

ENCLOSURE (B) 4

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SYNTHESIS OF ISOPARAFFINS  
(In Two Parts)

by

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## ENCLOSURE (B)4

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P A R T ISTUDIES ON THE SYNTHESIS  
OF ISOMERIC HEXANES

by

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Research Period: 1940-1941

SUMMARY

Studies were made of the synthesis of isomeric hexanes, useful as a high octane rating aviation blending fuel, from pinacone,  $(\text{CH}_3)_2\text{-C-(OH)-(OH)-C-(CH}_3)_2$ , and pinacolone,  $(\text{CH}_3)_3\text{-C-CO-CH}_3$ , obtained by the electrolytic reduction of acetone.

By the high pressure catalytic reduction of pinacone with the mixed Copper-Chromium-oxide as catalyst, high yields of tetramethylethane were obtained and the best condition and yield were as follows:

Reaction temperature .....	350°C
Reaction time .....	1 hr
Amount of catalyst .....	10%
Yield .....	87%

Pinacone anhydride was produced from pinacone hydrate with sodium carbonate. This method is simple and gives as good yields as the "Benzole method".

By the high pressure catalytic reduction of pinacolone with Copper-chromium-oxide catalyst, high yields of tetramethylethane were obtained and the best condition and yield are as follows:

Reaction temperature .....	330°C
Reaction time .....	2 hr
Amount of catalyst .....	8%
Yield .....	above 90%

Results of experiments on the production of isomeric hexanes from pinacolone with molybdenum oxide or nickel oxide were as follows:

1. With molybdenum oxide catalyst, cracking occurs and the yield of isomeric hexanes is lowered. 2-2-dimethyl-butane is produced with tetramethylethane.

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2. With nickel oxide catalyst, dehydrating power is not as great and, therefore, unreacted alcohol remains and the produced hexanes are mostly tetramethylethane.

1. When nickel oxide is used with diatomaceous earth or acid clay as catalyst carrier, the yield of hexanes is raised. Using the acid clay catalyst, 2,2-dimethylbutane is also formed as in the case of the molybdenum oxide catalyst. Though the mixed catalyst of molybdenum oxide and nickel oxide shows better yields than either alone, it is less effective than the copper-chromium oxide catalyst.

Continuous hydrogenation of pinacolone takes place readily, and the best conditions and yield of isomeric hexanes having an octane rating of 94 are as follows:

Reaction temperature .....	330-340°C
Space velocity .....	1
Initial hydrogen pressure .....	100 atm
Yield .....	above 80%

I. INTRODUCTIONA. HISTORY OF PROJECT

H. Adkins and R. Connor obtained 17% yield of isopropyl alcohol and 16% yield of isopropyl dimethylcarbinol from pinacolone and 100% yield of 2,2-dimethyl butanol from pinacolone with a Copper-chromium-oxide catalyst at 250°C.

B. Mal'dvskii and T. Nizovkina obtained 65% yield of tetramethylethane from pinacolone with molybdenum sulphide catalyst at 340-350°C.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

Chem. Eng. Capt. S. YAMAGUCHI  
Chem. Eng. Lieut. S. NISHINO

Date begun; April, 1940; Date finished; March, 1941.

II. DETAILED DESCRIPTIONA. DESCRIPTION OF TEST APPARATUS

A standard 2.4L rotating autoclave was used in most cases. In the case of the continuous hydrogenation of pinacolone, the high pressure hydrogenating unit described in Figure 1(B)<sub>4</sub> was used.

B. TEST PROCEDURE

Conventional hydrogenation procedure was used.

C. EXPERIMENTAL RESULTS.

1. The best results of the experiments of hydrogenation of pinacolone with the Copper-chromium-oxide catalyst were as follows:

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Food (B.P. 170-173°C. Mp. 35-38°C)	120gm used
Catalyst (Cu-Cr-O)	10gm
<del>Reaction temperature</del>	<del>350°C</del>
Reaction time	1 hr
Initial hydrogen pressure	100 atm
Upper layer of products	75gm
Properties of product:	
$d_{4}^{18}$	0.6620
$n_{D}^{15}$	1.3765
Distillation data	Boiling range 47-59.5°C
Yield	73gm from 75gm
$d_{4}^{18}$	0.6631
$n_{D}^{15}$	1.3770
Theoretical yield of isohexane	86%
Actual yield of isohexane	62%

2. The best results of the experiments producing isomeric hexanes from pinacoline with the copper-chromium oxide catalyst were as follows:

Food	100gm
Catalyst (Cu-Cr-O)	10gm
Reaction temperature	330°C
Reaction time	1 hr
Initial pressure	115 atm
Products	
Upper layer	81gm
Lower layer	13gm
Physical properties of upper layer	
$d_{4}^{18}$	0.6625
$n_{D}^{15}$	1.3755
Distillation data	47-49°C; 79gm
Theoretical yield	93%
Actual yield	79%

3. Results of continuous hydrogenation of pinacoline were as shown in Table I(B)4.

### III. CONCLUSIONS

Since pinacone is easily produced by electrolytic reduction of acetone which is readily obtainable as a by-product of the fermentation industry, 2,3, di-methylbutane will be easily produced by high pressure catalytic reduction of pinacoline which has been dehydrated by waste sulphuric acid from the electrolytic preparation of pinacone.

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TABLE I(B)4

## HYDROGENATION OF PINACELINE

	Catalyst components		
	Cu-Cr-O	NiO 1 Cu-Cr-O 2 diatomaceous earth 5 acid clay 2	
Reaction temperature, (°C)	330-340	330-340	
Space Velocity	1	1	
Initial-hydrogen pressure atm.	100	100	
Duration, (hr.)	48	112	
Reaction rate. (%)	85	90	
Hydrogen charge, (l/hr)	260	260	
Waste gas, (l/hr)	150	150	
Oil charged, (cc/hr)	197	195	
Oil produced, (cc/hr)	202 (H <sub>2</sub> O 1/5)	200 (H <sub>2</sub> O 1/5)	
Distillation of upper layer	38-62°C 75% d <sub>18</sub> 0.662 d <sub>4</sub> (55-60°C 82%) 62-73°C 10% 0.670 73-115°C 10% loss 5%	34-73°C 90% d <sub>18</sub> 0.560 (unsaturated 5% 55-60°C 83%) 73-110°C 7% loss 5%	198 (H <sub>2</sub> O 1/5) 30-62°C 50% d <sub>18</sub> 0.660 (47-57°C 27%) (57-60°C 45%) 62-75°C 10% 0.675 75-110°C 20%
Yield of tetramethylethane, %	82	83	
mixture unleaded		94	
Octane rating	0.05% Pb added	103	
	0.1% Pb added	110	

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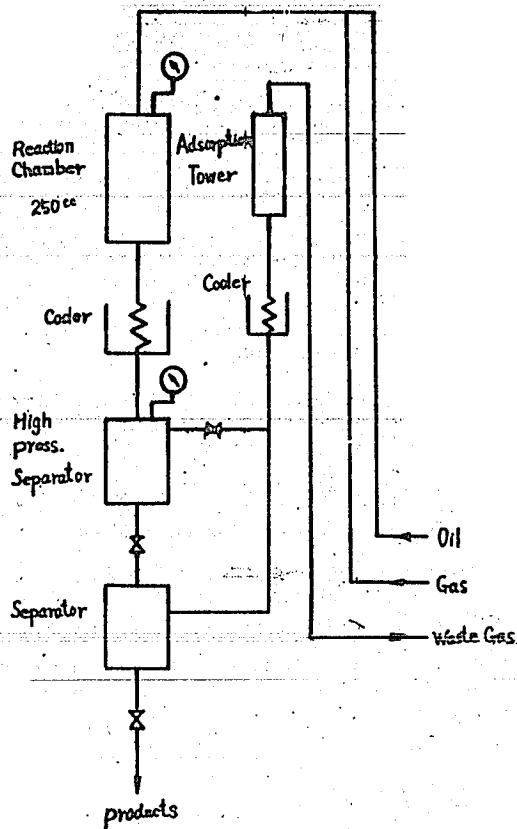


Figure 1(B)4  
FLOW SHEET OF LABORATORY HIGH PRESSURE  
HYDROGENATING UNIT

ENCLOSURE (B)4

PART II

STUDIES ON THE SYNTHESIS  
OF ISODODECANE

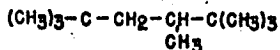
by

Chem. Eng. Lt.  
Comdr. S. NISHINO

Research Period: 1941-1942

SUMMARY

Synthesis of an isododecane having the following formula was tried because of the low vapour pressure and high octane rating of this compound:



Self-condensation, dehydration, and hydrogenation of pinacoline yielded 51% of the pure isododecane mentioned above, having a boiling range of 178-182°C.

Polymerization of 2,3-dimethylbutene (2) by sulphuric acid yielded 85% of another isododecane, having a boiling range of 170-190°C, under the following conditions:

Polymerization temperature ..... 20 ± 5°C  
Concentration of sulphuric acid ..... 81-84%  
Contact time ..... 5-15 min

Isododecane was easily obtained from isododecene by hydrogenation and had an octane number of 93, and vapour pressure of 0.01 kg/cm<sup>2</sup>.

INTRODUCTION

A. HISTORY OF PROJECT

In view of the demand for an aviation fuel having a low melting point, a high octane number, and a low vapour pressure, for use at high altitudes, an attempt was made to synthesize a pure isododecane from the pinacoline condensation and to investigate its physical properties. Moreover, an attempt was also made to synthesize isododecane for use as a safety fuel from the polymerization of isohexene using sulphuric acid.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

Chem. Eng. Capt. S. YAMAGUCHI  
Chem. Eng. Lt. S. NISHINO

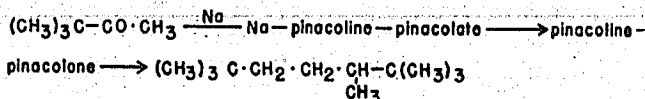


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Date of beginning: April 1941; Date of finish: March 1942.

II. DETAILED DESCRIPTIONA. ISODODECANE BY THE CONDENSATION OF PINACOLINE

From the experiments on the condensation of pinacolone, it appeared that sodium was the most useful of the following: sodium, alkali hydroxides, barium hydroxide and sulphuric acid, in carrying out the reaction:



Details of procedures were as follows:

- a. 1 mol. of pinacolone and 1 mol. of sodium are heated in an autoclave with hydrogen at atmospheric pressure and at 100-110°C for 12 hrs.
- b. The produced yellow solid, sodium-pinacolone-pinacolate, is dissolved in 2 volumes of ether and water is added slowly.
- c. Pinacolone-pinacolate is separated from the upper layer, dried by Glauber's salt and dehydrated by anhydrous oxalic acid to remove hydroxyl radicals.
- d. The product is hydrogenated using mixed copper-chromium oxide catalyst in an autoclave and is purified by distillation in a Podbielniak distillation apparatus.

2. Experimental results:

The yield of isododecane was 51% of the theoretical and the physical and chemical properties of the intermediates were as tabulated in Table II(B)4.

TABLE II(B)4

## PHYSICAL AND CHEMICAL PROPERTIES OF INTERMEDIATES

	Sample		
	Condensate	Dehydrate	Crude Product of Hydrogenation
Specific gravity ( $d_4^{20}$ )	0,8511	0,8283	0.7991
Refractive index ( $n_D^{20}$ )	1.4488	1.4443	1.4358
Iodine value		156.56	9.34
Elemental Analysis	C	80.82	81.77
	H	12.56	14.59
	O	7.53	3.64

Physical and chemical properties of the purified product, isododecane, are tabulated below:

Boiling range	178-182°C
Specific gravity $d_4^{20}$	0.7469
Refractive index $n_D^{20}$	1.4259
Freezing point	-110°C
Vapour pressure	0.009 kg/cm <sup>2</sup>
Octane rating	98%
Elemental analysis	determined      calculated
C%	84.75      84.70
H%	15.18      15.30

B. ISODODECANE BY POLYMERIZATION OF ISOPRENE IN PRESENCE OF SULPHURIC ACID

1. Details of procedures were as follows: 300gm. of sulphuric acid are cooled to -5°C in a three-necked flask fitted with a condenser and a stirrer.

150gm. of 2,3-dimethylbutene-(2) ( $d_4^{20} = 0.7011$ ;  $n_D^{20} = 1.4113$ ) are added slowly. The temperature is kept at 15°C and the mixture is stirred at the rate of 300 revolutions per minute.

2. Experimental results:

The comparative results of experiments in which various concentrations of sulphuric acid were used are tabulated in Table III(B)4.

TABLE III(B)4

EFFECT OF CONCENTRATION OF SULPHURIC-ACID ON THE YIELD OF DIMER OF ISOPRENE

Conc. of H <sub>2</sub> SO <sub>4</sub> (%)	Duration of stirring (min.)	Upper layer produced (gm)	Yield of dimer (%)
82	30	135	no reaction
85	15	140	90%
87	30	140	50%
92	15	141	70%
94	--	143	10%

As shown in Table III(B)4, 85% concentration of sulphuric acid was the most effective of the concentrations studied.

The physical and chemical properties of the final products of hydrogenation of the polymer are tabulated below.

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Specific gravity of product ( $d_{4}^{20}$ )	0.7682
Refractive index of product ( $n_D^{20}$ )	1.4325
Elemental analysis	determined      calculated
C% .....	84.69 .....
H% .....	15.30 .....

Distillation data of product

Boiling range	percent
170-175°C .....	5%
175-180°C .....	30%
180-185°C .....	35%
185-190°C .....	30%
Octane rating	
unleaded .....	93.1
lead added 0.1% .....	105.4
Vapour pressure .....	0.01kg/cm <sup>2</sup>
Flash point .....	54°C
Freezing point .....	below 80°C

C. RESULTS OF PERFORMANCE TEST OF ISODODECANE

Isododecane has a high octane rating and a low vapour pressure and is promising as a safety aviation fuel.

Determinations of octane rating and vapour pressure of blended samples of isododecane and the sub-standard fuel were carried out and the results are shown in Figure 2(B)4.

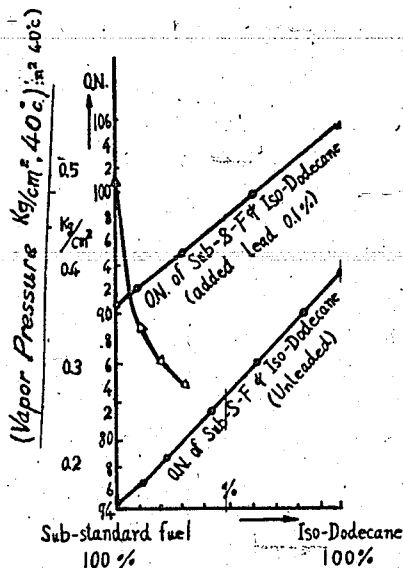


Figure 2(B)<sub>4</sub>

GRAPH OF OCTANE RATING AND VAPOR PRESSURE  
ISODODECANE AND SUB-STANDARD FUEL

ENCLOSURE (B)4

III. CONCLUSIONS

- A. Isododecane was synthesized and its physical properties were determined.
- B. The prepared isododecane was considered to have good blending properties and to be of value as a safety fuel.
- C. The mechanism of the polymerization of isohexene and the condensation of pinacoline were also studied.