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~~X-38(N)-2~~

ENCLOSURE (B) 20

PREPARATION OF n-HEPTANE  
AND ISO-OCTANE  
FOR STANDARD FUEL

by

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SUMMARY

When butyric acid was passed through thorium oxide heated at 380-430°C, butyrene was formed in a 98% yield of theoretical value. Butyrene was reduced with hydrogen in the presence of a mixture of Cu-Cr oxide or Cu-Ni oxide and activated acid clay; the reduced product was then fractionated after being washed with conc. sulphuric acid and water. The yield of pure n-heptane thus formed was about 40% to butyric acid.

Iso-butylene formed by the contact action of alumina from iso-butanol, was polymerized to iso-octene by the action of 63% cold sulphuric acid, and the iso-octene was reduced with hydrogen in the presence of reduced nickel to iso-octane. The yield of iso-octane was about 20% to butanol.

I. INTRODUCTION

The lack of standard fuel had become serious since 1941, and consequently the study of the following methods of preparation were started:

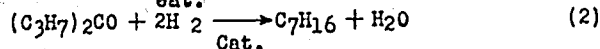
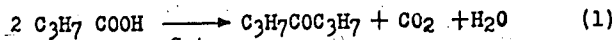
A. In Japan, the raw material for the preparation of pure n-heptane is n-butyric acid which was prepared from n-butyl alcohol. In this laboratory, methods for preparing butyrene from n-butyric acid and n-heptane from butyrene were examined. From these results, a small plant was planned and construction was started in August 1941. The manufacture of n-heptane began in February 1942.

B. The raw material for the preparation of pure iso-octane (2-2-4-trimethyl pentane) is iso-butanol obtained as by product of methanol production. The reactions for making pure iso-octane from iso-butanol are dehydration by the contact action of alumina, cold acid treatment and hydrogenation in the presence of reduced nickel.

After these experiments the construction of a small plant for preparing iso-octane was begun in August 1941 and production was started in June 1942.

II. DETAILED DESCRIPTIONA. Preparation of n-Heptane

The chemical reactions used in the preparation of n-heptane from butyric acid are shown in the following equations:

1. Preparation of butyrene (Reaction 1)

a. There are two methods of converting butyric acid to butyrene: by dry distillation of the calcium salt of butyric acid or by catalytic pyrolysis. The former method was carried out at high temperatures (about 500°C) so that the distillate was frequently impure. Thus, it appears that pure butyrene from butyric acid is not available by this method. Hence, a catalytic method for producing pure butyrene from butyric acid was adopted.

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b. Experimental apparatus and method. Butyrene was prepared from butyric acid using the apparatus shown in Figure 1(B)20.

Various catalysts, feed rates, and reaction temperatures were used. The catalyst was placed in a silica tube (22mm x 1200mm) and the temperature was determined by Ni-Cr thermocouples enclosed in silica sheaths.

The composition of the condensate was determined by the following method: The unreacted butyric acid is titrated with N/10 sodium hydroxide solution, and the volume of butyrene in the condensate is determined by distillation.

Pure butyrene is obtained from the condensate by fractionation after washing with a 5% NaOH solution to remove the unreacted butyric acid and then washed with water.

c. Experimental results. In these experiments the catalytic action was clarified and the favorable conditions of temperature and space velocity were determined.

The butyric acid used was obtained from Sanwa-Kagaku Manufacture and had the following properties:

Sp. gr. ( $d_4^{20}$ ) .....	0.957
B.P. (760mm Hg) .....	162.5°C

The following catalysts were investigated:

- (1) Powdered  $\text{CaCO}_3$
- (2)  $\text{CaCO}_3$ -Active clay (2:1)
- (3)  $\text{CaCO}_3$ - $\text{BaCO}_3$ -Active clay (1.1:0.5:1.0)
- (4)  $\text{CaCO}_3$ - $\text{MgCO}_3$ -Active clay (1.7:0.5:1.0)
- (5) ThO on pumice: Prepared by dipping in thorium nitrate solution, drying, and igniting at 500°C. Concentration of ThO is 25.8% by weight.
- (6)  $\text{U}_3\text{O}_8$  on pumice: Prepared by same method as (5). Concentration of  $\text{U}_3\text{O}_8$  is 48.4% by weight.

The results are recorded in Table I(B)20.

It was found that  $\text{U}_3\text{O}_8$  and ThO supported on pumice were excellent catalysts. Using these catalysts, the reaction temperature could be decreased to 400-430°C compared to a reaction temperature of about 500°C using other catalysts, and the feed rate could be increased.

The yield of butyrene from butyric acid is shown to be about 90% by volume to the feed used, and this value corresponds to a yield of 90% of the theoretical.

Additional butyrene is present in the lower and higher boiling fractions of the distillate.

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TABLE I(B)20  
 PREPARATION OF n-BUTYRONE FROM n-BUTYRIC ACID BY ACTION OF CATALYSTS

Catalyst:	Experiment No.										
	1	2	3	4	5	6	7	8	9	10	
Name	CaCO <sub>3</sub>	CaCO <sub>3</sub> Clay	CaCO <sub>3</sub> BaCO <sub>3</sub> Clay	CaCO <sub>3</sub> MgCO <sub>3</sub> Clay	ThO on pumice						U <sub>2</sub> O <sub>8</sub> on pumice
Mixing ration (by weight)		2:1	1.7:10.5:1:0	1.7:10.5:1:0	25%						48.4%
Weight used (gm)	50	90	74	60.5	45	45	52	64	64	64	
Volume of feed used (ml/hr)	38	81	95	75	98	83	37	81.5	103	200	
Reaction temperature (°C)	500	500	500	470	450	430	415	400	430	440	
Yield of condensate: (\$ by vol.)	86.7	80.2	66.2	70.5	76.6	76.1	76.5	77.2	76.7	76.5	
Sp. Gr. (42°)	0.9100	0.8920	0.8648	0.8433	0.8123	0.8235	0.8180	0.8170	0.8170	0.8153	
I.B.P. (°C)	65	68	65	65	80	70	65	72	72	64	
Distillation pt	27	25	21	17	60	4.0	5.0	5.0	5.0	5.0	
~114°C (\$ by vol.)	18	31	45	52	87	84	90	88	88	90	
115~115°C (\$ by vol.)	55	44	34	31	7.0	12.0	5.0	7.0	7.0	5.0	
To used feed (\$)	15.6	24.9	29.8	36.6	66.6	64.0	68.8	68.0	67.0	69.0	
To the theoretical (\$)	20.2	32.4	36.7	47.5	86.5	83.0	90.6	88.2	87.0	89.6	
Volume of gas formed: (l/hr)	36.3	11.3	16.9	12.7	12.0	10.5	99.0	11.0	13.9	25.6	
CO <sub>2</sub> (\$)	67.4	61.9	56.3	72.6	98.6	99.2	99.0	98.8	100.0	99.5	
O <sub>2</sub> (\$)	0.4	0.3	0.3	0.2							
Gas analysis: (by vol.)	C <sub>2</sub> (\$)	4.4	4.6	5.6	2.4						
	C <sub>2</sub> H <sub>4</sub> (\$)	10.5	11.6	15.1	6.1						
	C <sub>2</sub> H <sub>6</sub> (\$)	4.7	6.8	4.7	8.0						
	CO (\$)	2.9	5.5	7.6	3.4						
H <sub>2</sub> (\$)	1.3	1.2	1.7	0.8							
C <sub>2</sub> H <sub>5</sub> O~2 (\$)	5.8	6.7	8.5	4.2							
H <sub>2</sub> (\$)	2.6	1.4	0.2	2.1							
C <sub>2</sub> (\$)	1.5	1.6	1.6	1.4							
Volume of condensate (\$)	In condensate (\$)	52	41.8	23.7	13.7	trace	5.1	trace	0.7	1.1	
	To used feed (\$)	45	33.5	15.7	9.2	trace	3.9	0.6	0.8	0.8	

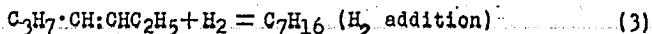
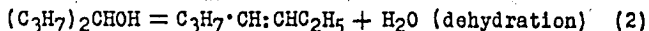
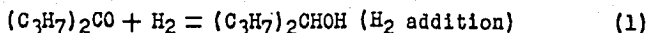
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The properties of the pure n-butyronone were as follows:

$d_{20}^4$ .....	0.8156
$n_D^{20}$ .....	1.4070
B.P. ....	144°C

2. Preparation of pure n-heptane from n-butyronone by hydrogenation.  
(Reaction 2)

a. The reactions by which n-heptane is formed from n-butyronone consist of 3 steps.



The usual method for forming n-heptane from butyronone is as follows: Butyronone is hydrogenated in the presence of  $MoS_3$  catalyst in 3 stages (1) hydrogenation of butyronone to heptanol ( $(C_3H_7)_2CHOH$  at  $230-235^\circ C$  and 100 atm. pressure; (2) dehydration of heptanol to heptene ( $C_3H_7CH : CHC_2H_5$ ); (3) hydrogenation of the latter to n-heptane ( $C_7H_{16}$ ) at  $350^\circ C$  and 135 atm. pressure. It was said that the last step proceeded very slowly and the presence of considerable amounts of heptene were observed in the product.

b. Catalyst.

The object of our research was to discover a more effective catalyst. Catalysts used for this purpose were Ni-Cu oxide and Cu-Cr oxide used for hydrogenating hydrocarbons and ketones. These catalysts were prepared as follows.

(1) Ni-Cu oxide. A mixture of nickel and copper nitrates in the ratio 2.NiO:1.CuO by weight was treated with  $NaCO_3$  solution and the precipitate was filtered, washed, dried, at  $90^\circ C$ , pulverized, and ignited at  $300^\circ C$ . The mixed oxide was mixed with activated acid clay in the ratio of 1 Ni-Cu oxide:3 clay before use.

(2) Cu-Cr oxide; This was prepared by the ordinary method for preparing Adkin's catalyst and was mixed with activated acid clay in the ratio of 1:4 by weight.

c. Experimental procedure for hydrogenation of butyronone.

400 gm of butyronone and 40-80 gm of catalyst were put in a rotating autoclave of 5 liters capacity under a hydrogen pressure of 100 atm. and heated with an electric heater. When the reaction temperature was reached, the reaction was continued for one hour. At the end of this time, the products were removed and examined. The results are shown in Table II(B)20.

d. From these results, it appears that the catalysts studied, mixtures of Ni-Cu oxide or Cu-Cr oxide and activated acid clay, were more effective than  $MoS_3$ . The yield of n-heptane to the ketone used was more than 85% by volume.

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TABLE II(B)20  
PREPARATION OF n-HEPTANE FROM BUTYRONE BY HYDROGENATION

		Experiment No.				
		1	2	3	4	5
Catalyst:	Name	Cu-Ni oxide mixed with active clay				
	Mixing ratio	1:2	1:3		1:4	1:4
	Ratio to used feed (%)	15	20	10	20	20
Reaction temperature (°C)		250	250	350	290	250
Reaction time (hr)		1	1	1	1	1
Initial H <sub>2</sub> pressure (atm)		110	110	110	110	110
Maximum H <sub>2</sub> pressure (atm)		169	171	220	184	168
Final H <sub>2</sub> pressure (atm)		68	68.2	81.2	74.8	70.7
Pressure difference (atm)		42	41.8	28.8	35.2	39.3
Yield of product (% by vol.) to used Butyrone		95.3	96.0	100.5	96.0	93.3
Sp. Gr. (d <sub>4</sub> <sup>20</sup> )		0.6857	0.6865	0.7420	0.6859	0.6853
I.B.P. (°C)		78.0	90.0	51.0	62.3	52.0
~97° (°)		3.0	4.0	5.2	3.6	5.0
97~98° (°)		91.2	89.9	44.8	90.4	90.0
98~ (°)		5.8	6.1	48.9	4.8	5.0
Yield of pure n-heptane fraction (97~98°)		86.9	86.4	45.0	86.8	84.0
Yield of pure n-heptane fraction (98~)		59.8	59.4	31.0	59.9	58.0
To use butyrone (% by vol.)						
To feed butyric acid (% by vol.)						

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The Ni-Cu oxide catalyst was more desirable than Cu-Cr oxide, since the reaction temperature was lower and the preparation of ~~the catalyst was easier.~~

The properties of the n-heptane formed by this method are completely suitable for a standard fuel and are as follows:

B.P. (at 760mm Hg.) .....	98.400
$d_{4}^{20}$ .....	0.6836
$n_{D}^{20}$ .....	1.38777

### 3. Pilot plant for n-heptane

From the results of these fundamental studies, a plant for producing n-heptane from n-butyric acid was designed and built in 1942. A detailed flow sheet is shown in Plate I(B)20.

This plant has a capacity of 30 l/day of pure n-heptane and consists of the following units:

#### a. Unit for producing n-butyronone.

When the volume of the unreacting butyric acid is increased to 3% by volume in the product, the catalyst was reactivated at 500°C and reused. This catalyst could be used for a month. The yield of butyronone using this unit is identical with that obtained in the laboratory.

30 liters of the product were washed with 10 liters of a 5% NaOH solution once and then 4 times with 10 liters of water. 40 liters of the washed product were distilled as follows: The first fraction was a 5% cut, the 2nd fraction a 75% cut and the 3rd the residue. Then the 1st fraction and residue were re-distilled in the same manner.

#### b. Hydrogenation unit.

The pure n-butyronone prepared was hydrogenated by the action of Ni-Cu oxide catalyst under a hydrogen pressure of 200 atm. and at 250°C.

#### c. Purification unit

The hydrogenated product was distilled and the following cuts obtained: The 1st fraction was a 10% cut, and the 2nd fraction a 75% cut. The 1st fraction and residue were redistilled in the same manner.

40 liters of the 2nd fraction was washed 3 times with 10 liters of 96% H<sub>2</sub>SO<sub>4</sub> and then once with 10 liters of 5% NaOH and finally, 4 times in 10 liters of water.

The washed crude n-heptane was then rectified by the last distiller. The distillates from this still were divided into 10 cuts, and each fraction was tested. The fractions meeting the specifications were then sent to a product tank and packed in 3 liter cans. Other fractions were redistilled and tested.

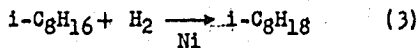
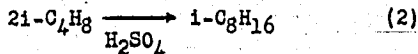
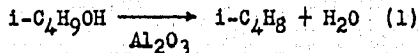


ENCLOSURE (B)20

The properties of n-heptane prepared by this plant are identical with those obtained in the laboratory.

### B. Preparation of iso-octane (2-2-4-trimethylpentane)

The reaction system for the preparation of iso-octane is shown in the following equations:



#### 1. Preparation of iso-butylene from i-butanol (Reaction 1)

a. Generally, the iso-butylene is produced from iso-butanol by the action of catalysts such as  $Al_2O_3$  and activated acid clay, but alumina was adopted in this study, since in the presence of n-butylene is formed activated acid clay.

#### b. Experimental apparatus:

The apparatus used is shown in Figure 2(B)20.

#### c. Procedure

Iso-butyl alcohol was introduced into the reaction tube at about 0.5 space velocity and at  $400^\circ C$  reaction temperature. The reaction products leaving the reaction tube were condensed and the condensate was collected in the receiver and the uncondensed matter is passed through another condenser to separate the gas and liquid. The condensate is removed from the receiver and the unreacted iso-butanol is recovered by distillation. The produced gas is collected in a bottle by displacement of water. The volume of iso-butylene formed is determined by absorption with 65%  $H_2SO_4$ . The ratio of reacted alcohol to used alcohol is calculated from the volume of unreacted alcohol.

The iso-butanol used in this study was obtained from the market, and its properties were as follows: sp.gr. ( $d_4^{20}$ ) is 0.8025, B.P. is  $106-108^\circ C$ .

The alumina used as the catalyst was prepared by heating at  $600^\circ C$ . The precipitate formed by the addition of  $CO_2$  gas to a NaOH solution of aluminum.

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d. Results

~~The results obtained were as follows:~~

Reaction temperature ..... 400°C.  
 Space velocity, (Feed vol./cat. vol./hr.) ..... 0.5  
 Alcohol converted ..... above 95% by vol.  
 Volume of iso-butylene in product ..... above 98% by vol.  
 Yield of iso-butylene from iso-butanol . approx. 74% by wt.

Notes: The theoretical yield of i-butylene from i-butanol is 75.7% by weight (= 56.06/74.08). The catalyst could be used without activation for more than a month.

2. Preparation of iso-octene from iso-butylene by cold acid process. (Reaction 2)

a. There are three well known processes for the polymerization of iso-butylene to iso-octene: (1) The phosphoric acid process, (2) the hot acid process, (3) the cold acid process. The first two processes are used on a commercial scale to prepare iso-octane from cracked gas, the latter process is used for the production of pure iso-octane (2-2-4-trimethylpentane) by selective polymerization of the iso-butylene in cracked gas.

b. Experimental apparatus:

The apparatus used is shown in Figure 3(B)20.

c. Procedure

Iso-butylene gas, dried by calcium chloride, is led into a 3 liter absorbing flask, charged with 1 liter of 63% H<sub>2</sub>SO<sub>4</sub> and is agitated with a glass stirrer at 5-15°C. The unabsorbed gas is passed through a gas bottle and the volume is determined. The rate of absorption of iso-butylene is calculated from the volume of unabsorbed gas.

The flask containing sulphuric acid and absorbed iso-butylene was dipped into another oil bath heated to 110°C. After reaching 90°C, the reaction was allowed to proceed for one minute, and then the flask was cooled with ice water as soon as possible. By this method, the iso-butylene was polymerized to iso-octene.

The polymer separated from sulphuric acid was washed with 5% NaOH solution and water and was distilled to separate the iso-octene (dimer) from the trimer.

d. Results

The experimental results obtained were as follows:

Condition of polymerization

Concentration of sulphuric acid ..... 63%  
 Volume of sulphuric acid used ..... 1 liter (1.5 kg)  
 Volumes of iso-butylene charged (1/hr.) .... 6, 8, 10, 12  
 Absorption temperature (°C) ..... 5, 10, 15, 20, 30  
 RPM of stirrer ..... above 300

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The rate of absorption of iso-butylene was above 95% at 6-8 liter/hr of charged volume and at 5-20°C of absorption temperature. When the charged volume of iso-butylene was increased to more than 10 liters/hr, the absorption rate decreased to less than 90%.

The desirable absorption temperature range is from 5-15°C. If the temperature is increased to above 15°C, the volume of iso-octene in the polymer is decreased to less than 60%.

The stirring speed has a marked effect upon the absorption of iso-butylene. A speed of at least 300 RPM is desirable for optimum yields.

The results of polymerization under the best operating conditions are as follows:

Absorption temperature .....	50°C
Volume of iso-butylene charged .....	8 liters/hr
Iso-butylene absorbed .....	approx. 98% by vol.
Polymerization temperature .....	90°C
Polymerization time (at 90°C) .....	one minute
Iso-butylene polymerized .....	approx. 90%
Iso-octene in product .....	approx. 65% by vol.
Yield of iso-octene to used iso-butylene .....	approx. 34% by wt.

The sulphuric acid can be used repeatedly.

### 3. Preparation of iso-octane from iso-octene by hydrogenation.

It is known that iso-octene is reduced to iso-octane in the presence of reduced nickel at 180°C and 10 atm. of hydrogen pressure.

400 gm of iso-octene and 40 gm of reduced nickel were put in a rotating autoclave of 5 liter capacity under a hydrogen pressure of 50 atm. and was reduced at 180°C. The yield of hydrogenation product was about 90% by volume to iso-octene used, and the concentration of pure iso-octane in the hydrogenation product was about 80%.

The iso-octane prepared by this method is suitable as a standard fuel and its properties are as follows:

B.P. (at 760mm Hg.) .....	99.30°C
$d_{4}^{20}$ .....	0.6921
$n_{D}^{20}$ .....	1.3916
Bromine value .....	below 0.01

Complete data relative to these experiments are not available.

### 4. Pilot plant for iso-octane.

From the results of these laboratory studies, a pilot plant for producing iso-octane from iso-butanol was designed and built in 1942. A detailed flow sheet is shown in Plate II(B)20. This plant has a capacity of 20 liters/day of pure iso-octane.

Results obtained in the pilot plant were as follows:

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Iso-butylene gas was produced by dehydration of iso-butanol vapour with alumina catalyst at 380°-400°C with a space velocity of 0.5. Its dehydration yield was 90%.

Then the gas was polymerized at 90°C for 5 minutes, after absorption by 63% conc.  $H_2SO_4$  at 5-15°C. The i-butylene absorbed was 10% by weight of  $H_2SO_4$ .

In the absorption unit, the depropanizer was used for the separation of iso-butylene and the lower hydrocarbon gases, and the separated iso-butylene was recycled.

The contents of iso-octene (dimer) in the polymerized product was about 65%, and the remainder was trimer. The polymerized product was washed with 5% caustic soda solution to remove the traces of  $H_2SO_4$ , and then the iso-octene fraction, boiling from 98-102°C, was distilled.

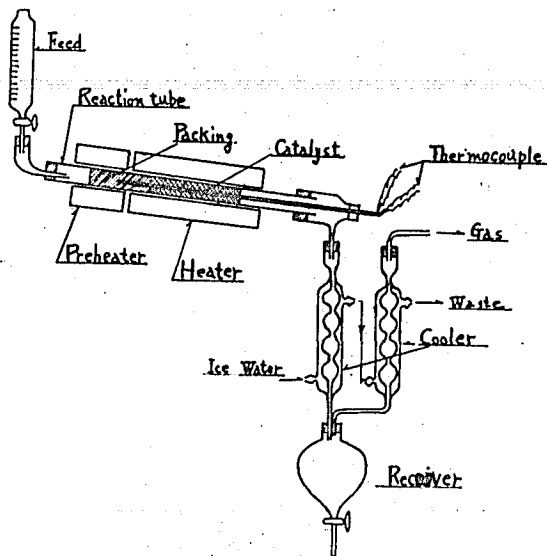
This product was hydrogenated in the presence of a nickel catalyst at 180-200°C and 10-30 atm. of hydrogen with a space velocity of 0.3-0.5. The completely hydrogenated product, having a bromine value below 0.01, was fractionated in 10% cuts, and the refractive index, specific gravity, and boiling point was determined for each fraction. The octane value of the iso-octane cut was determined using a C.F.R. engine.

The yield of pure iso-octane was about 70% by volume to iso-octene.

The capacity of the pilot plant is approximately 20 liters/day of pure iso-octane (about 15% by weight to charged iso-butanol)

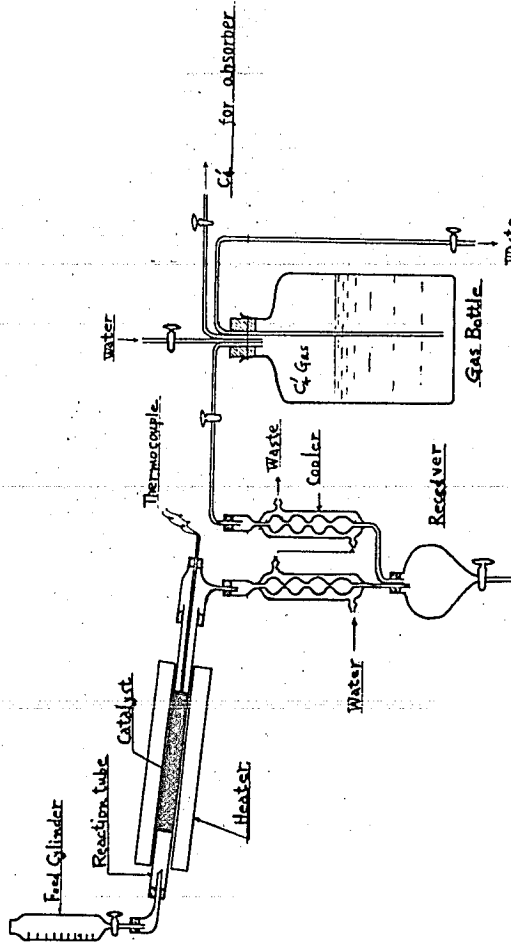
Figure 1(B) 20

## APPARATUS FOR PREPARATION OF BUTYRONE FROM BUTYRIC ACID



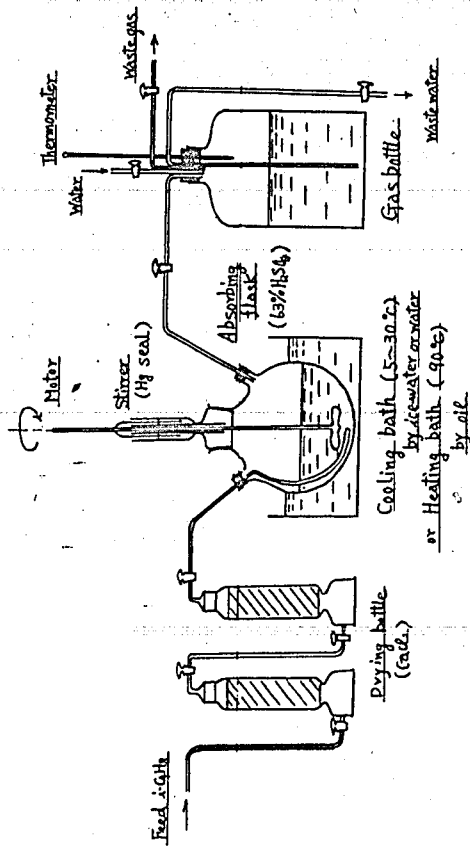
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Figure 2(B)20  
APPARATUS FOR PREPARATION OF  $i\text{-C}_4\text{H}_{10}$  FROM  $i\text{-C}_4\text{H}_9\text{OH}$



ENCLOSURE (B)20

Figure 3(B)20  
APPARATUS FOR PREPARATION OF  $i-C_4H_{10}$  FROM  $i-C_4H_8$



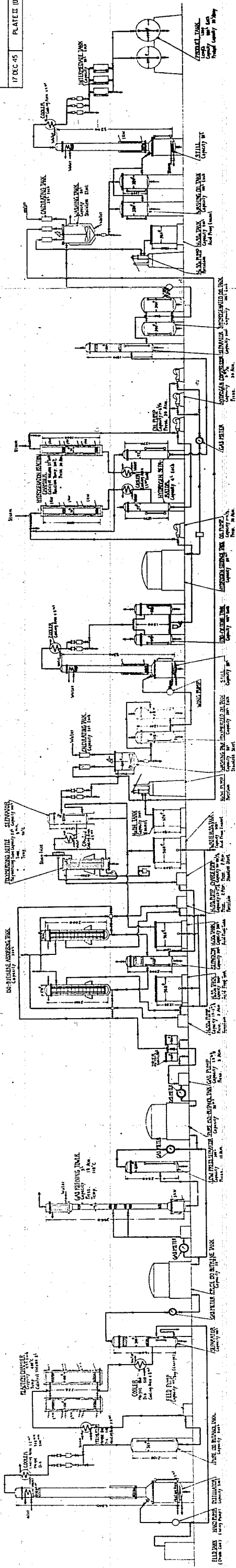


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U.S. NAVAL TECHNICAL MISSION TO JAPAN RESTRICTED  
FLOW SHEET OF PILOT PLANT FOR  
PREPARATION OF ISO-OCTANE

17 DEC 45 X-38(N)-2



FUEL OIL TANK Capacity 1000 gal  
 WATER TANK Capacity 100 gal  
 INTERMEDIATE TANK Capacity 100 gal  
 CONDENSER Capacity 100 gal  
 SEPARATOR Capacity 100 gal  
 DISTILLATION COLUMN Capacity 100 gal  
 GAS REFINING TOWER Capacity 100 gal  
 GAS REFINER Capacity 100 gal  
 ISO-OCTANE TANK Capacity 100 gal  
 AIR COMPRESSOR Capacity 100 gal  
 NITROGEN COMPRESSOR Capacity 100 gal  
 SAFETY VALVES  
 RELIEF VALVES  
 CONTROL PANELS