| Butanol fract. (%) | | 97.0 | 85.1 | 60.8 | 60.4 | 50.7 |
| Wt. % of product to charge | | 52.0 | 60.5 | 68.3 | 79.5 | 80.9 |

### Table XIII(B)10
### DATA OF CONTINUOUS HYDROGENATION OF CROTONALDEHYDE

| Time Elapsed (hr) | Vol. of Liq. Crotonaldehyde in Lit./hr | Vol. of Hydrogen in Lit./hr | Purity of Hydrogen (%) | Vol. of Hydrogenated Product in Lit./hr | % of Butylaldehyde Fract. in Product | % of Crotonaldehyde Fract. in Product | Vol. of Waste Hydrogen in Lit./hr | Purity of Waste Hydrogen (%) | Temp. of Upper Part of Reac. Tube | Temp. of Lower Part of Reac. Tube |
|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 1.148/4 | 2696/4 | 78.0 | 0.980/4 | 0.0 | 0.0 | 2242/4 | 73.3 | 160 | 145 |
| 28 | 2.296/8 | 5392/8 | 85.4 | 2.133/8 | 0.9 | 0.4 | 4490/8 | 79.2 | 170 | 150 |
| 68 | 2.296/8 | 5392/8 | 86.0 | 2.280/8 | 0.0 | 0.9 | 4556/8 | 79.0 | 165 | 150 |
| 100 | 2.296/8 | 5392/8 | 84.6 | 2.215/8 | 0.0 | 0.6 | 4467/8 | 74.1 | 165 | 150 |
| 140 | 2.296/8 | 5392/8 | 80.7 | 2.220/8 | 0.3 | 0.4 | 4022/8 | 72.9 | 165 | 150 |
| 186 | 2.296/8 | 5554/8 | 80.7 | 2.100/8 | 0.0 | 1.2 | 4613/8 | | 170 | 160 |
| 234 | 2.296/6 | 5462/8 | 88.0 | 2.240/6 | 0.0 | 0.9 | 4652/8 | 87.0 | 175 | 155 |
| 314 | 2.296/8 | 5605/8 | 83.0 | 2.345/8 | 0.0 | 0.9 | 4387/8 | 80.3 | 170 | 160 |
| 335 | 2.296/8 | 4044/8 | 91.6 | 2.250/8 | 0.0 | 1.5 | 4487/8 | | 170 | 165 |
| 399 | 2.296/8 | 4044/8 | 98.6 | 2.370/8 | 0.0 | 0.6 | 2780/8 | 93.0 | 170 | 160 |
| 431 | 2.296/8 | 4147/8 | 95.3 | 2.500/8 | 0.3 | 1.2 | 2933/8 | 90.0 | 170 | 160 |
| 471 | 2.296/8 | 4065/8 | 90.6 | 2.320/8 | 0.3 | 0.9 | 3048/8 | 83.3 | 170 | 160 |
| 503 | 2.296/8 | 4257/8 | 90.6 | 2.446/8 | 1.8 | 2.1 | 3313/8 | 83.3 | 178 | 160 |

It is obvious that the low yields of butanol are due to the local heating of the catalyst layer. The tests of the No.2 ~~reaction vessel were made under the same conditions as the~~ No.1 reaction tube. The hydrogen used was diluted with nitrogen to the extent of 81 - 98.5% to test the effect of concentration. The experimental data is tabulated in Tables XIII(B)10 and XIV(B)10.

c. Conclusions.

From these data, it is obvious that the reaction progressed very smoothly. The content of butanol in the hydrogenated product was 95% or more. The activity of the catalyst did not decline during a period of three weeks. Crotonaldehyde saturated with water can be used as a raw material. In the commercial application the linear velocity of the raw material through the catalyst layer should be low to avoid local heating of the catalyst layer. Thus, the catalyst activity will be maintained for a long period. Hydrogen of 85% purity can be used as a raw material.

## D. On the Preparation of Butene from n-Butanol

In order to find the best Japanese acid clay for use as the dehydrating catalyst of n-butanol, the following experiments were made.

### 1. Apparatus and Procedure

Two reaction tubes of quartz were used. The diameters of these tubes were 2cm and 3cm for catalyst volumes of 100cc and 200cc respectively. Butanol was added from a dropping burette to the reaction tube which was packed with the catalyst and heated by an electric furnace. The volume of the gas produced was measured and its composition was analyzed at one hour intervals. The percentage yield of butene produced was calculated by the following formula.

$$\text{Yield (\%) of butene} = \frac{V \times a \times \dfrac{p-w}{760} \times \dfrac{273}{273+t}}{v \times d \times \dfrac{22.4}{74.0}} \times 100$$

V Measured gas volume in litre
a Butene concentration in gas produced, %
p Atm. pressure in mm Hg.
w Water vapour tension at room temperature in mm Hg.
t Room temperature
d Density of butanol at room temperature
v Volume of butanol used in cc

Total butene in the gas produced was determined by 90% $H_2SO_4$ and isobutene was determined by 61% and 69% $H_2SO_4$ using a special method, details of which are as follows: At first most of the isobutene in the sample was absorbed in 61% $H_2SO_4$ and then the remaining isobutene was absorbed by contacting with 69% $H_2SO_4$ several times for 10 seconds until the volume decrease became constant. The sum of the absorbed volumes in 69% $H_2SO_4$ and 61% $H_2SO_4$ indicates the volume of isobutene.

ENCLOSURE (B)10

## Table XIV(B)10
## DATA OF CONTINUOUS HYDROGENATION OF CROTONALDEHYDE

| | First Week | Second Week | Third Week |
|---|---|---|---|
| Vol. of Crotonaldehyde Charged (lit/lit) | 50.512 | 47.355 | 48.212 |
| Sp. Gr. of Crotonaldehyde Used | 0.870 | 0.875 | 0.873 |
| Purity of Crotonaldehyde (%) | 90.0 | 87.4 | 88.5 |
| Calc. Wt. of Crotonaldehyde as 100% Pure (gm) | 39.551 | 36.215 | 27.252 |
| Vol. of Condensed Product (lit) | 49.443 | 46.743 | 49.826 |
| Sp. Gr. of Condensed Product | 0.837 | 0.840 | 0.835 |
| Butanol in Condensed Product (%) | 98.7 | 98.1 | 97.0 |
| Sp. Gr. of Butanol Fraction in Condensed Product | 0.830 | 0.820 | 0.833 |
| Butanol Content in Butanol Fract. (%) | 90.35 | 89.2 | 88.0 |
| Calc. Wt. of Butanol in Condensed Product (kg) | 36.925 | 35.026 | 36.612 |
| Calc. Yield of Butanol to Theoretical (%) | 88.3 | 91.7 | 93.0 |
| Measured Wt. of Butanol Vaporized in Waste Hydrogen (kg) | 1.465 | 1.361 | 0.998 |
| Calc. Wt. of Total Butanol (kg) | 38.331 | 36.387 | 37.510 |
| Calc. Yield of Butanol Condensed and Vaporized to Theoretical (%) | 91.7 | 95.3 | 95.2 |

## Table XV(B)10
## THE SOURCE AND COMPOSITION OF CLAYS

| No. | Source (Prefecture) | Ignition Loss (%) | $SiO_2$ (%) | $Al_2O_3$ (%) | $Fe_2O_3$ (%) | MnO (%) | CaO (%) | MgO (%) | $SO_3$ (%) | $P_2O_5$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | YAMAGATA | 7.55 | 75.43 | 13.75 | 2.52 | 0.10 | tr. | 0.32 | 0.26 | |
| 4 | YAMAGATA | 10.54 | 72.38 | 13.12 | 2.32 | 0.47 | 1.03 | | 0.27 | |
| 5 | YAMAGATA | 11.67 | 71.42 | 12.46 | 2.22 | 0.55 | 1.62 | tr. | 0.44 | tr. |
| 7 | ISHIKAWA | 11.44 | 67.03 | 11.04 | 5.03 | tr. | 1.15 | | 4.23 | |
| 9 | IWATE | 11.01 | 70.39 | 12.96 | 2.00 | 0.78 | 2.50 | tr. | 0.40 | |
| 10 | FUKUSHIMA | 6.87 | 75.45 | 12.37 | 2.42 | 0.80 | 1.27 | | 0.73 | |
| 11 | OKAYAMA | 3.32 | 74.42 | 21.06 | 0.35 | 0.51 | | | 0.38 | |
| 12 | Unknown | 7.71 | 73.98 | 10.31 | 5.33 | 1.10 | 1.53 | | 0.29 | |
| 14 | NIIGATA | 10.22 | 69.16 | 14.81 | 2.03 | 0.92 | 2.37 | tr. | 0.46 | |
| 15 | IWATE | 9.48 | 67.33 | 16.13 | 3.41 | 0.85 | 2.07 | tr. | 0.57 | |
| 18 | SAGA | 9.54 | 72.79 | 11.66 | 3.66 | 0.88 | 0.74 | tr. | 0.56 | |
| 19 | NIIGATA | 8.58 | 71.54 | 13.66 | 4.03 | tr. | 0.95 | 0.58 | 0.55 | |
| 20 | NIIGATA | 5.73 | 71.35 | 14.86 | 3.33 | 0.47 | 1.86 | 0.99 | 0.86 | |
| 21 | CHIBA | 7.99 | 73.89 | 12.62 | 2.70 | 0.35 | 1.45 | tr. | 0.93 | |
| 22 | YAMAGATA | 7.52 | 63.74 | 14.38 | 0.45 | | 1.24 | 2.96 | 0.18 | 0.10 |
| 23 | YAMAGATA | 7.28 | 67.16 | 13.83 | 7.89 | | 1.42 | 2.37 | 0.27 | 0.09 |
| 24 | YAMAGATA | 6.09 | 69.66 | 18.42 | 3.14 | 0.77 | 3.33 | 2.75 | 0.48 | |
| 25 | YAMAGATA | 5.94 | 69.69 | 17.17 | 3.58 | 0.32 | 2.67 | 1.53 | 0.67 | |
| 27 | SAITAMA | 6.94 | 73.79 | 13.22 | 1.55 | | 4.72 | | 0.68 | |
| 28 | Unknown | 3.78 | 76.94 | 14.80 | 2.38 | | 1.29 | 0.66 | 0.21 | |
| 29 | TOCHIGI | 6.18 | 70.53 | 17.27 | 2.75 | | 3.12 | | 0.28 | 0.05 |
| 30 | GIFU | 11.02 | 52.83 | 36.57 | 1.89 | 1.56 | 0.90 | 0.37 | 4.54 | |
| 31 | CHIBA | 7.31 | 72.96 | 13.53 | 2.38 | | 2.18 | 1.78 | 1.14 | |
| 37 | NAGASAKI | 2.41 | 76.30 | 15.00 | 0.60 | | 1.26 | 0.99 | 1.35 | |
| 44 | SHIZUOKA | 9.59 | 78.89 | 5.56 | 1.91 | 1.29 | tr. | 2.19 | 1.01 | |
| 45 | TOCHIGI | 20.25 | 44.86 | 28.43 | 2.68 | 0 | 2.26 | 0.48 | 0.47 | 0 |
| 46 | SHIZUOKA | 21.76 | 61.54 | 6.77 | 4.97 | 0 | tr. | 1.96 | 0.74 | tr. |
| 47 | ISHIKAWA | 15.01 | 61.65 | 16.85 | 2.16 | tr. | 0.87 | 2.06 | 1.06 | 0 |

Note: Table XVI(B)10 is the duplicate of Table XV(B)10 except for its title which is PLACE OF PRODUCTION AND COMPOSITION OF ACID CLAYS.

The butanol used had the following constants:

B.P. 116 - 117°C, $d_4^0$ 0.8247, $d_4^{20}$ 0.8099

Acid clays were used both with and without acid treatment. They were dried at 110°C for three hours after being kneaded with water and shaped into cylinders 3mm in diameter and 5 - 10mm in length.

The acidity of the clays was measured by the following method. Centi-normal NaOH solution, previously coloured red by phenolphthalein, was added to a 0.5 gm sample of dried clay until the colour of the supernatant liquid began to reappear. The acidity was represented by the quantity of NaOH solution required.

The acid treatment was carried out in the following manner. A 150 gram sample of acid clay was dipped into 300cc of 4 normal hydrochloric acid, heated for 3 hours on a water bath under reflux, filtered, and washed until the filtrate was free of chloride ion.

## 2. Experimental Results

The source of the various acid clays used and their compositions are tabulated in Table XV(B)10. Table XVI(B)10 shows the results of the experiments using these clays. In this table, previous acid treatment of the clay is indicated. Generally, the dehydrating action of acid clays increases by acid treatment. In general the acidity of the clays increases considerably by acid treatment and the clays having the highest acidities show the strongest dehydrating action. Figure 9(B)10 shows the relation between the acidity and yield of butene at a reaction temperature of 300°C and space velocity of 1 by liquid volume of butanol per volume of catalyst per hour. The content of isobutene in the product is below 2% at space velocity of 1, but is 4 - 5% at 0.2 space velocity.

## 3. Conclusions

There appears to be no relation between the yield of isobutene and the acidity of the clays. There also appears to be no definite relation between the dehydrating action and the composition of clay. The acidity of the clays is a surface phenomenon. The soluble impurities, e.g., alkalies, alkali earths, etc., which are absorbed on the surface of acid clay, are removed by the acid treatment. The dehydrating action is increased by the acid treatment, hence the dehydration reaction also appears to be a surface phenomenon. Since the effect of acid treatment of the clay on the isomerization is not appreciable, it is presumed that the isomerization reaction is related to the atomic arrangement in the acid clay, and is not a surface phenomenon.

## E. The Isomerization of n-Butene by Means of Phosphoric Acid Catalyst

To obtain isooctane having a sufficiently high octane value as a blending fuel, the n-butene obtained from n-butanol must be isomerized. There are very little research data pertaining to the isomerization reaction of n-butene. A procedure by which n-butene is isomerized to isobutene, using phosphoric acid supported on charcoal as the catalyst, was developed in this laboratory. In order to obtain a butene mixture suitable for polymerization to isooctane the following experiments were carried out.

### 1. Experimental Procedure

~~The butene used was prepared by the dehydration of n-butanol at~~ 350°C on an acid clay catalyst produced in YAMAGATA Prefecture.

The composition of gas produced was as follows.

| | |
|---|---|
| Butene - 1 | 23 - 24% |
| Isobutene | 2 - 3% |
| Butene - 2 | 73 - 75% |
| Air | 1 - 2% |

The catalyst was prepared by the following method.

Ordinary charcoal was crushed to 5 - 10 mesh, mixed with phosphoric acid (Sp. gr. 1.75), and dried at 130°C for 3 hours.

### 2. Experimental Results

The relation between the quantity of phosphoric acid in the catalyst and the isobutene content in the produced gas is shown on Table XVII (B)10 and Figure 10(B)10.

The relation between the reaction temperature, the space velocity of gas and isobutene content in the gas produced in shown on Table XVIII(B)10.

The most suitable reaction temperature for the isomerization reaction was from 350 to 400°C, and the desirable space velocity was from 20 to 100. Above these temperatures the decomposition of butene took place and below 300°C the polymerization reaction occured.

## F. On the Catalytic Polymerization of Butene under Pressure

### 1. Apparatus and Procedure

Partly isomerized butene was polymerized under pressure using $H_3PO_4$ - $BaSO_4$ catalyst to clarify the relationship between polymerization products and the applied pressure. The catalyst used was prepared as follows. Phosphoric acid and barium sulphate were mixed in the ratio of 1 to 9 and shaped into cylinders having a diameter of 6mm and length of 6mm.

Butene containing 2% isobutene was prepared by dehydrating n-butanol on acid clay at 350°C. Butene containing 20% isobutene was prepared by dehydrating and isomerizing n-butanol on the mixture of phosphoric acid and charcoal. Figure 11(B)10 shows a diagram of the apparatus used. The volume of the reaction tube was 500cc. The polymer obtained was fractionated into four fractions as follows:

| Fraction No. | Range of b.p. | Principal Comp. |
|---|---|---|
| 1 | -95°C | unreacted gas |
| 2 | 95 - 120°C | dimer |
| 3 | 120 - 150°C | trimer |
| 4 | 150°C- | higher polymers |

The dimer was hydrogenated in an autoclave under a pressure of 100 atmospheres of hydrogen using reduced nickel as the catalyst and the

ENCLOSURE (B)10

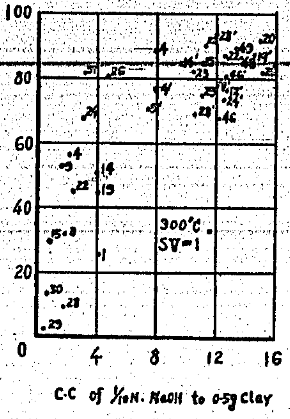


Figure 9(B)10
Yield of Butene to Theoretical

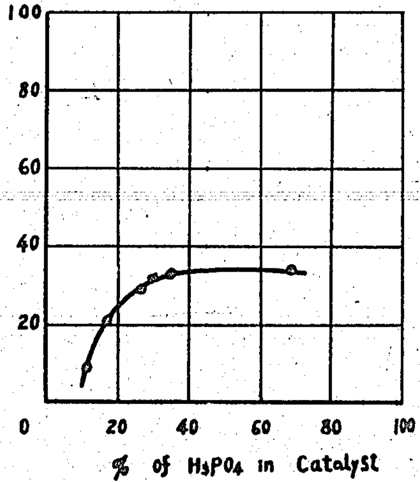


Figure 10(B)10
% of $i\text{-}C_4H_8$ in Gas Produced

octane rating of the hydrogenated dimer was measured by the C.F.R. motor method.

2. Experimental Results

a. The effects of the pressure on the polymerization.

In order to determine the effect of pressure on the polymeriza-

Table XVII(B)10
EFFECT OF AMOUNT OF PHOSPHORIC ACID IN CATALYST ON ISOMERIZATION OF BUTENE

| Content of $H_3PO_4$ in Cat. | Reaction Temp. | Space* Velocity | Composition of gas produced | | Oil produced per liter of gas |
|---|---|---|---|---|---|
| | | | i-$C_4H_8$ | Total $C_4H_8$ | |
| (% Wt.) | (°C) | | (%) | (%) | (cc) |
| 11.2 | 400 | 30 | 8.2 | 98 | 0 |
| 17.7 | 400 | 30 | 20.6 | 96 | 0 |
| 23.3 | 400 | 30 | 30.6 | 95 | 0.2 |
| 28.4 | 400 | 30 | 33.2 | 93 | 0.2 |
| 35.2 | 400 | 30 | 34.0 | 85 | 0.2 |
| 69.0 | 400 | 30 | 34.0 | 84 | 0.3 |

Table XVIII(B)10
COMPOSITION OF ISOMERIZED GAS AT VARIOUS TEMPERATURE AND SPACE VELOCITY

| React. Temp. (°C) | Space* Velocity | Composition of gas produced | |
|---|---|---|---|
| | | % of i-$C_4H_8$ | % of Total $C_4H_8$ |
| 300 | 50 | 13.2 | 92.2 |
| 300 | 100 | 9.8 | 93.4 |
| 350 | 50 | 26.0 | 94.6 |
| 350 | 100 | 18.6 | 94.6 |
| 400 | 20 | 33.0 | 93.0 |
| 400 | 100 | 24.2 | 95.0 |
| 450 | 50 | 27.6 | 85.0 |
| 450 | 100 | 20.4 | 92.0 |

*Space velocity is vols. of gas per vol. of Catalyst per hour.

### Table XIX(B)10
### POLYMERIZATION UNDER VARIOUS PRESSURES

(Reaction Temperature 120°C)

| Exp. No. | Pressure (Atms.) | Fractionation of Polymer (Vol %) | | | | | Butene Polymerized (%) | Octane value of Hydrogenated (dimers) | Isobutene in spent gas (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | -95° | 95-120° | 120-150° | 150° | loss | | | |
| 1 | 0 | 3.8 | 61.3 | 12.5 | 18.8 | 3.6 | 13.9 | | |
| 2 | 5 | 4.5 | 29.3 | 23.0 | 37.2 | 5.8 | 15.5 | | |
| 3 | 10 | 0.8 | 41.3 | 32.4 | 22.2 | 3.3 | 14.7 | 88.4 | 2.5 |
| 4 | 20 | 1.1 | 64.5 | 22.2 | 10.5 | 1.7 | 26.8 | | 2.5 |
| 5 | 30 | 0.9 | 67.1 | 13.1 | 15.6 | 3.3 | 45.9 | 83.3 | 3.5 |
| 6 | 40 | 0.7 | 67.4 | 16.9 | 12.1 | 2.9 | 53.8 | 82.3 | 3.5 |

Figure 12(B)10 (120°C) Polymerization under Various Pressures

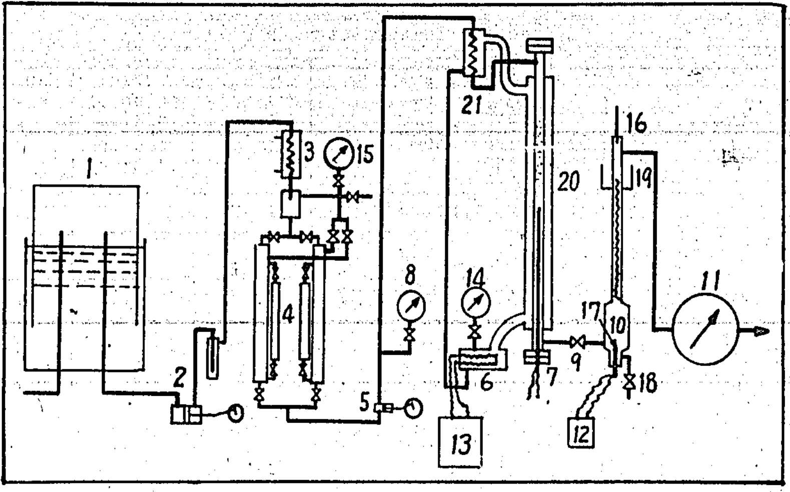
### Table XX(B)10
### POLYMERIZATION UNDER VARIOUS PRESSURES

(Reaction Temperature 150°C)

| Exp. No. | Pressure in atms. abs. | Fractionation of Polymer | | | | | Butene Polym. (%) | Octane Value of Hydrogenated dimers | Isobutene in spent gas (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | -95°C I | 95-120°C II | 120-150°C III | 150°C- IV | loss | | | |
| 7 | 0 | 1.3 | 52.1 | 22.6 | 19.6 | 4.4 | 2.7 | 88.3 | 3.0 |
| 8 | 10 | 0.8 | 33.4 | 36.8 | 27.6 | 1.4 | 22.7 | 88.5 | 2.5 |
| 9 | 20 | 0.4 | 39.3 | 30.1 | 28.8 | 1.4 | 24.2 | 86.8 | 2.4 |
| 10 | 35 | 0.4 | 64.5 | 21.7 | 10.1 | 3.3 | 32.4 | 84.1 | 3.0 |
| 11 | 45 | 0.5 | 64.5 | 20.7 | 8.5 | 5.8 | 28.4 | 84.5 | 3.0 |

Figure 13(B)10 (150°C) Polymerization under Various Pressures

ENCLOSURE (B)10



1. GAS HOLDER
2. COMPRESSOR
3. CONDENSER
4. MEASURING VESSEL OF LIQUID BUTENE
5. PUMP OF LIQUID BUTENE
6. WATER BOILER WITH ELECTRIC HEATER
7. THERMOCOUPLE
8. PRESSURE GAUGE OF REACTION PRESSURE
9. REDUCING VALVE
10. STILL WITH ELECTRIC HEATER
11. GASMETER FOR WASTE GAS
12. TRANSFORMER FOR CONTROLLING DISTILLATION TEMPERATURE
13. TRANSFORMER FOR CONTROLLING REACTION TEMPERATURE
14. PRESSURE GAUGE OF HOT WATER
15. PRESSURE GAUGE OF LIQUID BUTENE
16. THERMOMETER OF COLUMN TOP
17. THERMOMETER OF COLUMN BOTTOM
18. SAMPLING VALVE OF POLYMER
19. TOP COOLER OF COLUMN
20. REACTION TUBE
21. PREHEATER

Figure 11(B)10

APPARATUS FOR PRESSURE HYDROGENATION OF BUTENE TRIMER tion reaction and the yield and properties of the product, butene containing some isobutene was polymerized at different ~~pressures ranging from 0 - 40 atmospheres (on gauge) at temper~~atures of 120°C and 150°C. The butene used had a purity of 96.8% as $C_4H_8$ and contained 1.9% isobutene. The catalyst volume was 500cc, and the space velocity of butene was 500 expressed as the volume of gas per volume of the catalyst per hour. The results are shown in Tables XIX(B)10 and XX(B)10, Figures 12(B)10 and 13(B)10. The effect of pressure was considerable and the rate of the reaction increased with increasing pressure. At 150°C the rate of the reaction was nearly constant above 30 atmospheres pressure. At 120°C the polymers produced at pressures below 20 atmospheres contained less dimer than the polymers formed at atmospheric pressure. At both 120°C and 150°C a minimim yield of dimer was obtained. This minimum yield was found at five atmospheres pressure at 120°C and at 10 atmospheres pressure at 150°C. The octane rating of the hydrogenated dimer decreased with increasing reaction pressure.

The results of the polymerization of butene rich in isobutene are shown in Table XXI(B)10 and Figures 14(B)10 and 15(B)10. These experiments were carried out at 120°C and space velocities of 200 and 600. The butene used had a purity of 96.6% and contained 19.6% isobutene. In this case the yield of polymerized butene also increased with pressure. The dimer content of the polymer showed a minimum at 10 atmospheres and remained constant at pressure above 20 atmospheres. The octane rating of the hydrogenated dimer was generally above 92.

### b. The effects of varying space velocity on the polymerization under pressure.

In order to clarify the effect of space velocity, experiments were carried out under the following conditions: Temperature 120°C, pressure 10 atmospheres and 30 atmospheres. The butene used had a purity of 96.6% and contained 19.6% isobutene. The results are tabulated in Table XXII(B)10 and Figure 16(B)10. As these results show, the increase of the space velocity lowers the rate of polymerization and increases the dimer content in the polymer.

### c. The effect of the use of solvent on the polymerization under pressure.

A survey of the above results shows that the dimer content of the polymer was approximately 65% and the remainder was higher polymers. It had been expected from other sources that the polymerization of the B-B fraction of cracked gas would yield at least 90% dimer in the polymer produced. It was assumed that this could be attributed to the butane contained in the cracked gas acting as a diluent in the liquid phase polymerization: and lowering the mean molecular weight of the polymer. In order to determine the effect of the solvent on the polymerization and the properties of the polymer, the following experiments were carried out. Cyclohexane was used as a solvent, since it is not affected by polymerization catalyst and is easily separated by fractionation of the polymer. The cyclohexane used had the following properties:

b. p. 80 - 81°C, $d_4^{20}$ 0.7789, $n_d^{20}$ 1.4276

ENCLOSURE (B)10

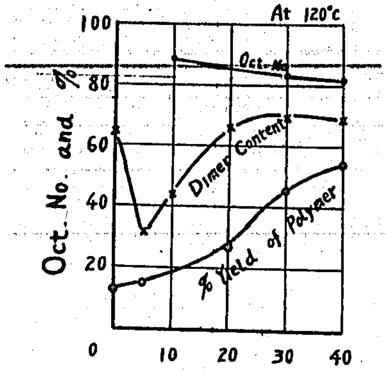


Figure 12(B)10

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

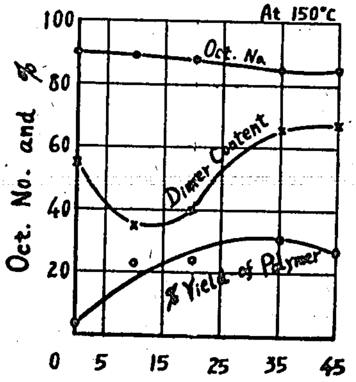


Figure 13(B)10

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSUR

### Table XXI(B)10
### POLYMERIZATION UNDER VARIOUS PRESSURES

| S. V. | Exp. No. | Pressure atms. | Fractionation of Polymer | | | | | Butene Polym. (%) | Octane Value Hydrogenated dimer | Iso-butene in spent gas (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | -90°C I (%) | 90-120°C II (%) | 120-150°C III (%) | 150°C- IV (%) | loss (%) | | | |
| 200 | 12 | 0 | 3.3 | 75.6 | 7.4 | 9.3 | 4.4 | 35.2 | 92.5 | 9.5 |
| 200 | 13 | 10 | 0.4 | 46.5 | 16.7 | 28.2 | 8.2 | 47.2 | 93.1 | 0.0 |
| 200 | 14 | 20 | 0.3 | 64.7 | 11.6 | 18.0 | 5.4 | 52.4 | 92.8 | 1.5 |
| 200 | 15 | 30 | 0.2 | 63.3 | 16.2 | 13.8 | 6.5 | 60.0 | 90.8 | 1.5 |
| 600 | 16 | 10 | 1.5 | 58.4 | 20.5 | 11.4 | 8.2 | 23.5 | 93.5 | 2.6 |
| 600 | 17 | 20 | 1.3 | 71.5 | 11.2 | 10.9 | 5.1 | 27.4 | 92.5 | 1.6 |
| 600 | 18 | 30 | 1.1 | 74.0 | 12.8 | 9.4 | 2.7 | 39.3 | 92.2 | 2.0 |

### Table XXII(B)10
### POLYMERIZATION AT VARIOUS SPACE VELOCITIES

| S. V. | Exp. No. | Pressure atms. | Fractionation of Polymer | | | | | Butene Polym. (%) | Octane value of hydrogenated dimer | Iso-butene in spent gas (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | -90° (%) | 90-120°C (%) | 120-150°C (%) | 150°C- (%) | loss (%) | | | |
| 200 | 19 | 10 | 0.4 | 46.5 | 16.7 | 28.2 | 8.2 | 47.2 | 93.1 | 5.0 |
| 400 | 20 | 10 | 0.2 | 63.5 | 10.8 | 17.2 | 8.2 | 33.4 | 94.0 | 4.0 |
| 600 | 21 | 10 | 0.2 | 76.0 | 7.1 | 12.2 | 4.5 | 26.4 | 94.0 | 3.9 |
| 400 | 22 | 30 | 0.3 | 64.7 | 13.2 | 12.6 | 9.2 | 56.9 | 92.2 | 2.4 |
| 600 | 23 | 30 | 0.4 | 70.7 | 10.7 | 9.7 | 8.5 | 39.2 | 92.2 | 3.2 |
| 800 | 24 | 30 | 0.3 | 80.4 | 6.2 | 7.7 | 5.4 | 35.9 | 94.0 | 6.4 |
| 1000 | 25 | 30 | 0.3 | 85.3 | 9.7 | 2.8 | 1.4 | 25.7 | 93.2 | |

ENCLOSURE (B)10

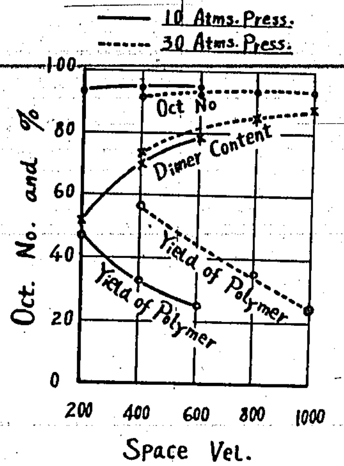


Figure 14(B)10
OCTANE NUMBER AND POLYMERIZATION AT
VARIOUS TEMPERATURES AND PRESSURES

Table XXIII(B)10
POLYMERIZATION AT VARIOUS SPACE VELOCITIES

| Pressure atms. | Exp. No. | S. V. | Butene Polym. | Distillation Test of Polymer | | | | | Octane Value of iso-octane | Isobutene in spent gas (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | I (%) | II (%) | III (%) | IV (%) | loss (%) | | |
| 10 | 26 | 200 | 43.4 | 5.2 | 69.0 | 13.8 | 9.2 | 2.8 | 93.0 | 3.3 |
| 10 | 27 | 400 | 34.6 | 8.1 | 75.5 | 9.6 | 6.9 | 0.0 | 92.2 | 4.2 |
| 10 | 28 | 600 | 30.7 | 16.7 | 70.0 | 5.5 | 7.5 | 0.8 | 92.7 | 3.4 |
| 30 | 29 | 200 | 51.0 | 8.6 | 78.5 | 4.9 | 6.1 | 1.9 | 91.7 | 1.6 |
| 30 | 30 | 400 | 44.2 | 9.2 | 77.1 | 2.0 | 6.3 | 5.4 | 92.0 | 1.4 |
| 30 | 31 | 600 | 31.1 | 9.0 | 83.5 | 2.9 | 3.9 | 0.7 | 91.4 | 1.6 |

ENCLOSURE (B)10

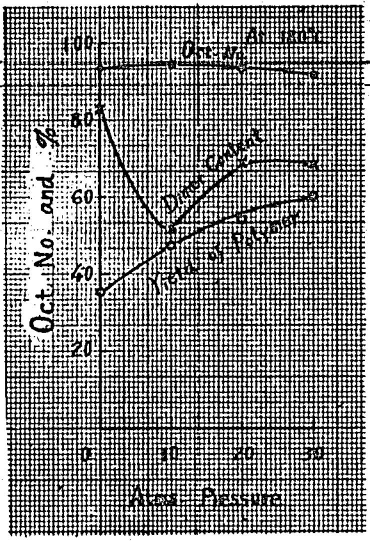


Figure 14

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

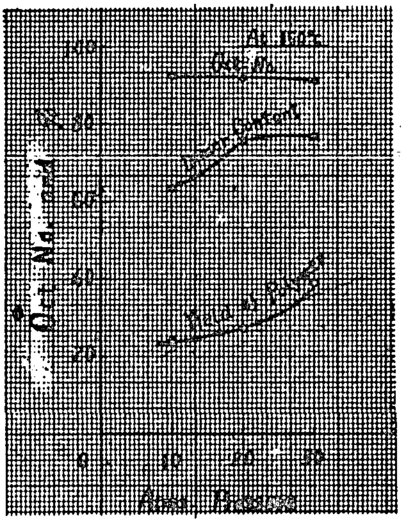


Figure 15

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

The experiments were conducted as follows: butene containing 20% of isobutene was mixed with cyclohexane. The mixture, consisting of 90% butene and 10% cyclohexane by volume, was charged at 120°C and pressures of 10 and 30 atmospheres. The results are tabulated in Table XXIII(B)10 and Figures 17(B)10 and 18(B)10. In these tables the space velocity is that of butene. Comparing these results with those obtained without solvent, the use of the solvent appears to lower the rate of polymerization, but the dimer content in the polymer increases considerably.

### 3. Conclusions

a. Generally, the application of pressure increases the rate of polymerization of butene.

b. In the pressure polymerization of butene the dimer content in the polymer shows a minimum at pressures of from 5 to 10 atmospheres. In the author's opinion, this phenomenon may be explained as follows: When the pressure is lower than 5 atmospheres the reaction occurs in the gas phase. The dimer formed on the catalyst surface evaporates with the unreacted gas and is removed from the surface of the catalyst with no further polymerization. At pressures of from 5 to 10 atmospheres the dimer formed on the catalyst surface remained in contact with the catalyst and is further polymerized. At pressures in excess of 20 atmospheres the reaction takes place in the liquid phase. In this case the dimer formed on the catalyst surface will be washed away and will not be further polymerized.

c. When butene containing only small amounts of isobutene is polymerized the product contains a little dimer. When hydrogenated this dimer has an octane rating below 90.

d. Butene containing 20% of isobutene was more easily polymerized, and the product was richer in dimer. The octane rating of the hydrogenated dimer was above 92.

e. The presence of solvent during the polymerization lowers the pressure required for liquid polymerization, and the yield of dimer in the polymer may be as high as 90%. In commercial operation the hydrogenated dimer may be used as the solvent.

## G. The Hydrogenation of Isooctene

### 1. The Influence of Residual Olefines in Isooctane on the Blended Fuel

In hydrogenating isooctene, residual olefines are apt to remain in the product especially when an old catalyst is used. The following experiments were carried out to determine the permissable limits of residual olefines. To prepare samples containing varying quantities of olefine, isooctene was added to completely hydrogenated isooctane. Isooctene was prepared from n-butanol as described previously and isooctane was prepared from isooctene by the complete hydrogenation in an autoclave at 100 atmospheres pressure of hydrogen using reduced nickel as the catalyst.

The bromine number of the isooctane was below 1. Isooctene mixed with isooctane at known volume ratios was regarded as the residual ~~olefine. Isooctane with added isooctene was blended with an equal~~ volume of N-1 gasoline having an octane number of 74.5. This gasoline is the substandard fuel for determining octane numbers by the C.F.R. motor method. The octane number of this blended fuel with 0.1% added lead was measured by the C.F.R. motor method. Figure 19 (B)10 shows the relation between the content of olefine in the isooctane and the octane number of the blended fuel.

The presence of olefines in isooctane lowers the octane rating of the blended fuel considerably, hence the hydrogenation of isooctene must be as complete as possible.

2. Activities of Various Hydrogenation Catalyst

The activities of some nickel catalysts were compared with that of mixed Ni-Cu catalysts supported on various carriers, and the change of octane rating of isooctane produced from the same raw material was measured by the C.F.R. motor method. The sample of isooctene was prepared as outlined above, and the catalysts were prepared as follows:

a. Cu-Ni.

Cupric nitrate and nickel nitrate solutions were mixed in the ratio Cu 3: Ni 1, a 10% solution of sodium carbonate was poured into the mixture until precipitation was completed. An excess of 10% sodium carbonate was added, and the precipitate was washed and dried.

b. Cu-Ni-Acid clay.

Acid clay of three times the weight of nickel was mixed with the Cu-Ni cake described above before drying.

c. Cu-Ni-MgO.

Magnesia instead of acid clay was used in preparing the catalyst described in (b).

d. Ni-diatomaceous earth.

Diatomaceous earth of 1.6 times the weight of nickel was mixed with nickel carbonate cake and was dried.

e. Reduced nickel.

Prepared in usual manner.

400cc of isooctene and the reduced catalyst (25 gm before reduction) were placed in an autoclave and hydrogen compressed to 100 atmospheres pressure was introduced and the mixture was heated to 200°C. The catalyst was filtered, and the iodine number of the hydrogenated product was measured by Hanus' method. The results are shown in Table XXIV(B)10.

The initial temperature was found from the temperature-pressure curve of the hydrogenation reaction. Although, in the case of ~~the Cu-Ni-MgO catalyst the initial reaction temperature is~~ relatively high, the pressure drop during hydrogenation is rapid. Since the Cu-Ni-MgO catalyst is easily tableted, has a strong activity and a low reduction temperature, it is suitable for practical use. The iodine values of the hydrogenated product were all below 1, and the octane numbers ranged from 90.4 to 91.5. Apparently, none of these catalysts affect the octane number of the product.

Table XXIV(B)10
PRESSURE HYDROGENATION OF BUTENE DIMER WITH VARIOUS CATALYSTS

| Exp. No. | Catalyst | Reducing temp. (°C) | Sample cc | Produced isooctane cc | Initial temp. of hydrogenation (°C) | Iodine Value | Octane No. |
|---|---|---|---|---|---|---|---|
| 1 | Cu-Ni | 200 | 400 | 350 | 90 | 0.4 | 91.1 |
| 2 | Cu-Ni-clay | 200 | 400 | 355 | 100 | 0.3 | 91.4 |
| 3 | Cu-Ni-MgO | not reduced | 400 | 351 | 110 | 0.5 | 90.5 |
| 4 | Cu-Ni-MgO | 200 | 400 | 355 | 100 | 0.4 | 90.6 |
| 5 | Ni-Diatom earth | 400 | 400 | 360 | 50 | 1.0 | 90.4 |
| 6 | Reduced Ni | 300 | 400 | 355 | below room temp. | 0.4 | 91.5 |

Table XXV(B)10
EFFECT OF RELATION OF REACTION TEMPERATURE ON HYDROGENATION OF BUTENE DIMER

| React. Temp. (°C) | Time of Exp. (hr) | Iso-octene used (gm) | Isooctane Produced (gm) | Exp. Loss (gm) | Purity of Waste $H_2$ (%) | Iodine No. of Product |
|---|---|---|---|---|---|---|
| 120 | 3.0 | 38.5 | 29.0 | 9.5 | 98.0 | 2.8 |
| 140 | 2.5 | 36.5 | 28.5 | 8.0 | 98.0 | 2.8 |
| 160 | 2.5 | 37.5 | 29.0 | 8.5 | 96.5 | 1.3 |
| 200 | 2.5 | 36.3 | 28.5 | 8.0 | 97.5 | 0.8 |

ENCLOSURE (B)10

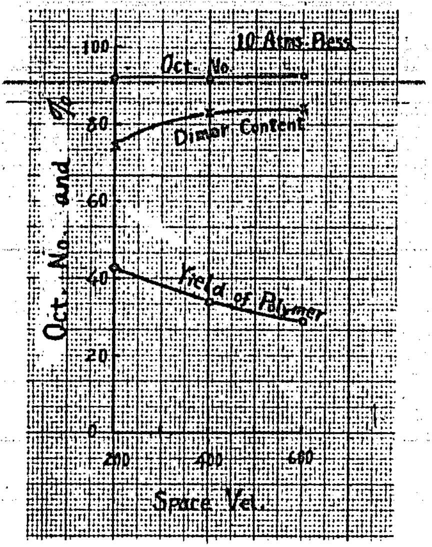


*Figure 16*

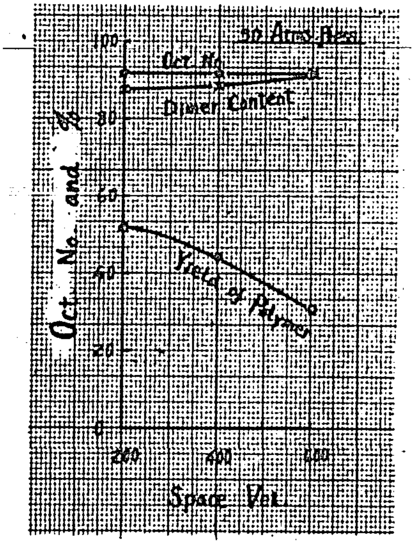


*Figure 17*

In the following experiments the Cu-Ni-MgO catalyst was used. Although, in general, copper catalyst has a weak hydrogenation ~~activity and is apt to be injured by action of heat and catalytic~~ poisons, it can be reduced in the hydrogenation reactor at steam heat, since it has a low reduction temperature. According to the literature, magnesia strengthens the heat resistance of the catalyst and nickel increases the activity of copper. This catalyst may be used since the synthesized isooctene contains no sulphur.

### 3. Pressure Hydrogenation of the Dimer by the Flow Method

The apparatus used is shown in Figure 7(B)10, and is the same as was used for the hydrogenation of crotonaldehyde. Twenty grams of tableted catalyst were packed in the center of the reaction tube, and isooctene was introduced at a velocity of 10cc-15cc per hour after reducing the catalyst with hydrogen at 210°C.for six hours. The quantity of hydrogen used was three times the theoretical. The pressure was kept at 10 $kg/cm^2$. At hydrogenation temperatures of 120, 140, 160, and 200°C, the results shown in XXV(B)10 were obtained. The results obtained at various velocities of isooctane at 160°C are shown in Table XXVI(B)10.

### 4. The Properties of Aviation Gasolines Blended with the Hydrogenated Trimer

Samples were prepared by mixing an aviation gasoline with the hydrogenated trimer, which was prepared from the fraction of 120 - 180°C of the butene polymer by hydrogenation in an autoclave. The distillation characteristics, the vapor pressure, and the octane number of blends of 10%, 20% and 30% hydrogenated trimer in aviation gasoline were obtained. The results are tabulated in Table XXVII(B)10. The octane numbers were determined with 0.1% added lead.

As these results show, the addition of hydrogenated trimer increases the distillation characteristics and the octane number, and lowers the vapour pressure of the blended fuel. The blend containing 10% of the hydrogenated trimer nearly conforms to the specification of the aviation gasoline now in use. The blending of hydrogenated trimer to gasoline having too high a vapor pressure would serve to lower the vapour pressure without lowering the octane number.

### 5. The Pressure Hydrogenation of Butene Trimer

As already mentioned butene trimer, the by-product of polymerization, was available as a blending fuel. The following experiments were carried out in order to determine the possibility of hydrogenating the trimer by the same method as was used for the dimer. The trimer was separated from the polymer as the fraction of 120°C - 180°C by fractionation. The catalyst used was the same as used in hydrogenating the dimer. The apparatus was the same as that used for the continuous polymerization of butene under pressure as shown in Figure 11(B)10. The outlet of the compressor was connected to the top of the reaction tube eliminating the cooler (3), and a cooler and a receiver were connected to the outlet of the reaction tube. Three times the theoretical amount of hydrogen was used. The waste hydrogen was separated from the receiver through a gas meter. The experimental results are shown in Table XXVIII(B)10. The hydrogenation

ENCLOSURE (B) 10

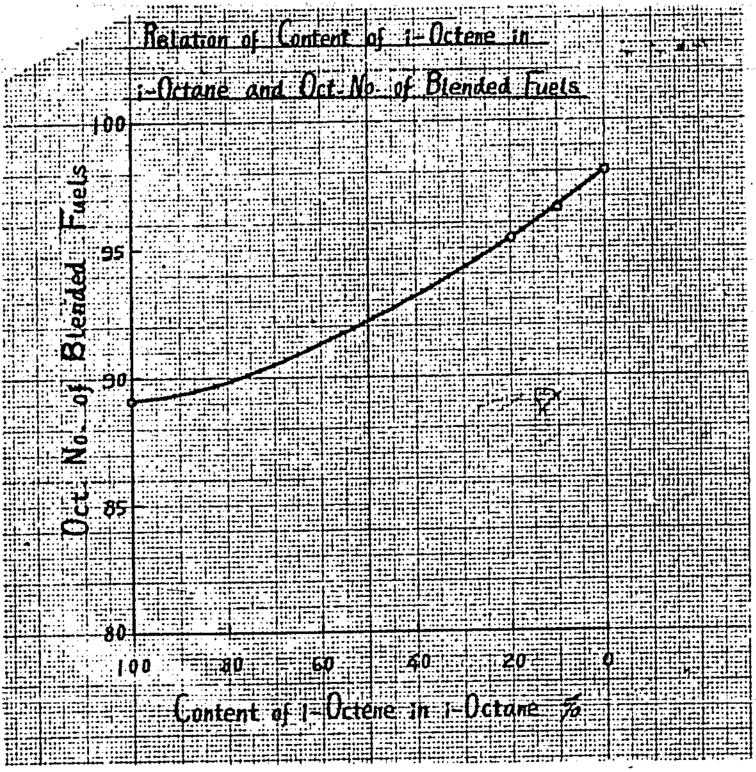


Figure 18

was completed at a temperature of 160 - 180°C, a pressure of 10 - 2 kgs/cm$^2$ and space velocity of the trimer of 0.5 - 1.0. It may be concluded that the hydrogenation of the trimer can be done under nearly the same conditions as the hydrogenation of the dimer.

Table XXVI(B)10
EFFECT OF SPACE VELOCITY ON HYDROGENATION OF BUTENE DIMER

| Time of Exp. (hr) | Wt. of Iso-octane used (gm) | Wt. of Iso-octane Produced (gm) | Purity of Waste Hydrogen (%) | Exp. Loss (gm) | Iodine No. of Product | Vol. of Isooctene per Vol. of Cat. per hr |
|---|---|---|---|---|---|---|
| 2.5 | 37.5 | 29.0 | 98.5 | 8.5 | 1.3 | |
| 2.5 | 72.5 | 64.5 | 97.8 | 8.0 | 1.6 | 0.71 |
| 1.25 | 92.5 | 84.5 | 98.0 | 8.0 | (1.0) | 1.8 |
| 1.5 | 109.0 | [illegible] | 98.0 | 12.5 | 1.9 | 3.1 |
| 1.0 | 91.0 | 81.5 | 98.0 | 9.5 | 8.7 | 4.5 |
| 0.83 | 91.5 | 84.5 | 98.9 | 7.5 | 11.4 | 5.4 |

Table XXVII(B)10
CHANGE OF CHARACTERISTICS OF AVIATION GASOLINE
BY BLENDING HYDROGENATED TRIMER

| Mix. Ratio of Hydro. trimer | Distillation Characteristics | | | | | | Reid Vapour Press kg/cm$^2$ | Octane Number 0.1% leaded |
|---|---|---|---|---|---|---|---|---|
| | I.b.p. | 10% | 50% | 90% | 97% | Sum. of 10+50+90% | | |
| 0 | 50.0 | 63.3 | 94.0 | 122.5 | 145.0 | 285.8 | 0.56 | 92.6 |
| 10 | 49.0 | 72.0 | 96.0 | 135.0 | 170.0 | 293.0 | 0.50 | 93.3 |
| 20 | 51.0 | 74.0 | 103.0 | 151.0 | 184.0 | 328.0 | 0.43 | 93.6 |
| 30 | 51.0 | 74.5 | 110.0 | 161.0 | 187.0 | 345.5 | 0.41 | 94.0 |

Table XXVIII(B)10
HYDROGENATION OF BUTENE TRIMER UNDER VARIOUS CONDITIONS

| Trimer Used (l) | Time of Exp. in (hrs.) | React. Temp. (°C) | Vol. of Trimer (vol./vol. of Cat./hr (hr) | Press (kg/cm$^2$) | Product (l) | Iodine Number of Product |
|---|---|---|---|---|---|---|
| 2.210 | 6 | 180 | 0.5 | 20 | 2.205 | 3.7 |
| 2.160 | 6 | 180 | 0.5 | 10 | 2.059 | 3.3 |
| 2.140 | 6 | 160 | 0.5 | 10 | 2.255 | 4.9 |
| 4.320 | 6 | 180 | 1.0 | 10 | 4.465 | 4.0 |