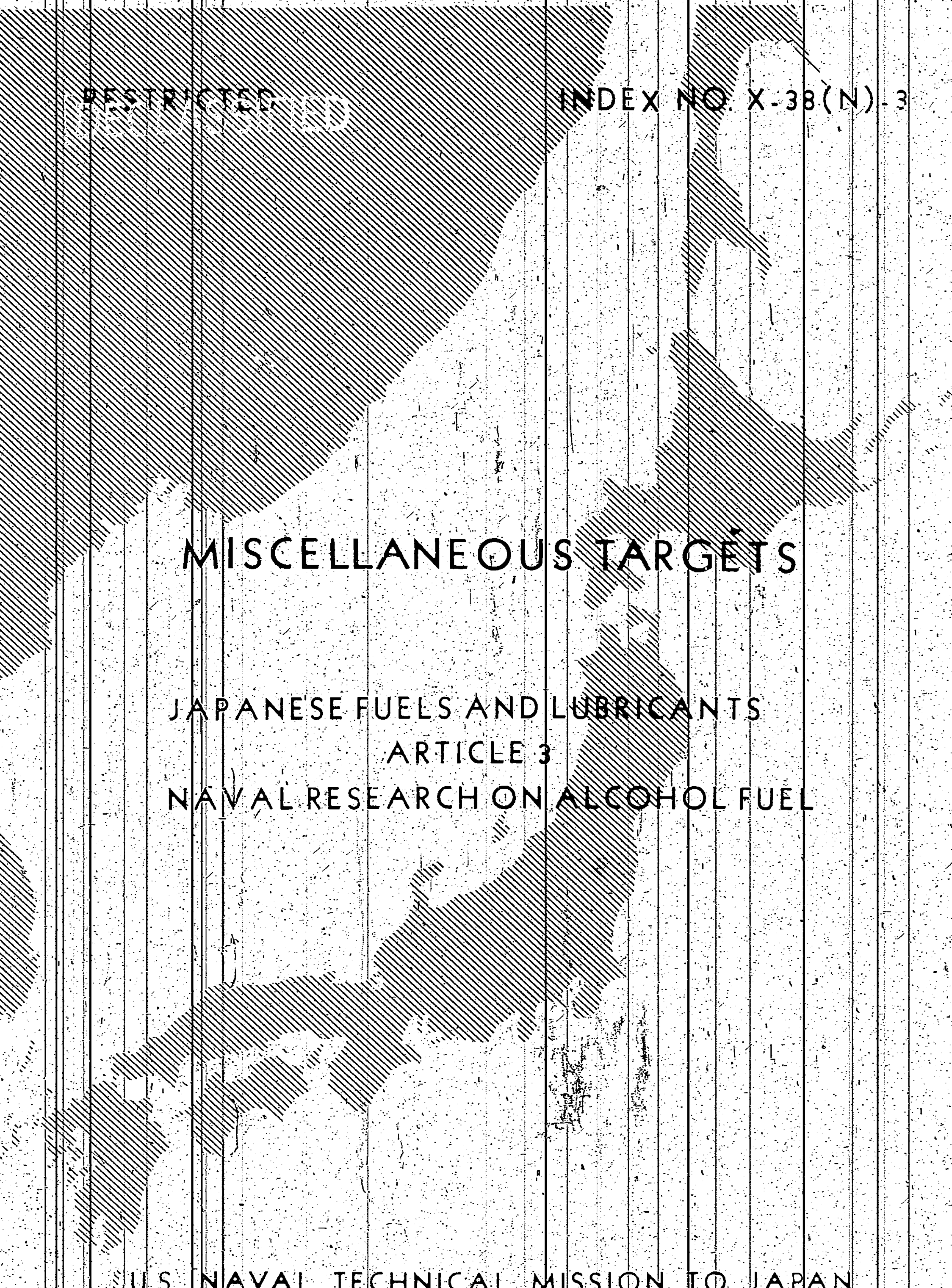
RESTRICTED INDEX NO. X-38(N)-3



MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS
ARTICLE 3
NAVAL RESEARCH ON ALCOHOL FUEL

U.S. NAVAL TECHNICAL MISSION TO JAPAN

NS/rk

U. S. NAVAL TECHNICAL MISSION TO JAPAN
CARE OF FLEET POST OFFICE
SAN FRANCISCO, CALIFORNIA

6 February 1946

RESTRICTED

From: Chief, Naval Technical Mission to Japan.
To : Chief of Naval Operations.

Subject: Target Report - Japanese Fuels and Lubricants, Article 3 - Naval Research on Alcohol Fuel.

Reference: (a)"Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Subject report, covering the alcohol fuel research program of the Japanese Navy as outlined by Targets X-09, X-10 and X-38(N) of Fascicle X-1 of reference (a), is submitted herewith.

2. The investigation of the target and the target report were accomplished by Comdr. G. L. Neely, USNR, Lt. Comdr. C. S. Goddin, USNR, and Lieut. W. H. Millet, USNR, assisted by Ens. E. R. Dalbey, USNR, as interpreter and translator.

C. G. Grimes

C. G. GRIMES
Captain, USN

RESTRICTED

X-38(N)-3

JAPANESE FUELS AND LUBRICANTS
ARTICLE 3
NAVAL RESEARCH ON ALCOHOL FUEL

"INTELLIGENCE TARGETS JAPAN" (DNI) OF 4 SEPT. 1945
FASCICLE X-1, TARGETS X-09, X-10, AND X-38(N)

FEBRUARY 1946

U.S. NAVAL TECHNICAL MISSION TO JAPAN

SUMMARY

MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 3
NAVAL RESEARCH ON ALCOHOL FUELS

Japanese Naval Research pertaining to the production of alcohols from various sources and the application of alcoholic aviation fuels has been investigated. This report deals primarily with the improvement of fermentation techniques, the synthesis of alcohols, and the practical testing of alcoholic aviation gasolines. This program was, for the most part, carried out during the last year of the war and was necessitated by the acute scarcity of conventional aviation gasoline. Interesting findings include the fact that approximately one pound of ethyl alcohol could be produced by fermentation from eleven pounds of sweet potatoes and that, after a year's research, it was found necessary to limit the use of ethyl alcohol fuels to training planes in view of its service performance characteristics.

TABLE OF CONTENTS

LIST OF ENCLOSURES

INTRODUCTION

This report is concerned primarily with research activities at the First Naval Fuel Depot, OFUNA, relative to the fermentation, synthesis and practical testing of various alcohols suitable for use as aviation fuels. A summary of the alcohol research program at the First Naval Fuel Depot has been prepared in English by Engineering Lieutenant Commander T. YAMAMOTO of the Japanese Navy and is submitted herewith as Enclosure (A). Detailed research reports, have been prepared in English specifically for, and reviewed with the Japanese authors by the Petroleum Section of the U.S. Naval Technical Mission to Japan. These reports are submitted as Enclosures (B)1 to (B)17 inclusive.

Since the research reports, drawings and other important documents of the First Naval Fuel Depot had been burned during August, 1945, under the orders of the Director of this institution, it was necessary to recall the Japanese technical personnel to the depot to reconstruct this information from laboratory notebooks, laboratory apparatus, and pilot plant equipment. This work required a period of nearly three months. Although this program was carried on under the supervision of the U.S. Naval Technical Mission to Japan, the reports submitted as Enclosures (A) and (B) do not conform to American standards because of the difficulties encountered in the translation and necessary revision of these articles. However, these reports do indicate with considerable accuracy the quality and extent of the Japanese research.

Additional information, supplementing that of Enclosures (A) and (B), has been obtained through interviews with cognizant personnel of the First Naval Technical Depot, YOKOSUKA, and Kyoto Imperial University. A typical plant for the fermentation of alcohol from sweet potatoes was visited at SHIMABARA, Kyushu, on 18 October, 1945. Related Army research activity at FUCHU has been discussed and the Preliminary Report of the Oil, Chemical, and Rubber Division of the United States Strategic Bombing Survey has also been reviewed.

The alcohol program is of interest since it emphasizes the extent to which Japan was forced to rely on substitute fuels because of the scarcity of aviation gasoline. The necessity for using alcohol and other substitutes is discussed in NavTechJap Report, "Japanese Fuels and Lubricants, Article 2-Naval Research on Aviation Gasoline," Index no. X-38(N)-2. No attempt has been made to evaluate the data which have been collected at the First Naval Fuel Depot. These data are presented as being typical of this particular field of Japanese research activity.

REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA, Kanagawa Prefecture

Shimabara Alcohol Plant of the Kyushu Regional Fuel Department, SHIMABARA, Kyushu.

Kyoto Imperial University, KYOTO.

First Naval Technical Depot, YOKOSUKA.

Japanese Personnel Interviewed:

S. KOMATSU, Ph. D., Civilian Advisor to Department of Fuel Research, First Naval Fuel Depot. (formerly Professor of Biochemistry at Kyoto Imperial University, foremost and very capable chemist of First Naval Fuel Depot).

K. NAKATA, Engineering Commander, Japanese Navy, Head of Aviation Gasoline Engine Test Section, First Naval Fuel Depot. (aeronautical test engineer of better than average capabilities).

T. UMEMURA, Engineering Lieutenant Commander, Japanese Navy, Head of Fermentation Section, First Naval Fuel Depot.

T. YAMAMOTO, Engineering Lieutenant Commander, Japanese Navy, Head of Gasoline Blending Section, First Naval Fuel Depot. (research chemist of better than average capabilities).

Research Assistants of the First Naval Fuel Depot, Whose Names are Included in Individual Japanese Reports:

B. YOSHI, Chief Engineer of the Shimabara Alcohol Plant.

S. TANAKA, Ph. D., Professor of Biochemistry, Kyoto Imperial University.

T. KONDO, Captain, Japanese Navy, Head of Aviation Gasoline Engine Testing, First Naval Technical Depot, YOKOSUKA, (of average capability, but not thoroughly versed in the details of work conducted by his staff).

S. SOMA, Engineering Lieutenant Commander, Japanese Navy, Aviation engine research engineer, First Naval Technical Depot.

Referenced Japanese Reports:

Technical Notes on Research Work, Army Fuel Research Institute, FUCHU.

Additional Referenced Reports:

United States Strategic Bombing Survey, Oil, Chemical and Rubber Division. Preliminary Report, 27 November 1945.

THE REPORT

PART I

FERMENTATION AND SYNTHESIS

A. FERMENTATION OF ALCOHOL

1. Ethyl Alcohol

By the spring of 1944 the shortage of hydrocarbon type aviation gasoline had become so acute that it became necessary to give immediate attention to the use of ethyl alcohol as a substitute. At that time, however, the supply of cane sugar and molasses from Formosa, Java, and the Philippines was decreasing, and it was found necessary to convert butanol plants to the production of ethyl alcohol; to utilize Japanese sweet potatoes and Manchurian grains as raw materials; and to install additional fermentation plants throughout Japan. Research relating to the transition from sugar and molasses to other raw materials was primarily concerned with the selection of proper nitrogen nutriments necessitated by the use of such substances as sweet potatoes and kaoliang. Detailed Japanese reports on these studies are given in Enclosures (B)1, (B)2, and (B)3.

In the meantime, other laboratories were studying these and related problems. At Kyoto Imperial University, for example, a survey was being made of some one hundred and fifty different varieties of sweet potatoes. The purpose of this research was to select the most suitable varieties for use as foods and as sources of alcohol, since the extensive utilization of sweet potatoes as a fuel source would seriously affect the Japanese food supply.

2. Butyl Alcohol

There were several butanol fermentation plants in Japan at the outset of the war. Most of the butanol thus prepared was to be used in the manufacture of iso-octane. The Army and Navy research laboratories investigated independently such subjects as the proper choice of bacteria and the selection of suitable nutriments for the acetone-butanol fermentation. Japanese reports on these studies are given in Enclosure (B)5.

3. Fermentation Plants

During the last year of the war the Japanese government assumed control of many of the alcohol plants throughout the islands. A typical example is the Shimabara Alcohol Plant of the Kyushu Regional Fuel Department. In 1944, with a yield of one pound of alcohol from eleven pounds of sweet potatoes, 3840 kiloliters of alcohol were produced by this plant. A brief description of this plant is submitted as Enclosure (C).

In 1945 the projected use of ethyl alcohol as an aviation fuel for training planes necessitated that many of the butanol plants be converted to the production of ethyl alcohol. In April, 1945, the Japanese Navy ordered the design of a simplified alcohol distillation plant which was to produce 500 kiloliters of alcohol per year from sweet potatoes. It was planned to erect a large number of these plants throughout Japan. Plant design details and test results are given in Enclosure (B)12.

4. Wood Hydrolysis

An interesting activity in connection with the alcohol research program was the investigation of the Bergius wood saccharification process as an alternate alcohol source. Studies on the hydrolysis of pine wood and the fermentation of wood sugar were underway at the First Naval Fuel Depot and are reported in Enclosures (B)4 and (B)2, Part I, respectively. A pilot plant, designed to treat 12 kilograms of wood per day, was constructed in 1945 but never operated. At the same time, Army laboratories were independently investigating the same process.

B. SYNTHESIS OF ALCOHOLS

1. Methyl Alcohol

Several plants producing methanol from carbon monoxide and hydrogen were visited in Japan. Typical of such plants was that of the Oriental High Pressure Company, OMUTA, Kyushu, and that of the Ube Plant of Teikoku Nenryo Kogyo K.K. A flow sheet of the methanol synthesis equipment at the Ube Plant is included in NavTechJap Report, "Japanese Fuels and Lubricants, Article 10- Miscellaneous Oil Technology and Refining Installations", Index No. X-38(N)-10, Enclosure (E). At the Third Naval Fuel Depot in TOKUYAMA a synthetic methanol plant was also in operation. (Refer to Enclosure (F) of above report). As a fuel, methanol-water blends (40-60) were used for auxiliary injection in fighter planes. It was reported that test work on auxiliary injection fluids showed that water was the most effective, methanol next, and ethanol third, but the Japanese Navy standardized upon the 40-60 blend of methanol and water in view of freezing point considerations.

The Oil, Chemical and Rubber Division of the United States Strategic Bombing Survey in a preliminary report has presented the following data relative to the production of methanol in Japan:

Year	Month	Methanol Production Rate (Tons per Year)
1933		100
1940	March	980
1942	March	20,350
1944	March	28,500
1945	March	13,900
1945	July	6,600

Research at the First Naval Fuel Depot was primarily concerned with increasing the yield of methanol and also in utilizing waste gases from the butanol fermentation as a source of raw material for methanol. The latter project was discontinued when the butanol fermentation program was stopped.

2. Butyl Alcohol

The synthesis of butanol, as an intermediate in the production of iso-octane, was extensively investigated by the Navy. A commercial plant with design capacity of 33,000 kiloliters of iso-octane per year from butanol (prepared from acetylene) was in operation in Korea. The First Naval Fuel Depot was actively interested in this project throughout the war. (NavTechJap Report, "Japanese Fuels and Lubricants, Article 2, Index No. X-38(N)-2, Enclosures (B)10,11,12,13).

PART II

SERVICE TESTS OF AVIATION FUELS

A. ENGINE TESTS

The utilization of ethyl alcohol as an aviation fuel had been investigated by the Third Naval Fuel Depot at TOKUYAMA some 15 years before the war, but the tests referred to in this report and carried out during 1944 and 1945 were necessary to supply information upon the use of ethyl alcohol in modern aircraft engines. Experimental work was initiated at the First Naval Fuel Depot, OFUNA, in April, 1944, and at the First Naval Technical Depot at YOKOSUKA in May of the same year. The laboratory work and some of the single and multi-cylinder tests were carried on at OFUNA, but most of the full-scale engine and all of the flight tests were carried out at YOKOSUKA.

The practical result of this one year period of research was the use of ethyl alcohol in training planes for the last three months of the war. It was found that 99% ethyl alcohol could be used in engines of 300 to 500 hp with full-power rating, but for high output engines, it could be used only under conditions of reduced power. In all carburetted engines, 94% ethyl alcohol gave acceleration difficulties; whereas, in solid injection engines, 94% ethyl alcohol could be used for the low-power range. Blends of equal parts of gasoline and 99% ethyl alcohol having the same octane number as the base gasoline could be used in high output engines at reduced power, but a sufficient amount of 99% ethyl alcohol could not be obtained in Japan due to the lack of manufacturing equipment. Blends of gasoline and 94% ethyl alcohol could not be used due to insolubility characteristics.

The first tests concerned the utilization of 10% blends of ethyl alcohol in aviation gasoline. However, with increasing shortages of aviation gasoline, the blending ratio of ethyl alcohol for experimental purposes was increased progressively, until in October of 1944, tests were made relating to the use of straight ethyl alcohol as fuel for training planes (Enclosures (B)11 to (B)17, inclusive). In these test programs many difficulties were encountered with ethyl alcohol due to its low specific heat, its low volatility, its high latent heat of vaporization, its pre-ignition tendencies, and its corrosive action on metals. These difficulties are summarized by Chemical Engineering Comdr. T. YAMAMOTO in Enclosure (A). Significant test results with 99% ethyl alcohol include the following:

1. Volatility of Ethyl Alcohol

In view of the low heat of combustion of alcohol and its high latent heat of vaporization, poor distribution resulted in multi-cylinder engines, causing wide differences in mixture strength in the several cylinders. These volatility aspects also caused difficulties in engine starting and acceleration, particularly at low atmospheric temperatures. (Enclosures (B)11, Part II, (B)12 and (B)17).

In order to improve the volatility characteristics of ethyl alcohol, tests were carried out with ethyl ether, acetone, and gasoline as blending agents, as reported in Enclosure (B)11, Part II. Ethyl ether, although imparting improved volatility characteristics, increased detonation, thus limiting its allowable concentration. A blend of [illegible]% ethyl ether in ethyl alcohol was used practically in training planes, and this concentration, plus the use of asbestos insulators between the cooling fins on the cylinders and the employment of a means for heating the intake gases by the exhaust, decreased the starting difficulties in cold weather (Enclosures (B)12 and (B)17).

2. Auto Ignition of Ethyl Alcohol

Extensive full scale engine tests showed that in spite of the high octane number of ethyl alcohol (92 octane number as determined in the CFR engine) its practical performance in Japanese combat multi-cylinder engines, operated at high boost, was unsatisfactory due to auto-ignition tendencies (Enclosure (B)17). Single cylinder full-scale aircraft engine tests showed that at lean mixtures auto-ignition occurred with straight ethyl alcohol. At rich mixtures the power dropped markedly, and the higher the boost, the narrower the air-fuel ratio band between these two performance limitations (Enclosure (B)11, Part I, Figure 1). This characteristic, coupled with its volatility aspects, prevented the successful utilization of straight ethyl alcohol in multi-cylinder engines of high output.

3. Detonation of Ethyl Alcohol

More than one hundred compounds were investigated for extending the limit of safe operation of anhydrous ethyl alcohol relative to mixture ratio and boost pressure by increasing its anti-knock properties. Of these, tetra ethyl lead was detrimental and di-ethyl selenide was the most effective, but this finding was not pursued due to the shortage of selenium in Japan. (Enclosure (B)12).

Spectrographic investigation of the mechanism of combustion of leaded ethyl alcohol in comparison with leaded iso-octane was carried out as reported in Enclosure (B)13.

B. CORROSIVE PROPERTIES OF ALCOHOL FUELS

1. Ethyl Alcohol

Certain samples of ethyl alcohol proved to be very corrosive to aluminum and brass in carburetor and engine induction systems. The cause of this corrosion was determined, and for its prevention, dibutyl amine and sodium arsenite were proposed as additives by the First Naval Fuel Depot and the First Naval Technical Depot, respectively, and the latter was actually used (Enclosure (B)12).

Ethyl alcohol caused the inside of steel drums to rust, and synthetic resin varnishes of vegetable oil base were found to be the most practicable. (Enclosure (B)16).

2. Methyl Alcohol

Magnesium and magnesium alloys were very subject to corrosion by anhydrous methanol. The addition of an alkaline solution of potassium chromate was found to be effective as an inhibitor. (Enclosure (B)15).

ENCLOSURE (A)

ENCLOSURE (A)

SUMMARY OF THE ALCOHOL RESEARCH PROGRAM AT THE FIRST NAVAL FUEL DEPOT

by

CHEM. ENG. LIEUT. COMDR.
T. YAMAMOTO

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (A)

I. INTRODUCTION

Studies on production of methanol, ethanol, and other alcohols were started prior to 1930 by the Navy. No attention was paid to the use of these alcohols for aviation fuel, since there was no demand for high octane fuel at that time. Owing to the rapid development of aircraft engines, and expansion of the air forces, an urgent demand for high octane fuel occurred in 1935. Consequently, research in fuel chemistry, and especially research on synthetic fuel, was greatly expanded by the Navy. In 1940, several alcohol factories were actually operated, producing both synthetic and fermented alcohol. Ethyl alcohol was first used as aviation fuel in 1945 to meet the shortage of natural gasoline.

II. GENERAL SUMMARY

The production of methanol on a semi-industrial scale was started in 1934 at the Naval Fuel Depot, TOKUYAMA. Methanol was first employed as a raw material in the manufacture of explosives, but in 1940, the use of methanol for aviation fuel was adopted to increase the output of aeroengines by taking advantage of its extremely high latent heat of vaporization. Since the supply of 100 octane fuel was scarce, the use of methanol was extended to various types of aircraft engines.

Research investigations were made to increase the yield of methanol by increasing space velocity and employing different catalysts. A copper catalyst gave a high space time yield but had low heat resistance. A zinc and copper chromite catalyst having high heat resistance was studied, and satisfactory results were obtained in commercial plants with its use. Studies were extended to the synthesis of methanol from carbon dioxide and hydrogen, waste gas from butanol fermentation. (Enclosure (B)7.) Almost the same conditions as for the water gas process, a space time yield of 0.5, were obtained. This process, however, was not developed commercially because the butanol fermentation program was stopped. The corrosion of the fuel system in aeroengines caused by the use of methanol was studied, and it was found that corrosion could be prevented by addition of 5% by volume of sodium bichromate and 0.1% caustic soda solution. (Enclosure (B)15).

In order to obtain isobutene as a raw material for the synthesis of iso-octane, the synthesis of isobutanol from water gas was studied, but the results were unsatisfactory. (Enclosure (B)10).

The cracked gas from petroleum, the hydration of propylene, butene, and isobutene in the presence of sulphuric acid ($H_2SO_4 \cdot 5H_2O$) was investigated. In spite of success in obtaining yields of the corresponding alcohols close to theoretical, this process was not developed on commercial scale. (Enclosure (B)8).

In 1937 a plant for synthesis of normal butanol from acetylene was planned at the Chosen Chisso Hiryo Co. (Korean Nitrogen Fertilizer Co.) to produce 60,000 kl of iso-octane per year. Research on this process was started independently at TOKUYAMA and at Korea, and continued up to the end of the war at the First Naval Fuel Dept. The butanol yield was more than 85% of theoretical. (Enclosure (B)10, Article 2 of this series). A plant based on this process was installed at KONAN, North Korea, with a capacity of 30,000 kl of iso-octane per year.

Before the war, butanol fermentation factories had been constructed to supply raw material for production of 100,000 kl of iso-octane per year. To improve the techniques of these factories, research was undertaken on new types of

ENCLOSURE (A)

fermentation bacteria. A strain superior to that of Weizmann was discovered. (Enclosure (B)5, Part II, Part III). Twenty per cent of butanol and ten per cent of acetone were obtained from sugar molasses. (Enclosure (B)5, Part I and (B)5, Part IV). Butanol could be produced in yields of only 20% by weight of sugar, whereas ethyl alcohol could be obtained in yields of 45%.

In 1944, the serious shortage of aviation gasoline forced the use of alcohol directly in aviation fuel, and the butanol fermentation factories were converted to produce ethanol. At first, the source of raw material for alcohol was cane sugar and molasses from Formosa, the Philippines, and Java; then it was necessary to change to grains from Manchuria and sweet potatoes from Japan. (Enclosures (B)1, (B)2, Part I and Part III.) Ethanol had been previously produced mainly from sweet potatoes by the amylo-process in Japan. For the alcohol-aviation program, however, the "Koji"-process was adopted which had been used formerly by the "Sake" brewers. The "Koji"-process when applied to grains and sweet potatoes gave a high yield of alcohol. (Enclosure (B)2, Part IV).

A simplified alcohol distillation plant was designed for production alcohol at "Sake" breweries. (Enclosure (B)6). Since food supplies were becoming critical, however, investigations of alternative sources of alcohol were necessitated, and in this connection the saccharification of wood cellulose and the hydrolysis of pine wood were studied. (Enclosure (B)4 and (B)2, Part I).

Many difficulties were encountered when alcohol was used in aviation fuel due to its low volatility, low anti-knocking properties, and corrosive action on metals. Ethyl ether and acetone were examined for increasing the volatility of alcohol. (Enclosure (B)11, Part II). The ethyl ether was produced from alcohol in the presence of acid clay at 200°C in a vapor phase. The yield was 90% of the alcohol. Acetone was also obtained from alcohol in yield of 90% with a mixed catalyst of zinc and iron oxides at 430°C. Ethyl ether was actually manufactured and used for facilitating starting and acceleration of training planes in cold weather. (Enclosures (B)9 and (B)12).

The uniform distribution of alcohol fuels to each cylinder of radial type aeroengines with carburetors was difficult, and tests were made in full-scale engines on alcohol-acetone, alcohol-ether, and other blended fuels. (Enclosures (B)11, Part II and (B)17). Acetone increased the volatility and anti-knocking properties of alcohol, but ethyl ether did not give satisfactory results.

In order to overcome the low anti-knocking properties and preignition caused by alcohol, as observed in the test with a mono-cylinder testing engine, many anti-detonants were studied, but none were successful.

The combustion characteristics of hydrocarbons and alcohols were studied spectroscopically, but these investigations had not been completed at the end of the war. (Enclosure (B)13).

To prevent corrosion of engine accessories, sodium arsenite and dibutyl amine were proposed as additives by the First Naval Technical Depot and the First Naval Fuel Depot respectively, and the former was actually used. (Enclosure (B)12). It was found that the corrosive action of alcohol on metals was caused by impurities such as chloride and copper ions present in the alcohol. (Enclosure (B)14.) To prevent the corrosion of alcohol tanks and containers, several types of paints were tested, and it was found that a paint made from synthetic resin and vegetable oil gave the best result. (Enclosure (B)16).

RESTRICTED

ENCLOSURE (B)

ENCLOSURE (B) 1

STUDIES ON ETHANOL FERMENTATION

by
TOSHINOBU ASAI,
Professor of Tokyo Imperial University

KAZUO SHIBAZAKI, Assistant

Research Period: 1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)1

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)1

SUMMARY

Various oil cakes were decomposed with protein decomposed fungi, and the decomposed matter was used as the nutriment for the alcohol fermentation of sugar.

The following significant results were obtained:

Nutriments	Percent (based on sugar) %	Ethyl-alcohol %	Fermenting time (days)
Soya bean cakes	3	86.4	3
Peanut bean cakes	5	92.7	4
Cotton seed cakes	3.5	87.0	4
Castor bean cakes	14	88.2	3
Cupura seed cakes	20	88.2	3
Pupa oil cakes	14	88.2	4

Note: In all cases the sugar concentration is 11.6%.

I. INTRODUCTION

A. History of Project

It was hoped that soya bean cakes or other oil cakes might be used as nutriments in the alcohol fermentation of sugar, but the nitrogen is mostly in the protein form, which is unsatisfactory for use as nutriments.

Decomposition of the cakes by acid or alkali is difficult because of the apparatus and materials required. Therefore, it was thought that various oil-cakes might be decomposed by protein decomposed fungi, and the decomposed matter used as nutriments for the alcohol fermentation of sugar.

B. Key Research Personnel Working on Project

Kazuo SHIBAZAKI

II. DETAILED DESCRIPTION

A. A protein of soya bean cakes is decomposed by bacteria, in the following manner:

A 2gm sample of powdered soya bean cakes and 10cc water in a 40cc erlenmeyer flask was digested for an hour under 13.6 kg/cm^2 pressure. After digestion it was innoculated with Bac. mesentericus Trevisan var. Proteolyticus II nov. var., and kept at 37°C. The sample was analyzed after 24 hours, 36 hours, and 48 hours, and the results obtained are shown in Table I(B)1.

B. The ethanol fermentation of sugar was studied, using the decomposed products of soya bean cakes as the nutriments.

The details of the test were as follows:

Powdered soya bean cakes (3 or 5% for total sugar) were diluted with five times as much water as the weight of soya bean cakes in a 40cc erlenmeyer flask. This was digested for an hour under 13.6 kg/cm^2 pressure. After digestion it was innoculated with Bac. mesentericus Trevisan var. Proteolyticus II nov. var., and cultivated at 37°C for 48 hours. After this

ENCLOSURE (B)

treatment, the decomposed products and 18gm of sugar in a 200cc erlenmeyer flask were diluted to a total volume of 150cc, and digested for 15 minutes under 6.8 kg/cm^2 pressure.

After cultivation at 30°C., the results tabulated in Table II(B)1 were obtained.

C. Studying the ethanol fermentation of sugar by the same method, but using the decomposed products of various oil cakes as the nutriments, the results tabulated in Table III(B)1 were obtained.

III. CONCLUSIONS

A. Using the decomposed products of soya bean cakes as the nitrogen source, (1.5% or 3.0%, vs. total sugar), and then fermenting mash of 11.58% sugar concentration for five days, the yield of alcohol obtained was 86% of the theoretical value. On the contrary, using 3% non-treated soya bean cakes (vs. total sugar), the yield of alcohol obtained was only 32.1% of the theoretical value for five days.

B. Using the decomposed products of other oil cakes as the nitrogen source, the results were as shown on Table III(B)1.

It is possible to increase the yield of alcohol and to shorten the fermenting time compared with contrast (using non-decomposed product of soya bean cakes as nitrogen source.).

C. The results of these findings have not been extended to commercial practice.

ENCLOSURE (B)1

Table I(B)1
NITROGEN ANALYSIS OF DECOMPOSED MATTER

Time of Culture	pH	Ammonia Type Nitrogen (%)		Amino Type Nitrogen (%)	
		In Soya Bean Cakes	Total	In Soya Bean Cakes	Total
0	5.7	0.165	2.30	0.185	2.59
24	6.4	0.250	3.51	0.685	9.56
36	7.4	0.635	8.80	0.850	11.83
48	7.8	1.110	15.45	1.475	20.51

Table II(B)1
SOYA BEAN CAKES IN ALCOHOL FERMENTATION

Soya Bean Cakes for Sugar (%)		pH	cidity (cc)	Sugar (%)		Alcohol Produced (%)	Fermentation	
				Rested	Fermented		Percent	Time*
Digested	3	3.9	2.24	7.94	31.4	2.5	32.1	—
	5	3.8	2.61	2.32	80.0	4.4	56.3	—
Bacteria Treatment	3	3.8	2.79	0.05	100	6.7	86.4	5
	5	3.8	2.65	0.05	100	7.0	89.8	3.5

Note. In all cases total sugar is 11.58% *Days

Table III(B)1
YIELDS FOR VARIOUS CAKES

	Amount Total Sugar Used (%)	Yield of Alcohol*	Ferment Time (days)
Peanut oil cakes	5	92.7	4
Cotton seed oil cakes	3.5	87.0	4
Castor bean cakes	14	88.2	3
Cupura seed cakes	20	88.2	3
Pupa oil cakes	14	88.2	4

* Percent of theoretical value

Table IV(B)1
VARIOUS OIL CAKES AS NITROGEN SOURCE IN SUGAR FERMENTATION

Oil Cakes	Total N %	Treatment	Cakes based on Sugar %	Total Sugar (gm)	pH	Acidity cc	Rested Sugar (gm)	Fermented Sugar(%)	Produced Alcohol %	Fermentation %	Fermented Time(days)
Peanut Oil Cakes	6.61	Digest only	3	12.44	3.6	2.24	7.78	37.46	2.1	25.41	
			5	12.44	3.6	2.25	5.80	53.34	3.5	41.85	
		Bacteria	3	12.44	3.3	2.52	1.38	88.90	5.3	62.78	5
			5	12.44	3.4	2.54	0.22	98.23	7.8	92.69	4
Cotton Seed Oil Cakes	3.72	Digest only	3.5	12.44	4.0	2.12	7.82	37.14	1.6	19.43	
			7	12.44	3.9	2.24	5.25	57.79	3.5	41.85	
		Bacteria	3.5	12.44	3.4	2.42	0.06	99.47	7.3	86.69	4
			7	12.44	3.4	2.70	0.06	99.47	7.4	88.19	2.5
Castor Bean Cakes	5.43	Digest only	7	12.44	4.1	2.20	8.16	34.45	2.1	25.41	
			14	12.44	4.0	2.98	5.42	56.43	3.0	35.87	
		Bacteria	7	12.44	3.2	2.60	3.08	75.24	4.8	56.80	5
			14	12.44	3.6	3.08	0.01	100.00	7.4	88.19	3
Cupura Oil Cakes	29.1	Digest only	10	12.44	4.2	1.90	7.88	36.65	2.5	29.89	
			20	12.44	4.1	2.24	5.21	58.12	3.7	43.34	
		Bacteria	10	12.44	3.6	2.52	0.25	97.99	4.8	56.80	5
			20	12.44	3.5	2.42	0.01	100.00	7.4	88.19	3
Pupa Oil Cakes	4.85	Digest only	7	12.44	4.0	2.24	8.47	31.91	1.8	20.93	
			14	12.44	4.0	2.80	6.05	51.36	2.9	34.38	
		Bacteria	7	12.44	3.2	3.18	1.74	86.01	5.2	61.29	5
			14	12.44	3.4	2.42	0.01	100.00	7.4	88.19	4

ENCLOSURE (B) 2

RESEARCHES ON ALCOHOL FERMENTATION

(In Four Parts)

by

CHEM. ENG. LT. COMDR. T. UMEMURA
CHEM. ENG. LIEUT. S. NAKAMURA
CHEM. ENG. SUB-LIEUT. T. FUKUZAKE
CHEM. ENG. LIEUT. Y. NODA
CHEM. ENG. LIEUT. M. TAKAHASHI

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

Research Period: 1944-1945

ENCLOSURE (B)2

LIST OF TABLES AND ILLUSTRATIONS

PART I

PART II

PART III

PART IV

ENCLOSURE (B)2

PART I

by

CHEM. ENG. LT. COMDR. T. UMEMURA

CHEM. ENG. LIEUT. S. NAKAMURA

Research Period: 1945

Ethanol fermentation of wood sugar produced by the Bergius method was studied. Production by Bergius method has not progressed far, since only 3 samples were studied. It was intended to continue this study, but time was not available.

Three samples were prepared in the following manner:

1. HCl in wood sugar neutralized with $BaCO_3$.
2. Ba in above mentioned sample was precipitated with H_3PO_4.
3. PO_4 in above sample was precipitated with $Ca(OH)_2$.

The sugar concentration of each sample was ca. 7%.

Rice bran (2%) and $(NH_4)_2SO_4$(0.7% based on total sugar) were used as a nitrogen source.

The percentage of produced alcohol in wood sugar mash was ca. 2.8-3.0%, and percentage of fermentation for theoretical value was ca. 72-78%.

The results of sample No.3 were most excellent, and sample No.2 was next. This data has not been kept because it was intended to repeat the experiment. No further data are available.

No commercial application of the Bergius process for obtaining alcohol from wood has been undertaken.

A photograph of the pilot plant used in fermentation tests is shown in Figure 1(B)2.

ENCLOSURE (B)2

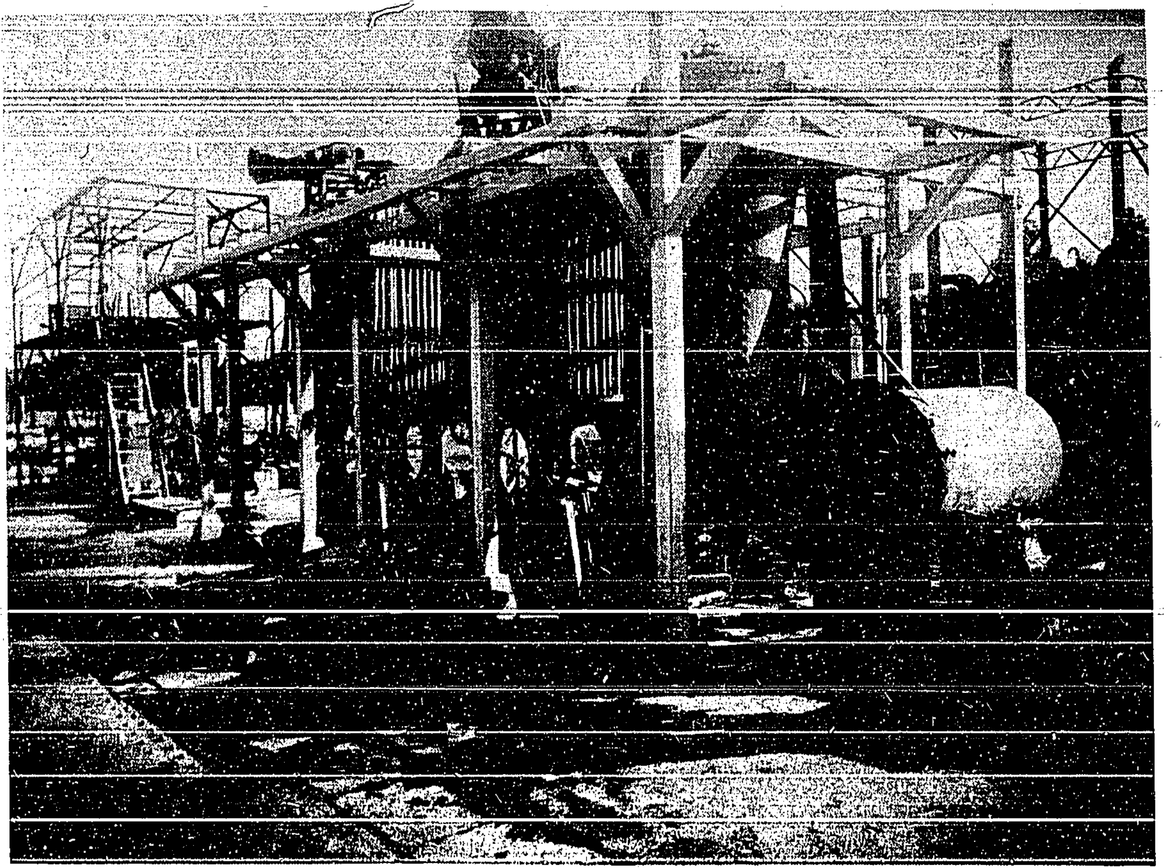


Figure 1(B)2
PILOT PLANT FOR FERMENTATION

ENCLOSURE (B)2

PART II

by

CHEM. ENG. LT. COMDR. T. UMEMURA

CHEM. ENG. SUB-LIEUT. T. FUKUZAKO

Research Period: 1945

SUMMARY

Flask-tests were conducted with the object of determining whether or not corn and kaoliang can be used for raw materials of alcohol manufacture by Koji process without the use of a nitrogen source. The following significant results were obtained:

Corn showed good results (a) for the manufacture of Koji, (b) for saccharizing power of Koji and (c) as a raw material of fermentation.

The saccharizing power of unrefined kaoliang is inferior to that of corn, and it was not found to be a satisfactory raw material for fermentation; that is to say, the fermentation was slow and subject to putrefaction. However, it may be possible that kaoliang can be used for alcohol manufacture.

I. INTRODUCTION

A. History of Project

Because of the increasing importance of alcohol as an aviation fuel in Japan, it was deemed necessary to study whether or not corn and kaoliang could be used as the raw materials of alcohol manufacture. It was expected that a large amount of corn would be imported from the continent. The work was begun by investigating the fermentation by the Koji process.

B. Key Research Personnel Working on Project

Chemical Engineering Sub-Lieut. T. FUKUZUKO

II. DETAILED DESCRIPTION

A. Test Procedures

1. Mold and Yeast Used for Test

For Koji: Aspergirus Oryzae (manufactured at TANAKAYA in KYOTO).

Yeast: Toki-yeast.

ENCLOSURE (B)2

2. Method of Analysis

Acid Value: Reported as cc of 0.1 N NaOH for neutralization of 10cc of sample.

pH: pH test paper (manufactured by Toyo Filter Paper Co. Ltd.)

Saccharide: Fixed quantity determined by Lehn's method.

Alcohol (Ethanol): The alcohol content of the distillate of 100cc sample was determined.

3. Manufacture of Koji

Koji was prepared in a large Petri dish in a thermostat maintained at 33°C. The Koji were removed after 48 hours without any additional treatment.

4. Soaking Apportionment:

Yeast mash*..........................	100cc
Koji..................................	40gm
Raw materials.........................	200gm
Water.................................	1300cc

Note: Yeast mash: Mash of rice was saccharized previously by Koji of bran. 1% lactic acid was added and then pure culture yeast mash (about 10%) was added to this mash. The mixture was then fermented.

B. Test of Koji for Saccharizing Power

1. Preparation of Enzyme

Twenty grams of Koji were added to 200cc of water (35°C) and kept for 2 hours in a thermostat at 35°C. This enzyme solution was filtered. Ten cc of above enzyme solution were added to 50cc of 2% starch solution and then saccharized for 2 hours in a thermostat at 55°C. A portion of this saccharized liquid was used for analysis. The quantity of saccharide was analized by Lehn's method and was recorded as glucose.

2. Experimental Results

Table I(B)2 shows the results of the saccharizing power test, and Table II(B)2 shows the results of the analysis of the products of the fermentation of Tests No. 7 and No. 6.

III. CONCLUSIONS

A. As shown in Tables I(B)2 and II(B)2, corn has a rapid fermentation of about 80%. This indicates that corn is a good source of Koji.

B. In the case of kaoliang, the rate of fermentation is slow, acid value is high, and putrefaction occurs. Kaoliang does not appear to be a good source of Koji. This may be due to the effect of tannin which is included in kaoliang bran. If this is the case, it will be necessary to test refined kaoliang.

ENCLOSURE (B)2

C. Industrial application of the use of kaoliang as a raw material will necessitate the following studies:

1. The steaming method.
2. Development of a satisfactory crusher.
3. The effect of steaming and crushing on soaking time.
4. The kaoliang mash is very viscous and the sugar content cannot be concentrated by high pressure steaming. Some other method must be devised for concentrating the sugar.

Table I(B)2
SACCHARIZING POWER TEST IN ALCOHOL FERMENTATION

Test No.	Apportionment of Koji	Enzyme Solution			Glucose in 60cc Saccharized Liquid (gm)	Quantity of Glucose Saccharized from Starch (gm)	Total Sacch. quantity in the Starch Soln. 50cc (gm)	The Rate of Saccharizing power (%)
		Acid Value (cc)	pH	Glucose (gm/10cc)				
1	Bran 10: Chaff 5	1.45	6.4	0.0540	0.5568	0.5028	0.8796	57.2
2	Corn 5: Bran 3: Chaff 4	1.10	5.8	0.0627	0.5376	0.4743	0.8796	53.9
3	Corn 10: Chaff 1	1.15	5.4	0.1785	0.7046	0.5261	0.8796	59.3
4	Corn 10: Chaff 1	0.90	5.6	0.1126	0.6221	0.5095	0.8796	57.8
5	Only Corn (Sifted to 1 mm mash)	0.90	5.4	0.0874	0.7478	0.5604	0.8796	75.2
6	Kaoliang 10: Chaff 1	0.80	5.3	0.1220	0.6053	0.4833	0.8796	54.9
7	Kaoliang 10: Chaff 1	0.70	5.4	0.0927	05784	0.4857	0.8796	55.2

Table II(B)2
ANALYSIS OF THE PRODUCTS OF ALCOHOL FERMENTATION

Test No.		Before Fermentation			Time of Total Ferment (hr)	Volume (cc)	Acid Value	pH	Total Residual Glucose	Ethanol (Vol %)	Rate of Consumption of Saccharide(%)	Rate of Ferment. (%)
		Acid value	pH	Total glucose (%)								
4	Corn-<u>Koji</u> Corn-Mash	3.6	4.7	11.81	64	1400	5.4	4.4	1.076	6.0	90.0	79.0
6	<u>Kaoliang-Koji</u> <u>Kaoliang-Mash</u>	2.8	4.7	11.9	93	1450	11.0	3.6	1.213	4.7	89.4	61.4

Note: Total glucose before fermentation includes saccharides from yeast mash. (17.75%)

ENCLOSURE (B)2

PART III

by

CHEM. ENG. LT. COMDR. T. UMEMURA

CHEM. ENG. LIEUT. Y. NODA

Research Period: 1945

SUMMARY

The conditions of ethanol fermentation when corn is digested at low pressures were investigated. The following significant results were obtained:

1. Corn was crushed to a 3mm-mesh powder, and digested for 7 hr under 1.75 kg/cm^2 pressure. When HF was added to this corn mash (ratio of HF to corn is 1/20000), the fermentation was 81% of the theoretical value.

2. Fine powder was not suitable for fermentation, since the pipes were clogged by the formation of dumplings which interfered with the fermentation.

3. The results shown in Table III(B)2 were obtained.

I. INTRODUCTION

A. History of Project

In Japan, cultures of aspergillus oryzae supply the diastase for the saccharification of grain starch in the manufacture of the drink known as koji made from rice, or take koji made from wheat bran.

Before saccharification, it is digested for sterilization and conversion of the starch in the grain by heating under pressure. When the corn is digested under low pressure, the conditions of ethanol fermentation are unsatisfactory. The purpose of this experiment was to investigate these conditions. In the original process, the procedure for the fermentation of grain was carried out in the following stages:

1. Conversion of the starch by heating under pressure.
2. Saccharification of the starch by diastatic action of the mould.
3. Fermentation of the sugar by yeast.

Figure 2(B)2 is a simplified flow sheet of the ethanol fermentation of corn.

B. Key Research Personnel Working on Project

Chem. Eng. Lt., Y. NODA

ENCLOSURE (B)2

II. DETAILED DESCRIPTION

A. The First Experiment

1. Material of Mash and its Analysis.

Corn	quartered
Starch value	61.24%
Directly reduced sugar	4.27%

2. Condition of Digestion.

Time	11 hrs
Pressure	1.75kg/cm^2

3. Condition of Saccharification. Saccharification was performed with take koji (aspergillus oryzae), the temperature of saccharification was 55°C, and the time of saccharification was 2.5 hr.

4. Material of Yeast. Dried strips of sweet potatoes were used and the conditions were as follows:

Alcohol	3.4%
Acidity	5.45 cc/10cc mash
pH	4.2
Volatile acid	0.1
Balling	6.5

5. Material of Koji. The material composition was as follows:

Dried strips of sweet potatoes	40%
Pupa oil cakes	10%
Wheat bran	20%
Rice hulls	30%
Total	100%

This koji material was cultivated with Aspergillus Oryzae.

6. The yield of alcohol was 45.8% of the theoretical and the results are tabulated in Table IV(B)2.

B. The Second Experiment

1. Material of Mash. The same corn as in previous experiment.

2. Conditions of Digestion.

Time	7 hr
Pressure	1.75 kg/cm^2

3. Condition of Digestion.

Temperature	55°C
Time	2 hr

4. Material of Yeast. The yeast was the same as in the previous experiment and was used under the following conditions.

Alcohol	2.4%
Acidity	5.3cc/10cc mash
pH	4.6
Volatile acid	0.3
Balling	4.6

5. Material of koji. Same as in previous experiment.

6. The yield of alcohol was 45.4% of the theoretical value and the results are tabulated Table V(B)2

C. The Third Experiment.

1. Material of mash. The same corn as in previous Experiment.

2. Condition of Digestion.

Time	6 hr
Pressure	1.75 kg/cm^2

3. Condition of Saccharification.

Temperature	55°C
Time	2.5 hr

4. Material of Yeast. It is the same as in previous experiment and was used under the following conditions:

Alcohol	2.6%
Acidity	4.7cc/10cc mash
pH	4.4
Volatile acid	0.15
Balling	8.57

5. Material of koji. It is the same as mentioned above.

6. The yield of alcohol was 63.4% of the theoretical and the results are tabulated in Table VI(B)2

D. The Fourth Experiment.

1. Material of mash and condition of digestion were the same as mentioned above.

2. Condition of saccharification.

Temperature	55°C
Time	2.33 hr

3. Material of Yeast. It is the same as mentioned above and was used under the following conditions:

Alcohol	2.8%
Acidity	4.9 cc/10cc
pH	4.6
Volatile acid	0.1
Balling	7.77

4. Material of Koji. Material components are the following:

Corn..80%
Rice hulls..................................20%

5. The Result. In this experiment, HF(40% aq. soln.) was added to the mash, and the ratio of HF/mash was about 1/20000. The yield of alcohol was 81.3% of theoretical and the results are tabulated in Table VII(B)2

I. CONCLUSIONS

ing HF in the fermentation, good yields of alcohol were obtained by the low ssure fermentation process.

Table III(B)2
SIGNIFICANT RESULTS OF CORN FERMENTATION AT LOW PRESSURES

(Pressure: 1.75kg/cm^2)

. of xp.	Degree of crush	Digested time, hr.	Added ratio of HF	Total sugar	Rested sugar	% of alcohol	% of fermentation
1	Quartered	11	0	11.69	4.59	3.5	45.8
2	Powder	7	0	12.38	3.55	3.6	45.4
3	Powder	7	0	10.05	2.13	4.1	63.4
4	Powder	7	1/2000	10.33	1.42	5.4	81.3

ENCLOSURE (B)2

Table IV(B)2
CORN FERMENTATION AT LOW PRESSURE

(Corn Was Quartered)

Time (hr)	pH	Acidity (cc)	Sugar (gm)	Temperature (°C)	Alcohol (%)
0	5.0	4.0	11.685	28	0
6	4.6	5.5	11.325	30	0.8
18	4.4	8.5	8.626	32	2.5
24	4.0	10.5	7.135	34.5	3.0
30	3.8	11.7	6.235	34.5	3.3
36	3.8	12.6	5.827	34.5	3.3
42	3.7	13.7	5.625	34.5	3.4
48	3.7	15.0	5.472	33	3.5
54	3.5	15.5	4.852	34	3.5
66	3.4	15.6	4.657	34	3.5
72	3.4	15.7	4.640	33	3.5
78	3.4	16.0	4.640	33	3.5
84	3.4	17.2	4.590	33	3.5

Table V(B)2
CORN (POWDER) FERMENTATION AT LOW PRESSURE

(Concentration of Mash: 12.38%)

Time (hr)	pH	Acidity (cc)	Sugar (gm)	Temperature (°C)	Alcohol (%)
0	5.2	2.8	12.38	29.5	0
6	4.8	4.5	10.21	31	0
12	4.6	5.5	7.34	35	2.9
18	4.6	6.9	7.08	36	3.0
24	4.4	8.6	6.73	36	3.5
30	4.4	10.4	5.46	36	3.5
36	4.4	12.0	5.23	36	3.5
42	4.2	13.0	4.97	35	3.5
48	4.2	13.3	4.03	35	3.6
54	3.8	14.0	4.02	35	3.6
60	3.7	14.8	3.97	34	3.6
66	3.6	15.4	3.94	34	3.6
72	3.6	15.4	3.92	34	3.6
78	3.2	15.6	3.62	34	3.6
84	3.4	16.4	3.55	34	3.6

ENCLOSURE (B)2

Table VI(B)2
CORN (POWDER) FERMENTATION AT LOW PRESSURE

(Concentration of Mash: 10%)

Time (hr)	pH	Acidity (cc)	Sugar (gm)	Temperature (°C)	Alcohol (%)
0	5.6	3.2	10.00	27.5	0
6	5.4	4.1	9.55	28.0	0.4
12	4.8	5.9	6.83	31.0	2.6
18	4.0	6.0	5.15	35	2.9
24	3.8	6.5	3.73	35	3.6
30	3.6	7.3	2.87	34.8	3.7
36	3.6	8.6	2.51	34.8	3.9
42	3.4	8.9	2.26	34.8	4.1
48	3.4	9.3	2.17	34.5	4.1
54	3.2	9.5	2.15	34.5	4.1
60	3.2	10.7	2.14	34.2	4.1
66	3.2	11.2	2.13	34.2	4.1

Table VII(B)2
EFFECT OF HF ON CORN FERMENTATION AT LOW PRESSURE

Time (hr)	pH	Acidity (cc)	Sugar (gm)	Temperature (°C)	Alcohol (%)
0	5.4	3.4	10.33	27.3	0
0	5.2	4.1	9.97	28	0.2
12	5.0	4.4	4.95	31	2.6
18	4.6	4.5	4.26	35	3.5
24	4.4	4.6	3.11	36	4.6
30	4.3	4.3	2.13	36	5.4
36	4.2	4.2	1.68	36	5.4
42	3.8	3.8	1.55	36	5.4
48	3.8	3.8	1.49	36	5.4
54	3.6	6.3	1.44	35.5	5.4
60	3.4	6.5	1.43	35	5.4
66	3.4	6.9	1.42	34.5	5.4

ENCLOSURE (B)2

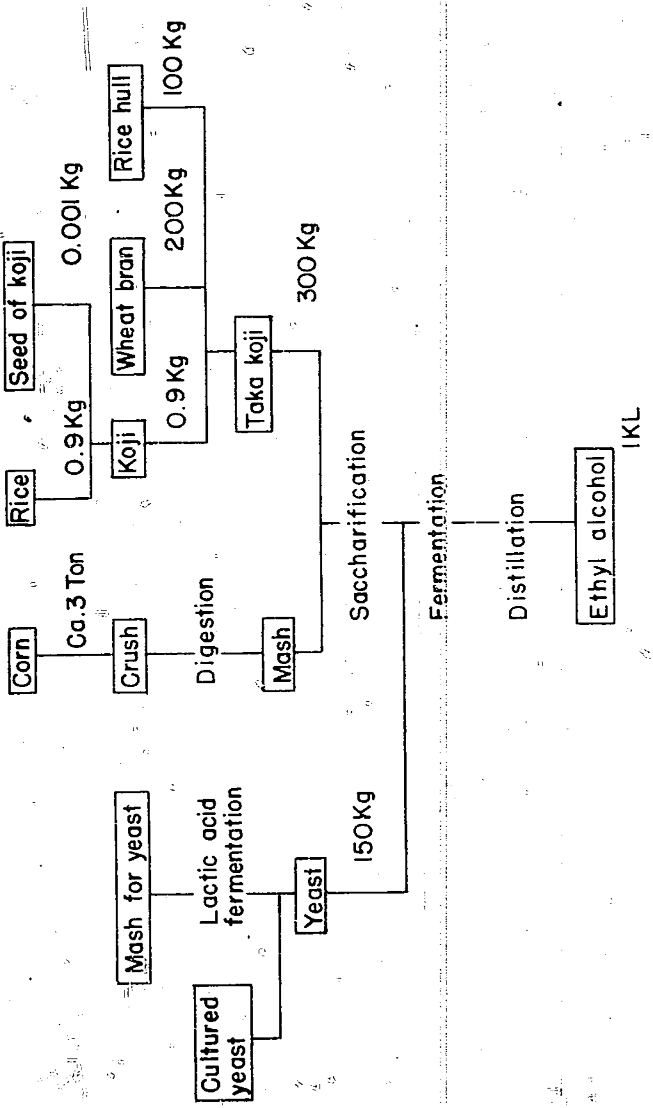


Figure 2 (B)2
FLOW SHEET OF THE ETHANOL FERMENTATION OF CORN
(This is not experimental data)

ENCLOSURE (B)2

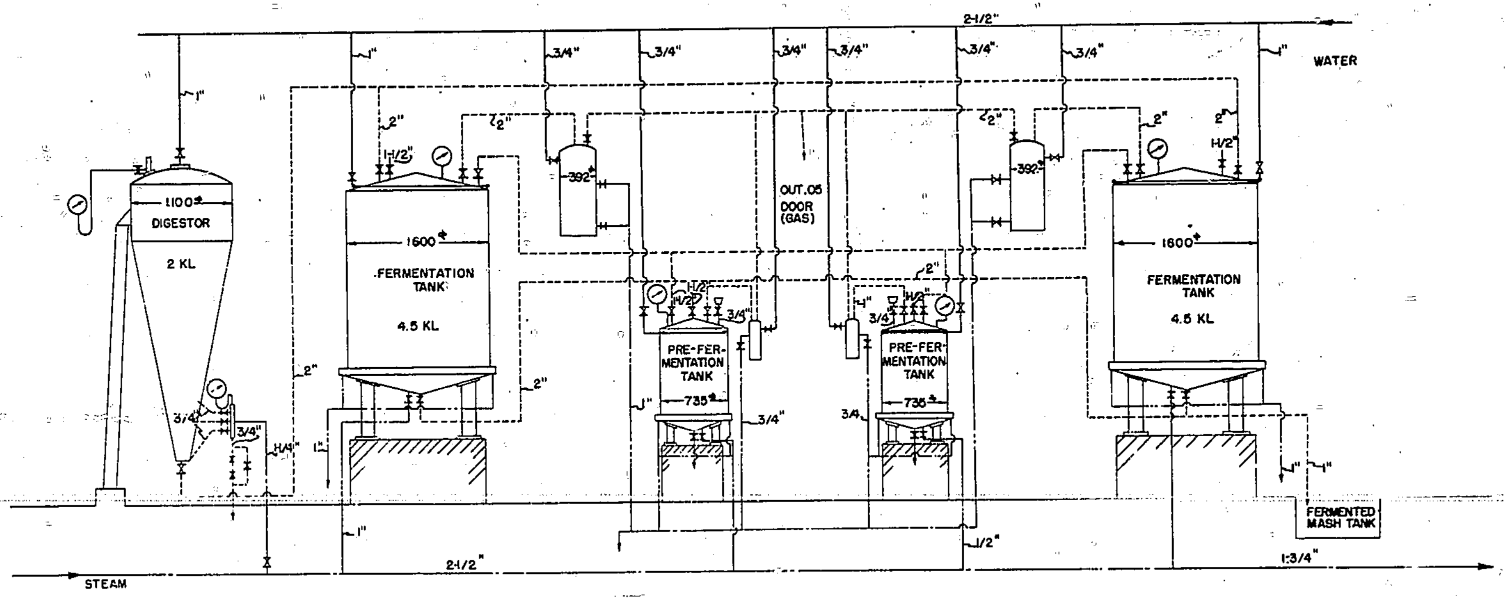


Figure 3 (B)2
FLOW SHEET OF FERMENTATION APPARATUS

ENCLOSURE (B) 2

PART IV

by

CHEM. ENG. LT. COMDR. T. UMEMURA
CHEM. ENG. LIEUT. M. TAKAHASHI

Research Period: 1944-1945

SUMMARY

The most suitable raw materials for the koji in the alcohol fermentation of sweet potatoes was studied. The corn-koji showed a good result, and it's saccharifying power was nearly 93% that of the wheat-koji.

I. INTRODUCTION

In alcoholic fermentation, the sweet potato must be saccharified before being subjected to the action of the yeast. There are three saccharifying processes used:

1. The Amyromyces method
2. The mineral acid method
3. The koji method

In this project the koji method was used.

There are two materials used in the Aspergillus group for saccharifying sweet potaotes; namely, aspergillus oryzae, the so-called "White Koji", and Aspergillus awamori, the so-called "Black Koji".

However, the raw materials in the culture of moulds have a great influence on the saccharifying power of the mould. The most suitable raw material for these moulds, from an economical point of view, has previously been rice bran. In this research, raw materials other than rice bran were used. In the case of Aspergillus oryzae or "White Koji", kaoling with rice bran, corn with rice bran, were selected as suitable raw materials for growth of the moulds.

The cultures of the mould of with these raw materials was not perfect since the power of saccharification was only 93% of the yield using rice bran. Aspergillus awamori (Black Koji) showed comparable results.

It is assumed that the culture superior in saccharifying power will give equally good results in fermentation experiments. Therefore, the authors studied the saccharifying power of various raw materials.

II. DETAILED DESCRIPTION

A. Details of Test Procedures and Conditions

1. The raw materials mentioned above were steebed for 14 hr, and then boiled for 50 min. After this treatment the spores of the mould were mixed with these meterials, and they were kept at 28°C,

for 48 hr in a thermostat. During this process the raw materials were stirred frequently to maintain an equal temperature.

2. Experimental method of determining the saccharifying power of koji

a. Enzyme solution:-Twenty grams of koji were added to 200cc water, kept for 2 hr in a thermostat at 35°C, and filtered.

b. Starch solution:-A 2% soluble starch solution was prepared.

The enzyme solution (50cc) and starch solution 910cc) were mixed in a flask, and kept for 2 hr at 55°C.

The quantity of reducing sugar after saccharification was determined and it was expressed as the degree of saccharification.

3. Method of Analysis

Sugar was determined by Hanes' method and calculated as glucose.

The pH value was determined by test paper specially made for the purpose by the Toyo Filter Paper Co, Ltd.

B. Experimental Results:

1. The results of experiments on the saccharifying power of Asp. Oryzae prepared from different raw materials are shown in Table VIII(B)2.

2. The results of the experiment on the saccharifying power of Asp. awamori prepared from different raw materials are shown in Table IX(B)2.

3. Experiment on the fermentation of sweet potato mash by koji.

Asp. oryzae was found to be more powerful than the Asp. awamori in saccharifying power as determined above. Hence, in this experiment, Asp. oryzae was used in the cultivation of rice or a mixture of corn and rice bran.

a. Anclyis of Sweet Potato. Name of the variety is Genji:

Water	70.1%
Crude fiber	1.0%
Total N.	0.1%
Starch value	24%

b. Preparation of Mash

A 385 gm sample of sweet potatoes was placed in a flask, and a small amount of water added. The mixture was ground slightly and was sterilized in the usual manner.

c. Yeast

A 10cc sample of koji extract (balling-10) was placed in a test tube, and sterilized by the usual method.

Yeast was innoculated to this medium and incubated for 24 hr at 30°C.

d. Saccharifying and Innoculation

Ten percent by weight of koji was added to the sweet potato in the flask and the mixture was incubated at 55°C with frequent shaking. After this treatment, the mash was cooled to 30°C, and the yeast was innoculated.

e. Method of Analysis

The pH and acidity were determined as usual. Total sugar was determined by Hanes' method. The alcohol in the distillate of the fermented mash was determined by specific gravity.

f. These results are shown in Table and Table XI(B)2.

III. CONCLUSIONS

1. It was recognized that the saccharifying power of Asp. Oryzae was greater than that of Asp. awamori.

2. The corn koji was shown to have a good saccharifying power, and it was nearly 93% that of the rice bran koji.

3. Other materials such as, kaoliang (1) plus corn (5), and a mixture of castor seed cakes, corn, and rice hulls, are also useful raw materials for the koji.

4. Experiment proved that other types of koji besides rice koji are capable of application in industry.

ENCLOSURE (B)2

Table VIII(B)2
DETERMINATION OF THE SACCHARIFYING POWER OF ASP. ORYZAE

Test No.	Raw materials	pH				Percent of Saccharification	Order of Saccharifying power
		Before Extract	After Extract	Before Saccharifying	After Saccharifying		
1	Rice	5.7	5.8	6.0	5.7	52	7
2	Rice bran	5.2	5.2	5.4	5.4	83	1
3	Vine of sweet potato	4.0	4.0	4.2	4.2	36	10
4	Corn 5: Rice hulls 1	4.4	4.4	5.0	5.0	77	2
5	Kaoliang 5 Rice hulls 1	4.8	4.8	5.6	5.4	74	4
6	Kaoliang	5.0	5.0	5.2	5.4	59	5
7	Corn 6 Castor seed oil Rice hulls 3	5.4	5.4	5.5	5.6	75	3
8	Corn 6 Castor seed cakes 1 Rice hulls 3	5.6	5.6	6.3	6.3	36	10
9	Cotton seed cakes 4 Vine of sweet potato 1 Castor seed cakes 1	5.0	5.0	4.8	4.8	40	9
10	Pupa seed cakes	4.2	4.2	4.5	4.5	36	10
11	Soya bean cakes	4.3	4.4	4.4	4.4	54	6
12	Rice bran (red)	4.0	4.0	4.2	4.2	47	8

Table IX(B)2

DETERMINATION OF THE SACCHARIFYING POWER OF ASP. AWAMORI

Test No.	Raw materials	pH				Percent of Saccharification	Order of Saccharifying Power
		Before extract	After extract	Before Saccharifying	After Saccharifying		
1	Rice	4.7	3.4	5.4	4.8	58	2
2	Vine of sweet potato	5.4	4.7	5.4	5.4	39	5
3	Corn	3.0	3.0	5.8	4.8	66	1
4	Kaoliang 5 Rice hulls 1	2.8	2.8	5.8	4.8	33	6
5	Kaoliang	4.4	3.8	5.0	5.0	31	7
6	Corn 6 Castor seed cakes 1 Rice hulls 3	5.2	4.6	5.0	5.0	52	3
7	Soya bean cakes 6 Rice hulls 3 Castor seed cakes 1	5.4	5.4	5.4	5.4	45	4
8	Cotton seed cakes 1 Vine of sweet potato 1	5.4	5.4	5.4	5.4	11	8

ENCLOSURE (B)2

Table X(B)2
EXPERIMENT ON THE FERMENTATIONS OF SWEET POTATOES

Test No.	After Fermentation				Ratio of Fermentation	Ratio of the Consumed Sugar Based on Total Sugar
	pH	Acidity cc	Rested Sugar gm/100cc	Alcohol %		
1	4.0	4.7	1.0	7.9	.97	.93
2	4.0	5.3	2.0	7.4	.84	.86
3	4.3	3.1	4.0	6.0	.74	.71
4	4.2	4.6	1.6	7.5	.92	.82

Note: Koji material is rice.
Before fermentation pH is 4.1, acidity is 3.2cc, and total sugar is 14.3 gm/100cc.

Table XI(B)2
EXPERIMENT ON THE FERMENTATION OF SWEET POTATOES

Test No.	After Fermentation				Ratio of Fermentation %	Ratio of the Consumed Sugar Based on Total Sugar %
	pH	Acidity cc	Rested Sugar gm/100cc	Alcohol %		
1	4.1	4.1	0.65	7.7	87.5	95
2	4.0	4.3	0.64	8.5	96	98
3	4.2	4.5	0.5	8.0	91	97
4	4.1	4.0	0.5	7.9	90	97

Note: Koji material: Corn 5: Rice hulls 1
Before Fermentation, pH is 5.0, acidity is 1.9cc, and total sugar is 15.5 gm/100cc

ENCLOSURE (B) 3

THE ABSORPTION OF INORGANIC NUTRIENTS IN THE ALCOHOLIC FERMENTATION BY YEAST

by

CHEM. ENG. LIEUT.
M. KUNO

Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)3

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)3

SUMMARY

The absorption of phosphate, sulphate, potassium and magnesium from the Knopp's culture solution during the fermentation by Saccharomyces formosensis Nakazawa, the distillery yeast employed for alcohol production from cane sugar, was investigated. The absorption of sulphate, phosphate, and potassium during the yeast growth increased during the first part of the fermentation. After 120 hours the concentration of those ions in the culture solution increased gradually with time. The absorption curves of these ions, therefore, indicated a minimum at about 120 hours.

The absorption of magnesium was not apparent throughout the growth of the yeast.

I. INTRODUCTION

A. History of Project

Many investigations of organic constituents in the course of alcoholic fermentation have been studied, but since the absorption of inorganic materials by the yeast had been studied by only a few investigators,* The present research was undertaken with Saccharomyces formosensis Nakazawa.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr. Y. MOMOTARI
Chem. Eng. Lt. M. KUNO

II. DETAILED DESCRIPTION

A. Test Procedure

1. Components of the culture solution.

Sucrose........	100.00 gm
KNO_3..............	2.00 gm
KCl..............	0.12 gm
KH_2PO_4...........	0.25 gm
$MgSO_4 \cdot 7H_2O$.......	0.25 gm
H_2O...........	1000.00 cc

2. Procedure.

Saccharomyces formosensis Nakazawa, distillery yeast No. 396, was cultivated for 3 days in 10 cc of Knopp's solution and introduced into 2990 cc of Knopp's nutrient kept at about 23°C. After each 30 hours, 200 cc portions were removed, boiled to stop fermentation, and the yeast cells filtered off. The filtrate was evaporated to dryness, dissolved in HCl, and diluted to 100 cc.

The procedures for systematic analysis are shown in Figures 1(B)3 and 2(B)3, and the results are shown in Table I(B)3 and Figures 3(B)3 and 4(B)3.

---

*S. Tanaka: Mem. Coll. Sci. Kyoto Imp. Uni., A, 129 (1939).

III. CONCLUSIONS

The experimental results show that potassium, sulphate, and phosphate are absorbed by the yeast during fermentation.

After the first 120 hours, the absorption of these constituents decreases and they are slowly removed from the yeast.

Magnesium does not appear to be necessary for the fermentation, since none is absorbed during the process.

Potassium, sulphate and phosphate appear to be absorbed by the yeast during fermentation, and hence their presence may be considered as necessary.

Table I(B)3

CHANGE IN CONCENTRATION OF SO_4, PO_4, K AND MG DURING FERMENTATION

Hour	SO_4		PO_4		K		Mg	
	mg/100cc	mol. ratio	mg/100cc	mol. ratio	mg/100cc	mol. ratio	mg/100cc	mol. ratio
0	9.4	0.965	17.2	0.986	90.5	0.998	2.6	1.056
30	7.9	0.811	15.7	0.900	89.8	0.991	2.5	1.016
60	7.6	0.780	14.6	0.838	88.3	0.974	2.7	1.095
90	6.0	0.616	13.2	0.757	84.3	0.930	2.4	0.975
120	2.7	0.277	8.9	0.510	77.2	0.852	2.5	1.016
150	3.0	0.308	9.1	0.522	75.8	0.836	2.4	0.975
180	4.2	0.431	10.7	0.613	75.5	0.833	2.4	0.975
210	4.7	0.482	12.0	0.688	77.0	0.849	2.5	1.016
240	5.5	0.564	13.2	0.757	81.0	0.893	2.3	0.934
270	6.9	0.708	14.5	0.831	82.0	0.904	2.4	0.975

(Tabulated Data for Curves Shown in Figure 3(B)3)

ENCLOSURE (B)3

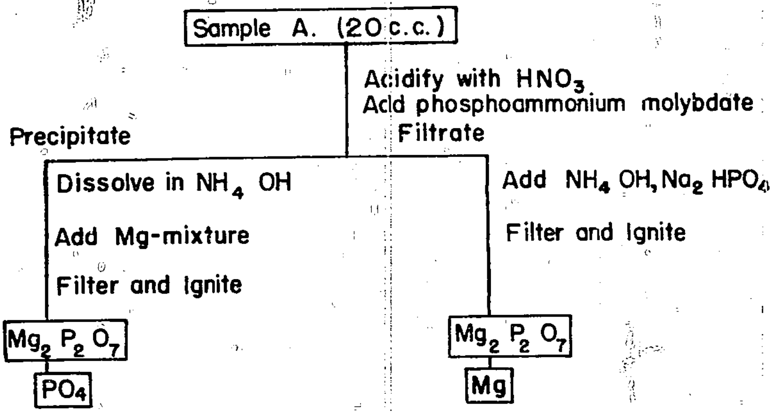


Figure 1 (B)3

SYSTEMATIC ANALYSIS OF CULTURE FOR Mg AND PO_4

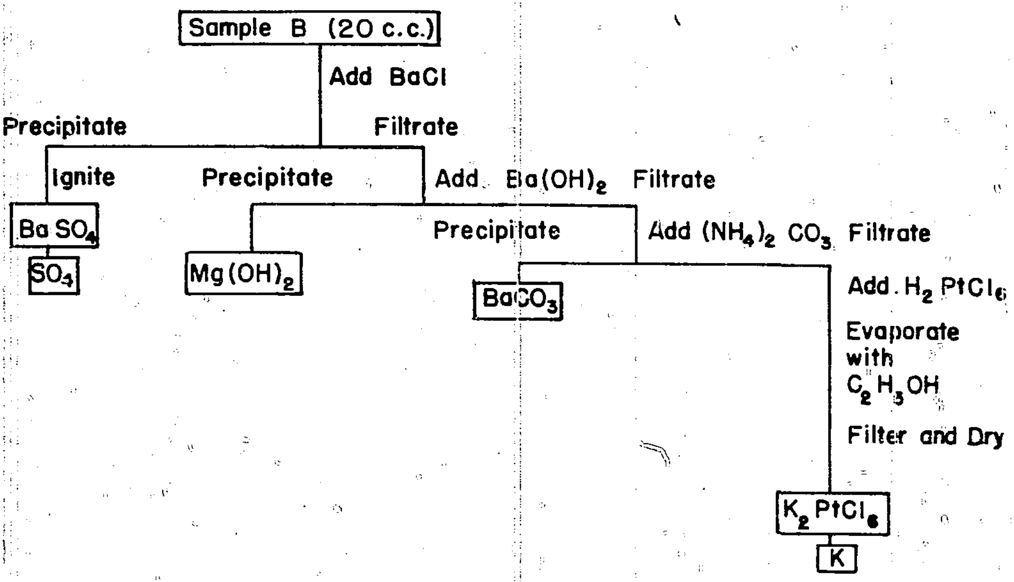


Figure 2 (B)3

SYSTEMATIC ANALYSIS OF CULTURE FOR SO_4 AND K.

ENCLOSURE (B)3

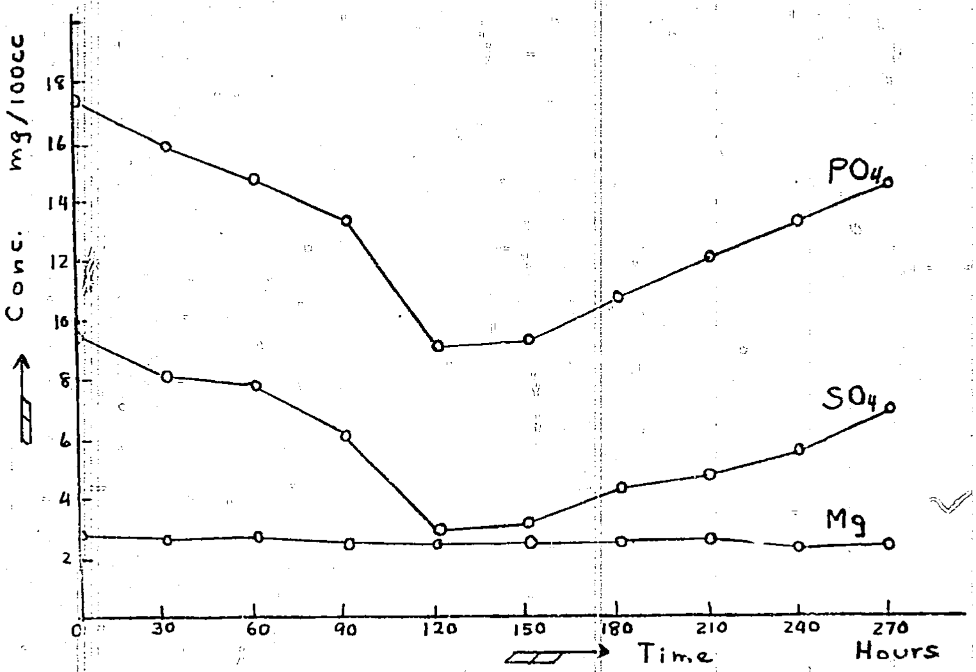


Figure 3 (B)3
CHANGE IN CONCENTRATION
OF Mg, SO_4 AND PO_4 DURING FERMENTATION

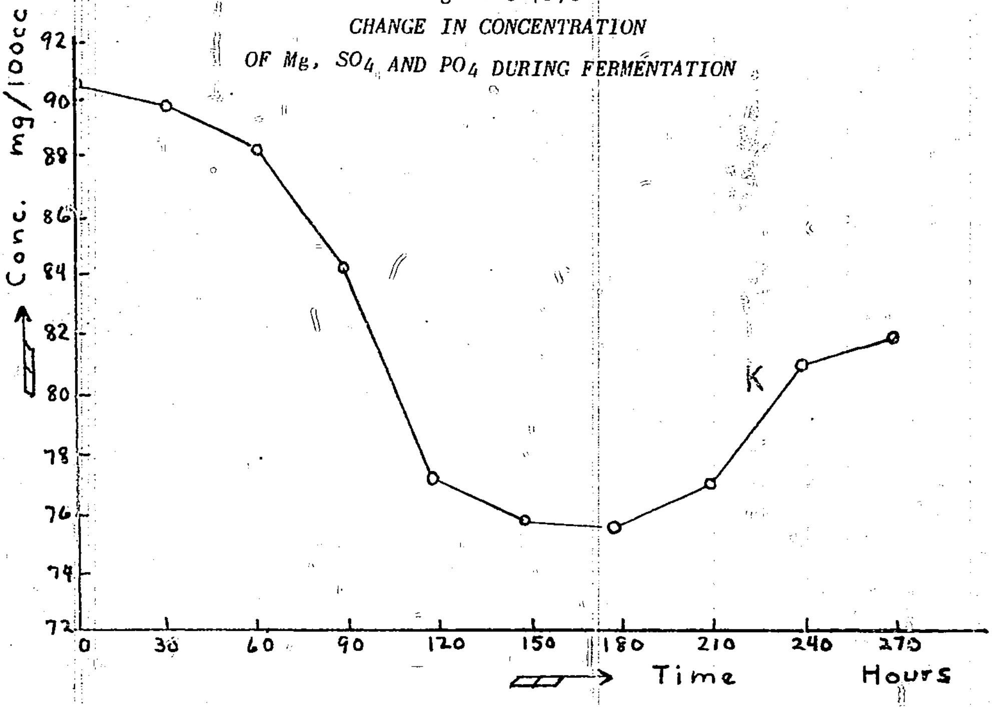


Figure 4 (B)3
CHANGE IN CONCENTRATION OF K. DURING FERMENTATION

ENCLOSURE (B) 4

STUDIES ON THE HYDROLYSIS OF PINE WOOD

by

ENG. COMDR.
H. FUJIMOTO

Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)4

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)4

SUMMARY

Laboratory tests of the hydrolysis of pine wood by the Bergius process using conc. HCl were repeated, and a pilot plant was erected for continuous operation treating 12 kilograms of wood per day. This pilot plant, however, was never operated.

I. INTRODUCTION

This research was started in January, 1945, to obtain fermentable sugar from pine wood. (Complete data not available.)

It was mainly carried out by Eng. Lieut. M. MURAKAMI.

II. DESCRIPTION

A. Chipped pine wood was immersed in concentrated hydrochloric acid (40%) and allowed to stand at room temperature. The optical rotarory power and reducing power of the solution was measured during reaction. After one hour, almost all of the celluloses in the wood were hydrolyzed to acid cellulose, and after 24 hours the hydrolysis reached equilibrium. About 80% of the total sugar was inverted to glucose.

B. The chemical stability of glucose towards HCl in the solution was studied, because it is important is deciding the maximum temperature for recovering hydrochloric acid from the hydrolyzed liquor by distillation. Glucose is easily polymerized to higher polymers by conc. HCl, but if the temperature of distillation is kept below 50°C., more than 90% is reinverted to glucose by boiling with dilute HCl.

C. Recovery of HCl by vacuum distillation from hydrolyzed liquor was investigated and 90% of the acid was recovered. The concentration of distilled HCl was 32% and the concentration of HCl remaining in the residual sugar solution was 5%.

D. Fermentation Test. The residual sugar solution from the distillation was neutralized by $PbCO_3$ diluted to a 7% sugar solution. The solution was subjected to fermentation test after inversion. Eighty percent of the total sugar was converted to ethyl-alcohol (3.96% of the original wood).

E. The separation of the acetic acid included in the distilled HCl solution was studied using a U-tube type separator, and it was separated into two components, 95% of HCl and 90% of acetic-acid in purity, respectively.

F. A pilot plant treating 12 kilograms of wood per day was erected in order to test continuous operation but it was not used. (See Figure 2(B)4.)

The flow chart and operating conditions of the pilot plant are shown in Figure 1(B)4.

ENCLOSURE (B)4

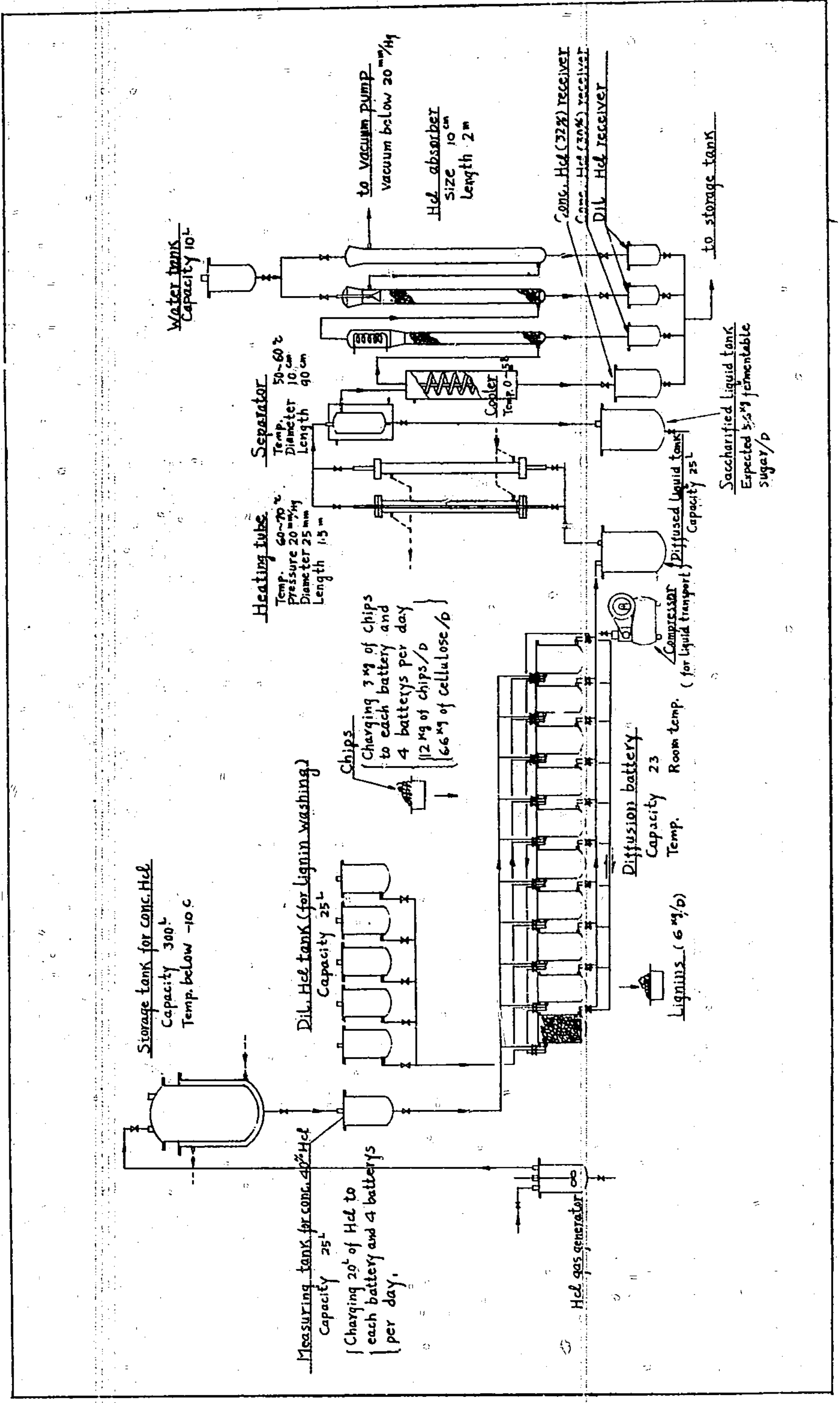


Figure 1 (B)4
APPARATUS OF WOOD SACCHARIFICATION

ENCLOSURE (B)4

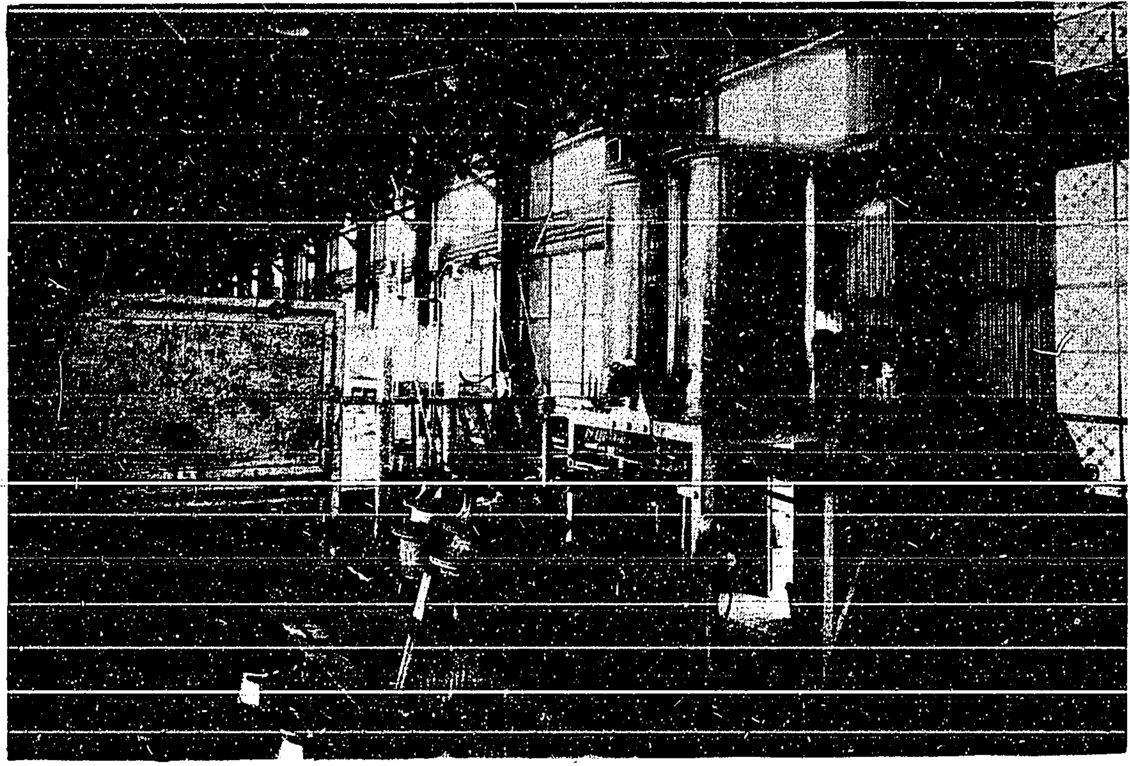


Figure 2 (B)4
PILOT PLANT FOR HYDROLYSIS OF WOODS

ENCLOSURE (B) 5

STUDIES ON BUTANOL FERMENTATION

(In Four Parts)

CHEM. ENG. LT. COMDR. T. UMEMURA
MR. Y. TAKEDA
MR. S. SHIMADA
CHEM. ENG. LIEUT. M. TAKAHASHI

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

Research Period: 1941-1944

ENCLOSURE (B)5

PART I

PART II

PART III

PART IV

ENCLOSURE (B)5

PART I

by

CHEM. ENG. LT. COMDR. T. UMEMURA

Research Period: 1941

SUMMARY

The production of butanol in quantity from the butanol fermentation of molasses was studied, and 9.6% acetone and 21.6% butanol were produced from the total sugar by the regulation of PH to 7, and using the proper nitrogen source such as soya bean cakes, etc.

I. INTRODUCTION

A. History of Project

In the past, many butanol bacteria were selected by the agricultual department of Tokyo Imperial University. The bacteria best fitted for the butanol fermentation of molasses of the above mentioned bacteria was found to be the No. 314 bacteria.

Therefore, using No. 314 bacteria, the conditions of butanol fermentation of molasses were investigated.

B. Key Reasearch Personnel Working on Project

Chem. Eng. Lt. Comdr. T. UMEMURA

II. DETAILED DESCRIPTION

A. Test Procedures

1. Analytical Methods.

Acetone: Acetone is determined by Messinger's method.

Butanol and Ethanol: Butanol and Ethanol is determined by Johnson's method.

Sugar: Directly reduced sugar is determined as glucose by Bertran's method. After saccharification by acid, total sugar is determined as glucose by Bertran's method.

pH: Measured with pH test paper.

2. Cultivation Method. This is in accordance with Weizman's method. The molasses mash is adjusted to a sugar concentration of 7-8%, and is sterilized for 30 minutes a day for 3 successive days. It is innoculated from a pure culture of butanol bacteria which may be maintained in corn mash. After innoculation, it is cultivated at 37°C in the incubator.

B. Experimental Results

1. Analysis of Molasses.

ENCLOSURE (B)5

Directly reduced sugar	43.12 gm/100cc
Total sugar	64.52 gm/100cc
Specific gravity (20°/4°)	0.8122
Ash	4.71%
Nitrogen	0.225%

2. Selection of Bacteria: In accordance with Weizman's method suitable bacteria for molasses are selected from the butanol bacterias which are kept in the Agricultual department of Tokyo Imperias University. Bacteria No. 314 was found to be suitable for molasses as indicated in Table I(B)5.

3. Effect of pH: Experiments were carried out and the following results were obtained.

a. pH change for sterilization. Molasses mash containing ca. 8% sugar as total sugar and 5% soya bean cakes in total sugar was sterilized for 30 minutes a day, continuing for 3 days. The changes of pH were obtained and are recorded in Table II(B)2.

b. Relation between pH-change and fermentations: Molasses mash containing 8% sugar as total sugar and 5% soya bean cakes in total sugar was sterilized for 30 minutes a day, continuing for 3 days. The molasses mash was adjusted to the desired pH by the addition of a measured quantity of alkali, and then innoculated with bacteria No. 314. The results obtained are listed in Table III(B)5 and IV(B)5.

4. Relation between Sugar Concentration and Fermentation: The molasses mash is adjusted to the desired sugar concentration and to a pH of 7 by the addition of a measured quantity of alkali.

Other treatment is the same as previously described. The results are tabulated in Tables V(B)5 and VI(B)5.

5. Relation between Nitrogen and Fermentation. The data showing the relation between the amount of nitrogen and fermentation are shown in Tables VII(B)5 and VIII(B)5. The molasses mash is adjusted to the desired ratio of soya bean cakes to total sugar.

Other treatment is the same as mentioned above.

III. CONCLUSIONS

Butanol bacteria for molasses fermentation were selected, and the best conditions of fermentation were studied.

It was found that No. 314 bacteria is suitable for molasses fermentation.

It has been found that it is best to adjust the pH to 7 and to use the proper nitrogen source such as 5% concentration of soya bean cakes to total sugar.

A sugar concentration of 5% in the molasses fermentation is suitable for the formation of butanol.

ENCLOSURE (B)5

Table I(B)5
EFFECT OF DIFFERENT BACTERIA ON MOLASSES FERMENTATION

Bacteria No.	pH		Directly Reduced Sugar	
	Before Fermentation	After Fermentation	Before Fermentation	After Fermentation
31	4.8	4.2	4.968	1.412
74	5.2	4.8	4.950	1.487
138	5.0	4.4	4.542	1.166
173	5.0	4.8	4.542	0.933
314	4.8	4.2	4.968	1.254

Table II(B)5
CHANGES IN pH DURING STERILIZATION

The Initial pH	The 1st Sterilization	The 2nd Sterilization	The 3rd Sterilization
4.8	4.7	4.6	4.6
6	5.4	5.2	5.0
7	5.6	5.3	5.3
8	5.8	5.6	5.6
9	5.4	5.6	5.6

Table III(B)5
EFFECT OF INITIAL pH ON FERMENTATION

(Analysis of mash before fermentation.)

No. of Experiment	Initial pH	Nitrogen Source	Acidity cc.	Total Sugar (%)
1	4.6	Soya bean cakes	2.57	8.569
2	6.2	"	0.78	7.626
3	6.9	"	0.02	7.550
4	8.3	"	"	7.626
5	6.2	none	0.88	7.335
6	7.2	"	"	7.339
7	8.1	"	"	7.345

ENCLOSURE (B)5

Table IV (B)5
EFFECT OF INITIAL pH ON FERMENTATION

(Analysis of mash after fermentation.)

No. of Experiment	Final pH	Acidity	Fermented Sugar (gm)	Fermented Sugar Based on Total Sugar	Produced Acetone (Mg/100cc)	Produced Butanol (Mg/100cc)	Produced Ethanol (Mg/100cc)
1	4.3	5.10	3.124	36.4	77		
2	4.4	4.16	4.638	60.8	226		
3	4.7	4.90	5.694	75.4	332	762	135
4	4.6	4.99	6.481	84.9	310	719	127
5	4.5	3.92	3.042	41.4	134		
6	4.6	4.38	2.236	30.4	82		
7	4.6	4.41	2.896	30.4	94		

ENCLOSURE (B)5

Table V(B)5
EFFECT OF SUGAR CONCENTRATION ON FERMENTATION

No. of Exp.	pH	Total Sugar (gm/100 cc)
1	7	4.445
2	"	5.850
3	"	6.321
4	"	7.018
5	"	9.588
6	"	10.392

Table VI(B)5
EFFECT OF SUGAR CONCENTRATION ON FERMENTATION

(Analysis of mash after fermentation)

No. of Exp.	Final pH	Acidity (cc)	Fermented Sugar (mg)	Fermented Sugar % Based on Total Sugar	Produced Acetone mg/100 cc	Produced Butanol mg/100 cc	Produced Ethanol mg/100 cc
1	4.8	2.56	4.032	90.7	274		
2	4.7	3.45	5.428	92.7	352	824	143
3	4.6	4.46	5.518	84.6	367	850	152
4	4.6	4.72	5.402	76.9	392	896	158
5	4.8	4.60	6.392	66.6	362	855	159
6	4.8	4.80	6.594	63.4	358	824	150

ENCLOSURE (B)5

Table VII (B)5
EFFECT OF AMOUNT OF NITROGEN ON FERMENTATION

(Analysis before Fermentation)

No. of exp.	Amount of Soya bean Cakes (gm/100cc)	Soya bean Cakes % based on Total Sugar	pH	Total sugar (gm/100cc)
1	0.5	8	7	6.172
2	0.25	4.5	"	5.591
3	0.05	0.7	"	6.651

Table VIII(B)5
EFFECT OF AMOUNT OF NITROGEN ON FERMENTATION

(Analysis after Fermentation)

No. of Exp.	Final pH	Acidity cc	Fermented Sugar (gm)	Fermented Sugar, % Based on Total Sugar	Produced Acetone (mg/100cc)	Produced Butanol (mg/100cc)	Produced Ethanol (mg/100cc)
1	4.6	4.75	4.316	69.9	232		
2	"	"	4.248	75.9	406	917	132
3	"	"	4.368	65.6	350	820	136

ENCLOSURE (B)5

PART II

by

Y. TAKEDA
Chief Engineer in Central Research
of Formosan Government General

S. SHIMADA
Engineer in Central Research
of Formosan Government General

Research Period: 1942

SUMMARY

Various bacteria for the acetone butanol fermentation were selected from different soils. Several effective bacteria were found and the following results were obtained:

1. When dried strips of sweet potatoes were fermented, using 21.4% of rice bran as a nitrogen source, the results were as tabulated in Table IX (B)5

2. When dried strips of sweet potatoes were fermented, using 1.86% of $(NH_4)_2SO_4$ and 1.4% of $CaCO_3$ as a nitrogen source, the results were as shown in Table X (B)5

I. INTRODUCTION

A. History of Project

Strong bacteria for acetone butanol fermentation were selected from various soils in order to ascertain which bacteria were the most suitable.

B. Key Research Personnel Working on Project

Engineer S. SHIMADA

II. DETAILED DESCRIPTION

A. Test Procedure

1. Examination of Bacteria

a. Collecting the Soil. Most of the soils were obtained from cane sugar or sweet potato farms.

b. Selection Method. Samples containing 7% dried strips of sweet potato mash (water 50cc dried strips of sweet potatoes 3.5gm, rice bran 0.5) were placed in a 3 x 2.5cm test tube, and digested for 40 min. under $2kg/cm^2$ pressure. The test soil was added to this mash, heating for 3 min. on a water bath. After cooling, it was cultivated at 37°C under 15mm-20mm Hg - pressure for 120 hr, and then a part of the cultivating mash was added to the new mash. This treatment was repeated 5-10 times, and the product was tested by the Iodoform reaction. Promising samples were then subjected to plate culture.

2. Plate Culture. The components of the artificial culture solutions were as follows:

Distilled water	100cc
K_2HPO_4	0.5gm
KH_2PO_4	0.5gm
$MgSO_4$	0.2gm
NaCl	0.0.gm
$FeSO_4$	0.01gm
$MnSO_4$	0.01gm
Peptone	5.0gm

An extract of yeast (50cc), glucose (15gm), and agar (6gm) was added to this artificial culture solution. This mash was sterilized 30 minutes a day for three successive days. After operating plate culture as in ordinary methods, the mash was kept at 37°C under 15mm-20mm Hg - pressure for 5 - 7 days.

3. Sand Culture. Sand is boiled in acid and alkali, washed with water, and dried. A small quantity of this sand is put in a sterilized test tube, sealed with cotton in a $CaCl_2$ - dessicator and then sealed with glass.

When using this sand for an experiment, the glass seal is broken, the sand is added to the unhulled rice mash, and kept at 37°C.

B. Test of Fermentation

1. Preparation of Mash and Analytical Methods. A mixture of sweet potato (21gm), rice bran (3gm), and water (300cc) were placed in a 500cc bottle, mixed well and digested for 40 minutes under $2kg/cm^2$ pressure in an autoclave. The mash volume was about 290cc, and when mash was analyzed, the total volume was put in a mortar and pulverized sufficiently.

a. Quantitative analysis of starch. A 20cc sample of starch was placed in a 300cc flask, 180cc of distilled water and 20cc HCl (specific gravity 1.125) were added, and the solution heated for 3 hrs. on a water bath. After cooling, it was neutralized with alkali and diluted to a total volume of 500cc with water. The total sugar in the mash, measured by Bertran's method, was about 20cc of the above-mentioned sample. The starch value in 100cc of mash was 0.9 times as much as the quantity of sugar.

b. Acidity. A volume of 20cc of mash were diluted with 100cc of distilled water in a 300cc flask, and titrated with N/10 NaOH, using phenolphthalein as an indicator. The acidity is expressed as cc of N/10 NaOH required to neutralize 100cc of mash.

c. pH. The pH was determined with pH test paper.

2. Analysis Method After Fermentation. The mixture was analyzed as follows 96 hrs. after innoculation.

a. Rested starch. After stirring the fermentation bottle, 20cc of mash in a 150cc flask were diluted with 80cc distilled water and 10cc HCl (specific gravity 1.125), saccharified for 3 hrs. on a water bath, cooled, neutralized, and then diluted to 200cc with water. The total sugar in the mash was measured by Bertran's method on a 20cc portion of above-mentioned sample. The starch value in 100cc of mash is 0.9 times as much as the quantity of sugar.

b. Acidity. After filtering the fermented mash, 10cc of filtrate is titrated with N/10 NaOh, using phenolphthalein as indicator.

Acidity is expressed as cc of N/10 NaOH to neutralize 100cc of fermented mash.

c. pH. Same as previously.

d. Acetone. Acetone was determined by Goodwin-Messinger's method, and is expressed as grams in 100cc of mash.

e. Butanol and Ethanol. Determined by Christansen's method.

3. Results. The results are as tabulated in Table XI(B)5.

C. Test of Fermentation Using $(NH_4)_2SO_4$ and $CaCO_3$ as Nutriments

The following results were obtained.

1. Dried strips of sweet potatoes (21gm), 0.39gm of $(NH_4)_2SO_4$, 0.3gm of $CaCO_3$, and 300cc water in a 500cc bottle were digested for 40 hrs. under 20kg/cm^2 pressure. The molar ratio of $(NH_4)_2SO_4$ to $CaCO_3$ was determined by experiment to be 1 : 1.

2. Result. The initial mash analysis was as follows:

Acidity	10.0
pH	5.4
Starch	5.0

The results of the experiment are tabulated in Table XII(B)5.

III. CONCLUSIONS

Bacteria for acetone-butanol fermentation were selected from various soils and the effectiveness of each was examined.

Ten excellent bacteria for the acetone-butanol fermentation were found.

Using rice bran or $(NH_4)_2SO_4 + CaCO_3$ as the nitrogen source, the following results were obtained.

Butanol for starch	about 20%
Acetone for starch	about 10%

ENCLOSURE (B)5

Table IX(B)5
RESULTS OF NEW SPECIES OF BACTERIA IN BUTANOL FERMENTATION (NITROGEN SOURCE: RICE BRAN)

Name of Bacteria	Yield of Butanol	Yield of Acetone	Time of Fermentation hr
KN 1	19.96	10.21	120
KN 12	19.46	10.24	120
KN 16	20.01	10.98	120
KN 20	20.89	11.26	120
KN 21	20.46	11.75	120
KN 26	18.71	9.74	96
Weizmann	19.26	9.72	120

Table X(B)5
RESULTS OF NEW SPECIES OF BUTANOL BACTERIA IN BUTANOL FERMENTATION*

Name of Bacteria	Yield of Butanol	Yield of Acetone	Time of Fermentation hr
KN 1	20.29	10.86	72
KN 19	21.00	10.78	48
KN 46	20.40	10.55	72
Weizmann	20.29	10.52	96

*Nitrogen source: $(NH_4)_2SO_4+CaCO_3$

Table XI(B)5
ANALYSIS OF FERMENTED MASH USING RICE-BRAN AS NITROGEN SOURCE

Analysis of Fermented Mash

Bacteria	pH	Acidity (cc)	Rested Starch (gm)	Acetone mg/100cc	Ethanol mg/100cc	Butanol mg/100cc
KN 1	4.4	46	0.5	0.5513	0.0972	1.0779
KN 12	4.4	56	0.5	0.5532	0.1050	1.0509
KN 14	4.4	46	0.8	0.5538	0.0754	0.9916
KN 16	4.6	38	0.6	0.5930	0.0384	1.0808
KN 19	4.2	75	0.7	0.5476	0.0480	0.9698
KN 20	4.6	40	0.6	0.6081	0.0469	1.1274
KN 21	4.6	40	0.6	0.6346	0.0352	1.1600
KN 23	4.4	51.5		0.3300	0.0409	0.5863
KN 27	4.4	58.0	0.8	0.5476	0.0384	0.9933
KN 46	4.3	59.0	0.8	0.5259	0.0570	1.0101

Original mash analysis

Starch	5.4gm
Acidity	10cc
pH	5.2

ENCLOSURE (B)5

Table XII(B)5
ANALYSIS OF FERMENTED MASH USING $(NH_4)_2SO_4$ AND $CaCO_3$ AS SOURCE OF NITROGEN

Bacteria	Acidity (cc)	pH	Rested Starch (gm)	Ethanol mg/100cc	Acetone mg/100cc	Butanol mg/100cc
KN 1	39.5	4.4	0.38	0.0649	0.5428	1.0147
KN 12	38.0	4.4	0.33	0.0574	0.5239	0.9436
KN 14	43.5	4.3	0.81	0.0639	0.4464	0.8517
KN 16	39.0	4.4	0.38	0.0654	0.3366	0.5732
KN 19	32.5	4.6	0.40	0.0876	0.5390	1.0502
KN 20	50.0	4.2	0.43	0.0978	0.4728	0.9572
KN 21	37.0	4.4	042	0.0538	0.1646	0.2387
KN 23	43.0	4.3	0.33			
KN 27	35.0	4.4	0.44	0.0796	0.3102	0.5073
KN 46	41.0	4.3	0.45	0.0632	0.5277	1.0199
Weizmann	34.5	4.4	0.41	0.1223	0.5258	1.0145

ENCLOSURE (B)5

PART III

by

CHEM. ENG. LT. COMDR. T. UMEMURA

CHEM. ENG. LIEUT. M. TAKAHASHI

Research Period: 1944.

A means of increasing or strengthening the fermenting power of clostridium acetobutyricum was conducted by the use of physical stimulations such as an electric lamp, x-rays and super sonics.

The significant results were as follows:

1. Super sonics slightly improved the fermenting power of organisms with short time exposure of the stimulant.

2. Incandescent lamps decreased the fermenting power of the organisms.

3. X-rays had varying influences in accordance with the wave length of the ray: viz, long waves increased the fermenting power of the organisms.

I. INTRODUCTION

A. History of Project

A device for increasing or strengthening the fermenting power of butanol bacteria was Weizmann's method, but the effect of physical stimulation was not studied. In this report various physical effects on fermenting power were investigated.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. M. TAKAHASHI.

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

1. Sand Culture. A test tube, half filled with dry pure sand, was sterilized by dry heating, and was then innoculated with clostridum Acetobutyricum.

2. The test tube containing the nourishing medium contained sucrose (3%) and soya bean cakes (0.3%).

3. A vacuum flask was evacuated to about 20 or 30mm pressure.

4. A flask containing 500cc of the culture medium consisting of 20gm sucrose and 2gm soya bean cakes.

ENCLOSURE (B)5

B. Details of Test Procedures and Conditions

As mentioned above, three physical stimulating agencies were used and the times of exposure of the sand culture of bacteria were 10, 30, and 60 seconds.

These cultures were subjected to the physical stimulation along with the control culture, and were cultured in an evacuated apparatus, at 20mm to 30mm pressure and at a temperature of 37°C for 24 hours. After 24 hours, these cultures were poured in a new medium containing sucrose (4%) and soya bean cakes (0.4%) at 37°C. After 48 hours, the butanol and acetone contents were determined. Other cultures in the medium containing sucrose (6%) and soya bean cakes (0.6%) were held at 37°C for 48 hours, and the effect was determined as above.

C. Experimental Results

1. Yields. In the case of the super sonics or W-anticathode X-ray, products were formed in the ratio of 6 parts of n-butanol, 3 parts of acetone, and one part of ethanol, just as in the normal butanol-acetone fermentation. However, the incandescent lamp and Cu-anticathode X-ray influence yielded an abnormal ratio of acetone butanol. In the former case, 120 grams of mixed solvent was obtained from 342 grams of sucrose. Detailed data are presented below.

2. Details of Tests.

a. Effect of super sonics.

Super sonics; 480 K.C., 300 Watts

Exposure of the sand cultures to super sonics was conducted as above mentioned, for 10, 30, and 60 seconds. In the case of 4% sugar mash, 10 seconds' exposure showed yields of butanol comparable to those obtained with the control, but 30 or 60 second exposures resulted in inferior yields. It was almost the same in the case of 6% sugar mash, except that the effect of 10 seconds' exposure was to give a considerable increase in in the yield of butanol.

The influence of super sonics in increasing the fermenting activity of organisms was not too promising. The results are tabulated in Table XIII(B)5.

b. The effect of incandescent lamp. A 320 Watts mercury lamp was used. The time of exposure of the sand culture to the incandescent lamp was 10, 30, and 60 seconds. The activity of fermentation was decreased in accordance with the duration of exposure. The results are tabulated in Table XIV(B)5.

c. The effect of X-rays.

(1) Cu-anticathode (3000 Volts 10 ma). All exposures to Cu-anticathode x-rays decreased the fermenting ability of the organism. This was especially true of the exposure to the rays for 60 seconds which gave extremely poor fermentation yields. The results are tabulated in Table XV(B)5.

(2) W-anticathode (65000 V, 3 ma). In exposing the sand cultures to W-anticathode for 30 seconds or 60 seconds, the activity of the organism increased and gave a better yield than the control in the culture of 4% sugar mash. The same was true of the effect of exposure on the 6% sugar mash. The yield of butanol after an exposure of 60 seconds was much superior to that obtained after 30 seconds' exposure or to that of the control. (See Table XVI(B)5.)

d. Summary of data. The percentage yields of butanol under the various stimulations studied are tabulated in Table XVII(B)5.

III. CONCLUSIONS

The effects of three types of physical stimulation, super sonics, incandescent lamps and x-rays, upon the sand culture of clostridium acetobutyricum were studied. Super sonics increased the fermenting activity of the organism slightly after 10 seconds' exposure, but decreased the activity after longer exposures.

Incandescent lamps showed an extremely bad influence on the fermentation activity. This influence increased with increasing time of exposure.

In the case of x-rays the results are different for Cu-anticathode and W-anticathode.

The Cu-anticathode rays decreased the fermenting ability, while W-anticathode was effective in increasing the activity of bacteria, viz; exposures of 30 seconds and 60 seconds gave an increased fermenting ability over the control. The 60 seconds' exposure was extremely effective in increasing bacterial action.

ENCLOSURE (B)5

Table XIII(B)5
INFLUENCE OF SUPER SONICS

(480 kc, 300 watts)

Time of Exposure (sec)	pH	Acidity (cc)	Sugar Content (%)	Ratio of Consumed Sugar to Total Sugar (%)	Acetone (mg/100cc)	Butanol (mg/100cc)	Time of Fermentation (hr)
0	4.2	2.7	4	95.4	420	820	48
0	4.4	2.8	4	95.4	432	825	"
30	4.4	3.2	4	94.2	398	725	"
60	4.3	3.1	4	94.1	446	756	"
0	4.1	5.7	6	74.7	440	926	48
10	4.2	2.7	6	85	520	1209	"
30	4.0	5.9	6	18.2	109	-	"
60	4.0	5.0	6	51.6	344	882	"

Table XIV(B)5
INFLUENCE OF INCANDESCENT LAMP

Time of Exposure (sec)	pH	Acidity (cc)	Sugar Content (%)	Ratio of Consumed Sugar to Total Sugar (%)	Acetone (mg/100cc)	Butanol (mg/100cc)	Time of Fermentation (hr)
0	4.4	2.5	4	92.5	427	779	48
10	4.6	2.4	4	90	404	715	"
30	4.4	3.9	4	92.4	227	405	"
60	4.6	2.2	4	92.4	248	455	"
0	4.6	2.4	6	64.5	412	959	48
10	4.2	3.1	6	58	387	893	"
30	4.2	3.2	6	32.9	208	593	"
60	4.6	3.2	6	32.7	228	673	"

ENCLOSURE (B)5

Table XV(B)5
INFLUENCE OF CU-ANTICATHODE

(3000 V, 10 ma)

Time of Exposure (sec)	pH	Acidity (cc)	Sugar Content (%)	Ratio of Consumed Sugar to Total Sugar (%)	Acetone (mg/100cc)	Butanol (mg/100cc)	Time of Fermentation (hr)
0	4.4	4.7	4	75	386		48
10	4.4	2.2	4	60	364	427	"
30	4.4	4.8	4	30	287	427	"
60	3.6	7.6	4	26			"
0	4.4	2.3	6	65.5	447	872	48
10	4.4	2.9	6	70	462		"
30	4.4	3.2	6	25	202	1015*	"
60	4.0	7.4	6	53			"

*Probably in error by infection.

Table XVI(B)5
INFLUENCE OF W ANTICATHODE

(65000 V, 3 ma)

Time of Exposure (sec)	pH	Acidity (cc)	Sugar Content (%)	Ratio of Consumed Sugar to Total Sugar (%)	Acetone (mg/100cc)	Butanol (mg/100cc)	Time of Fermentation (hr)
0	4.4	2.4	4	74	340	667	48
30	4.4	2.9	4	87.5	385	703	"
60	4.4	3.0	4	95	400	856	"
0	4.4	3.4	6	76.6	477	946	48
30	4.2	3.8	6	76.6	476	961	"
60	4.6	2.9	6	96.5	586	1355	"

ENCLOSURE (B)5

Table XVII(B)5
YIELD OF BUTANOL

(Fermentation Time 48 Hours)

	Conc. of Mash Exposure Time	4% Sugar Mash				6% Sugar Mash			
		0 sec	10 sec	30 sec	60 sec	0 sec	10 sec	30 sec	60 sec
Percentage Yield of Butanol	Super Sonics	20.5	20.6	18.1	18.9	15.0	20.0	-	13.3
	Incandescent Lamp	19.5	17.0	10.0	11.0	16.0	14.0	9.8	11.3
	Cu-Anticathode	-	10.0	10.0	-	14.0	-	16.0*	-
	W-Anticathode	16.0	-	17.0	21.0	15.1	-	16.0	22.0

* Probably in error by infection.

ENCLOSURE (B)5

PART IV

by

Y. TAKEDA
Chief Engineer in Central Research
of Formosan Government General

S. SHIMADA
Engineer in Central Research
of Formosan Government General

Research Period: 1941-1942

SUMMARY

A promoter for the acetone-butanol fermentation of dried strips of sweet potatoes was desired.

It was found that rice bran, peanut bean cakes, soya bean cakes, banko beans, and the powdered Formosan brewer's grains on which Ryzopus Delemer has been bred, and $(NH_4)_2SO_4+CaCO_3$ gave excellent results as promoters of butanol fermentation from dried Formosan sweet potatoes.

I. INTRODUCTION

A. History of Project

In the acetone-butanol fermentation from dried strips of sweet potatoes, a good result can not be obtained because of the lack of nitrogen and other nutriments for the bacteria.

In regard to this, the question arose as to what kind of materiels should be added to the principal raw materials. At present, rice bran is considered to be the best fitted for the purpose, but it has disadvantages in the following respects:

1. It must be used in large quantities (20% based on raw material).
2. The rice bran is a good fodder, and is difficult to obtain in large quantity.
3. According to the literature, fermentation is retarded when rice bran is added.
4. Rice bran is comparatively expensive and is difficult to preserve since it contains oil. Hence, it is considered to be desirable to find the material having as few of the above disadvantages as possible in considering the fermentation efficiency on an industrial scale.

B. Key Research Personnel Working on Project

Eng. of Formosan Central Research S. SHIMADA

II. DETAILED DESCRIPTION OF FERMENTATIONS TESTS

A. The Testing of Rice Bran

The fermentation was carried out in the usual manner by adding rice bran to a mash containing 7% dried strips of sweet potatoes.

The percentage of rice bran is the percentage based on the total amount of mash. The results are as tabulated in Table XVIII(B)5. In the following experiments, rice bran is used as a control.

B. The Testing of Peanut Bean Cakes

The fermentation was carried out by adding different percentages of peanut bean cakes. The addition of 0.5% cake was sufficient for normal fermentation. The results are as tabulated in Table XIX(B)5.

C. The Testing of the Soya Bean Cakes

The fermentation was, in general, unsatisfactory. The optimum results were obtained with 0.5% soya bean cakes. This quantity is 7% of the sweet potato content. The results are tabulated in Table XX(B)5.

D. The Testing of Black Sesame Seed Cakes

The fermentation was carried out by adding 0.1, 0.3, 0.5, 0.8, and 1.0% black sesame seed cakes to the mash.

In this case the fermentation was poor, and the cake was not effective as a promoting material.

E. The Testing of Banko Beans

Banko beans were tested in the same manner and the adequate quantity of banko beans was found to be 0.5 or 0.8%. (This is 7 or 10% based on the sweet potatoes.)

The results are tabulated in Table XXI(B)5.

F. The Testing of the Rice Bran with Fungi Powder

1. The fermentation was carried out using rice bran and Asp. Oryzae or Rhyzopus. Delemer.

The fermentation was normal, when 0.5% rice bran and 0.5% Asp. Oryzae, or 0.5% of rice bran and 0.5% Rhyz. Delemer was added. The results are tabulated in Table XXII(B)5.

2. The Testing of Rice Bran With the Extract of Fungi. When the extract of the fungi was used, the fermentation was poor. The results are tabulated in Table XXIII(B)5.

The extracts were made as follows: 45 gr. of the fungi were boiled in 250cc of water for 2 hrs., filtered, and concentrated to 100cc.

G. The Testing of Formosan Brewer's Grains

1. The filtrate of Formosan brewer's grains was used instead of water, both with and without rice bran.

In every case, acidity was very high, and the fermentation failed.

2. Formosan brewer's grains were ineffective as the promoting material. The results are tabulated in Table XXIV(B)5.

3. Formosan Brewer's Grains on which Rhyz. Delemer had been bred were used. The results are tabulated in Table XXV(B)5. Using 1% of the grain, the fermentation was normally carried out and the yield of the solvent was satisfactory.

H. The Testing of the Green Tea Waste

The results using green tea waste were unsatisfactory, since the fermentation was very poor.

I. The Testing of $(NH_4)_2SO_4$+$CaCO_3$ or $(NH_4)_2SO_4$ + Rice Bran

1. Using only $(NH_4)_2SO_4$ as a nitrogen source, the fermentation was not normal, while using both $(NH_4)_2SO_4$ and $CaCO_3$, the result was comparatively good and was superior to the control in respect to the rested starch.

The results are tabulated in Table XXVI(B)5.

2. Varying amounts of $(NH_4)_2SO_4$- $CaCO_3$ were used, and it was found that the yield of solvent decreased with increasing amounts of $(NH_4)_2SO_4$- $CaCO_3$. In all cases, the acidity was low and the rested starch was small. Since Calcium was used, it appears that Ca-salts are formed by the acid produced during the fermentation process.

If this is the case, an excess of $CaCO_3$ should be advantageous in lowering the acidity. The results are tabulated in Table XXVII(B)5.

3. Varying ratios of $CaCO_3$ to $(NH_4)_2SO_4$ were used. It was found that the optimum ratio was 1 : 1.

The results are tabulated in Table XXVIII(B)5.

4. Consideration of Experiments on use of $CaCO_3$- $(NH_4)_2SO_4$.

a. In the case of the 7% mash of dried strips of sweet potatoes, the addition of 0.08 or 0.1% of $(NH_4)_2SO_4$ (1.14 or 1.43% based on the sweet potato content) and 0.08 or 0.12% $CaCO_3$ (1.14 or 1.71% based on the sweet potato content) is considered to be adequate.

b. Adding $(NH_4)_2SO_4$ and $CaCO_3$, if the $(NH_4)_2SO_4$ was in excess, the yield of acetone was increased and the butanol yield was decreased.

If $CaCO_3$ was in excess, the yield of ethanol was increased.

5. The Testing of Fertilizer in Place of Pure $(NH_4)_2SO_4$. $(NH_4)_2SO_4$ used as fertilizer can be used as effectively as chemically pure $(NH_4)_2SO_4$. The results are tabulated in Table XXIX(B)5.

6. The Testing of a new species of Bacteria with $(NH_4)_2SO_4$+$CaCO_3$. Using the new species of soil bacteria developed in this laboratory and reported herewith, the superiority of the new species was recognized and the characteristic effect of $(NH_4)_2SO_4$ and $CaCO_3$ was obtained.

The results are tabulated in Table XXX(B)5.

III. CONCLUSIONS

The best material as a nitrogen source in the fermentation of dried strips of sweet potatoes was found to be rice bran.

Satisfactory materials for use as nitrogen source, in order of effectiveness, are listed below.

The following materials were found to be unsatisfactory:

Black sesame bean
Extract of Asp. Oryzae
Extract of Rhyzopus Delemer
Formosan brewer's grains
Green tea waste

When $(NH_4)_2SO_4$ and $CaCO_3$ were used, the yield of acetone was increased and the yield of butanol was decreased when the $(NH_4)_2SO_4$ was in excess.

When $CaCO_3$ was in excess, the yield of ethanol was increased.

Using the new species bacteria, adding 0.13% $(NH_4)_2SO_4$ and 0.1% $CaCO_3$, the superiority of the new species was recognized and the characteristic effect of $(NH_4)_2SO_4$ and $CaCO_3$ was obtained.

Table XVIII(B)5
EFFECT OF RICE BRAN IN SWEET POTATO FERMENTATION

Percent of Rice bran	After fermentation*					
	acidity** (cc)	pH	Rested starch gm/100cc	Ethanol gm/100cc	Acetone gm/100cc	Butanol gm/100cc
0.5	33.0	4.2	2.75	0.265	0.375	0.744
1.0	40.0	4.2	2.05	0.342	0.401	0.825
1.5	32.0	4.6	0.67	0.391	0.570	1.082
2.0	30.5	4.4	0.71	0.434	0.582	1.099

* Before fermentation; acidity 8.0cc, pH 5.0, Starch 4.94 gm/100cc.
** cc of 0.1 N NaOH required to neutralize 10cc of product.

ENCLOSURE (B)5

Table XIX(B)5
EFFECT OF PEANUT BEAN CAKES IN SWEET POTATO FERMENTATION

Exp.No.	Percent of Peanuts' Bean cakes	After fermentation*					
		Acidity (cc)	pH	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
	0.5	26.5	4.6	0.47	0.276	0.506	1.012
1	1.0	27.5	4.6	0.46	0.419	0.509	1.047
	1.5	25.5	4.7	0.45	0.361	0.588	1.077
	Rice bran 1.5	27.0	4.6	0.65	0.285	0.596	1.131
2	0.1	39.0	4.3	4.31	0.052	0.036	0.074
	0.3	19.5	4.7	0.52	0.392	0.486	1.033
	0.5	26.5	4.3	1.17	0.294	0.429	0.853
	Rice bran 1.5	25.0	4.8	0.23	0.371	0.552	1.047

* Before Fermentation; acidity 9.0cc, pH 5.0, Starch 4.94 for Exp. No. 1
Before Fermentation; acidity 8.5cc, pH 5.0, Starch value 5.06 for Exp. No. 2

Table XX(B)5
EFFECT OF SOYA BEAN CAKES IN SWEET POTATO FERMENTATION

Exp.No.	Percent of Soya Bean Cakes	After fermentation*				
		Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
1	0.1	24.5	3.38	0.078	0.208	0.396
	0.3	22.0	1.50	0.189	0.429	0.820
	0.5	27.0	1.01	0.200	0.502	0.918
	Rice bran 1.5	33.0	1.86	0.185	0.492	0.875
2	0.5	19.0	0.42	0.376	0.515	1.017
	0.8	24.0	0.44	0.429	0.495	1.008
	1.0	25.0	0.50	0.457	0.479	1.002
	Rice bran 1.5	27.0	0.59	0.432	0.547	1.125

* Before Fermentation; Acidity 9.5cc, Starch 5.06 for Exp. No. 1
Before Fermentation; Acidity 8.0cc, Starch 4.79 for Exp. No. 2

ENCLOSURE (B)5

Table XXI(B)5
EFFECT OF BANKO BEAN CAKES IN SWEET POTATO FERMENTATION

Percent of Banko beans	After fermentation*				
	Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
0.1	24.0	2.86	0.206	0.212	0.409
0.3	23.0	1.08	0.282	0.416	0.885
0.5	20.0	0.65	0.360	0.458	1.023
0.8	20.5	0.58	0.322	0.483	1.056
1.0	21.0	0.54	0.355	0.496	1.055
Rice bran 1.5	27.0	0.55	0.344	0.480	1.049

* Before Fermentation: acidity 9.5cc, starch 5.09

Table XXII(B)5
EFFECT OF RICE BRAN AND FUNGI IN SWEET POTATO FERMENTATION

Percent of rice bran & Fungi		After fermentation*				
		Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice	1.5	32.0	0.48	0.364	0.581	0.999
Rice A	0.5 0.5	26.5	0.52	0.278	0.546	1.104
Rice A	1.0 0.5	18.5	0.51	0.343	0.550	1.029
Rice R	0.5 0.5	26.0	0.43	0.315	0.575	1.062
Rice R	1.0 0.5	21.0	0.44	0.287	0.538	1.094

A: Asp. Oryzae R: Rhyzopus Delemer
* Before Fermentation: acidity 10.5cc, starch 4.79

ENCLOSURE (B)5

Table XXIII(B)5
EFFECT OF RICE BRAN AND THE EXTRACT OF FUNGI IN SWEET POTATO FERMENTATION

Percent of Rice Bran & Fungi extract	After fermentation*				
	Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice bran 1.5	35.0	0.57	0.506	0.533	1.002
Rice bran 1.5 AE 10cc	27.0	0.52	0.461	0.615	1.037
AE 10cc	25.0	2.21	0.300	0.311	0.615
Rice bran 1.5 RE 10cc	38.0	0.86	0.466	0.492	0.929
RE 10cc	26.0	2.72	0.315	0.258	C.467

AE: Extract of Asp. Orz. RE: Extract of Rhyz. Delemer
* Before Fermentation: acidity 9.5cc, Starch 5.03

Table XXIV(B)5
EFFECT OF FORMOSAN BREWER'S GRAINS IN SWEET POTATO FERMENTATION

Percent of Formosan brewer's grain	After fermentation*				
	Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
0.3	18.5	2.95	0.087	0.258	0.523
0.5	19.5	2.35	0.102	0.331	0.669
1.0	20.5	2.67	0.111	0.317	0.637
Rice bran 1.5	29.5	0.48	0.242	0.587	1.175

* Before Fermentation: acidity 10.25cc, starch 5.15

Table XXV(B)5
EFFECT OF FORMOSAN BREWER'S GRAINS ON WHICH RHYZOPUS DELEMER HAS BEEN BRED IN SWEET POTATO FERMENTATION

Percent of Formosan brewer's grains with Rhyz. Delemer	After fermentation*				
	Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice bran 1.5	34.5	0.59	0.095	0.514	1.049
R.E.b.g. 1.0	24.0	0.49	0.134	0.555	1.040
" 0.5	17.0	0.42	0.144	0.465	0.885
" 0.3	17.0	1.41	0.106	0.346	0.703

R.E.b.g: Formosan brewer's grains on which Rhyzopus Delemer has been bred.
* Before Fermentation: acidity 10.5cc, starch 4.89.

ENCLOSURE (B)5

Table XXVI(B)5
EFFECT OF $(NH_4)_2SO_4$ $CaCO_3$ OR $(NH_4)_2SO_4$ + RICE BRAN IN SWEET POTATO FERMENTATION

Percent of Material	After fermentation*				
	Acidity (cc)	Rested Starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice bran 1.5	44.5	0.70	0.138	0.580	1.185
$(NH_4)_2SO_4$ 0.1	70.0	4.17		0.027	
$(NH_4)_2SO_4$ 0.3	77.0	4.44		0.011	
$(NH_4)_2SO_4$ 0.1	30.5	0.31	0.167	0.456	1.095
$CaCO_3$ 0.2					
$(NH_4)_2SO_4$ 0.3	38.5	0.26	0.132	0.432	0.954
$CaCO_3$ 0.5					
Rice bran 0.5 $(NH_4)_2SO_4$ 0.07	55.5	3.69		0.161	

* Before Fermentation: acidity 11.3cc, Starch 5.02 gm.

Table XXVII(B)5
EFFECT OF $(NH_4)_2SO_4$ AND $CaCO_3$ IN SWEET POTATO FERMENTATION

Percent of Material	After fermentation*				
	Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice bran 1.5	33.0	0.504	0.161	0.597	1.264
$(NH_4)_2SO_4$ 0.05 $CaCO_3$ 0.1	26.5	0.509	0.203	0.479	1.036
$(NH_4)_2SO_4$ 0.10 $CaCO_3$ 0.2	23.5	0.333	0.259	0.463	1.003
$(NH_4)_2SO_4$ 0.2 $CaCO_3$ 0.4	22.0	0.223	0.201	0.444	0.965
$(NH_4)_2SO_4$ 0.3 $CaCO_3$ 0.6	23.5	0.311	0.105	0.412	0.927
$(NH_4)_2SO_4$ 0.5 $CaCO_3$ 1.0	38.0	0.245	0.064	0.312	0.722

* Before Fermentation: acidity 4.25cc, starch 4.89

ENCLOSURE (B)5

Table XXVIII(B)5
EFFECT OF $(NH_4)_2SO_4$ AND $CaCO_3$ IN SWEET POTATO FERMENTATION

Percent of material	After fermentation*				
	Acidity (cc)	Rested starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice bran 1.5	35.0	0.502	0.267	0.608	1.153
$(NH_4)_2SO_4$ 0.1 $CaCO_3$ 0.05	56.0	4.187		0.029	
$(NH_4)_2SO_4$ 0.1 $CaCO_3$ 0.01	56.0	4.139		0.020	
$(NH_4)_2SO_4$ 0.1 $CaCO_3$ 0.05	25.0	0.578	0.203	0.525	1.028
$(NH_4)_2SO_4$ 0.1 $CaCO_3$ 0.1	20.0	0.372	0.297	0.571	1.088
$(NH_4)_2SO_4$ 0.1 $CaCO_3$ 0.15	24.0	0.430	0.324	0.530	1.102

* **Before Fermentation:** acidity 9.00cc, Starch 4.98 gm.

Table XXIX(B)5
EFFECT OF $(NH_4)_2SO_4$ FOR FERTILIZER IN SWEET POTATO FERMENTATION

Percent of material	After fermentation*					
	Acidity (cc)	pH	Rested Starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
Rice bran 1.5	33.0	4.5	0.81	0.214	0.5487	1.006
$(NH_4)_2SO_4$ 0.08 $CaCO_3$ 0.1	22.5	4.6	0.39	0.194	0.5325	1.061
$(NH_4)_2SO_4$ 0.1 $CaCO_3$ 0.1	25.5	4.5	0.48	0.159	0.5619	1.012
$(NH_4)_2SO_4$ 0.13 $CaCO_3$ 0.1	29.5	4.4	0.40	0.080	0.6054	1.038

* **Before Fermentation:** acidity 9.5cc, Starch 5.18 gm.

ENCLOSURE (B)5

Table XXX(B)5
THE EFFECT OF $(NH_4)_2SO_4$ AND $CaCO_3$ USING NEW SPECIES OF BACTERIA*

Test No.	Species No.	After fermentation					
		Acidity (cc)	pH	Starch (gm)	Ethanol (gm)	Acetone (gm)	Butanol (gm)
1	KN1	39.5	4.4	0.38	0.065	0.543	1.015
2	KN12	38.0	4.4	0.33	0.057	0.524	0.944
3	KN14	43.5	4.5	0.81	0.064	0.446	0.852
4	KN16	39.0	4.4	0.38	0.065	0.337	0.573
5	KN19	32.0	4.6	0.40	0.088	0.539	1.050
6	KN20	50.0	4.2	0.43	0.098	0.473	0.957
7	KW21	37.0	4.4	0.42	0.054	0.165	0.239
8	KW23	43.0	4.3	0.33			
9	KW27	35.0	4.4	0.44	0.080	0.310	0.507
10	KW46	41.0	4.3	0.45	0.063	0.528	1.020
11	Weizmann	34.5	4.4	0.41	0.122	0.526	1.015

* $(NH_4)_2SO_4$ 0.13%
$CaCO_3$ 0.1%
Acidity 10.0cc

Table XXXI(B)5
NITROGEN SOURCE MATERIALS

Order	Material	Optimum Concentration (based on Mash)
1	Rice bran	0.5
2	$(NH_4)_2SO_4$ $CaCO_3$	0.1 0.1
3	Peanut bean cakes	0.1 - 1.5
4	Rice bran*	0.5
5	Banko bean	0.5 - 0.8
6	Soya bean cakes	0.5

* Plus Aspergillus Oryzae or Rhyzopus Delemer

ENCLOSURE (B) 6

THE DESIGN
OF A
SIMPLIFIED ALCOHOL DISTILLATION PLANT

by

CHEM. ENG. LIEUT. A. SHIOMI

Research Period: April - June, 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)6

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)6

I. INTRODUCTION

A. History of Subject

By order of the Naval Supply Office, work was started in April, 1945, on the design of a distillation plant to produce 500 kiloliters per year of second class Alcohol (alcoholic content above 94%) from spirit with alcoholic content of 30%, made from sweet potatoes by the sake-breweries.

On the basis of this design, the equipment was constructed by the Chemical Engineering Department and the plant erected at the Iinuma sake-brewery in CHIBA Prefecture. A performance test of this plant was made in July, 1945.

B. Key Research Personnel Working on the Project

Nav. Eng. T. SHIBAZAKI
Eng. Lieut. S. SHIOMI

II. DETAILED DESCRIPTION

A flow sheet of the process is given by Plate I(B)6.

The raw spirit to be rectified is pumped from the reservoir to the feed gravity tank and it flows down, under constant head, to the preheater, where it is heated to about 65°C, and the liquid is charged to the rectifier. The concentrated vapor (alcoholic content of about 95%) from the top of the column is sent to the preheater and condensers. The residual gases, such as aldehydes, are discharged to the atmosphere.

A part of the condensate from the preheater and condenser is cooled and sent to product, the remainder plus condensate from the reflux condenser is returned to the rectifier as reflux.

The waste, with alcoholic content of less than 0.1% by volume, is withdrawn from the bottom of the rectifier through an automatic liquid level regulator.

Heat necessary for the distillation is provided by stripping steam introduced at the bottom of the column. Two outlet pipes are provided to take out fusel oil accumulated in the column.

The design operating conditions and the material and heat balances summarized below and on Figure 1(B)6 and Table II(B)6

A performance test was made on July 31, 1945, and the results are summarized in Table I(B)6.

III. CONCLUSIONS

This apparatus was shown to be suitable for practical usage. It had reserve capacity; and only three men, including 1 distiller, 1 fireman, and 1 assistant, were required for its operation.

ENCLOSURE (B)6

Table I(B)6
PERFORMANCE TEST RESULTS

	Quantity	Concentration of Alcohol	Absolute Quantity of Alcohol
Input raw spirit	277.4kg/hr	25% by weight	69.35kg/hr
Output product	75.3kg/hr	92% by weight	69.30kg/hr
Loss of alcohol			0.05kg/hr

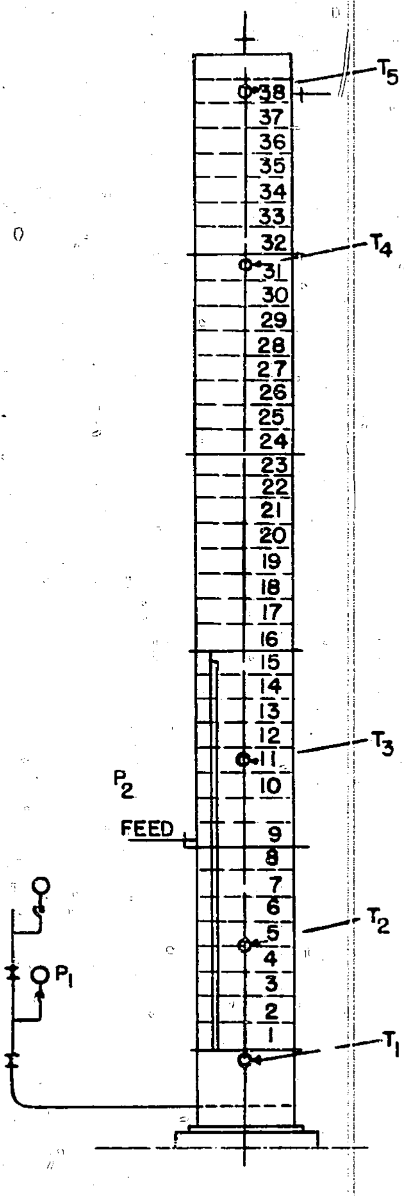
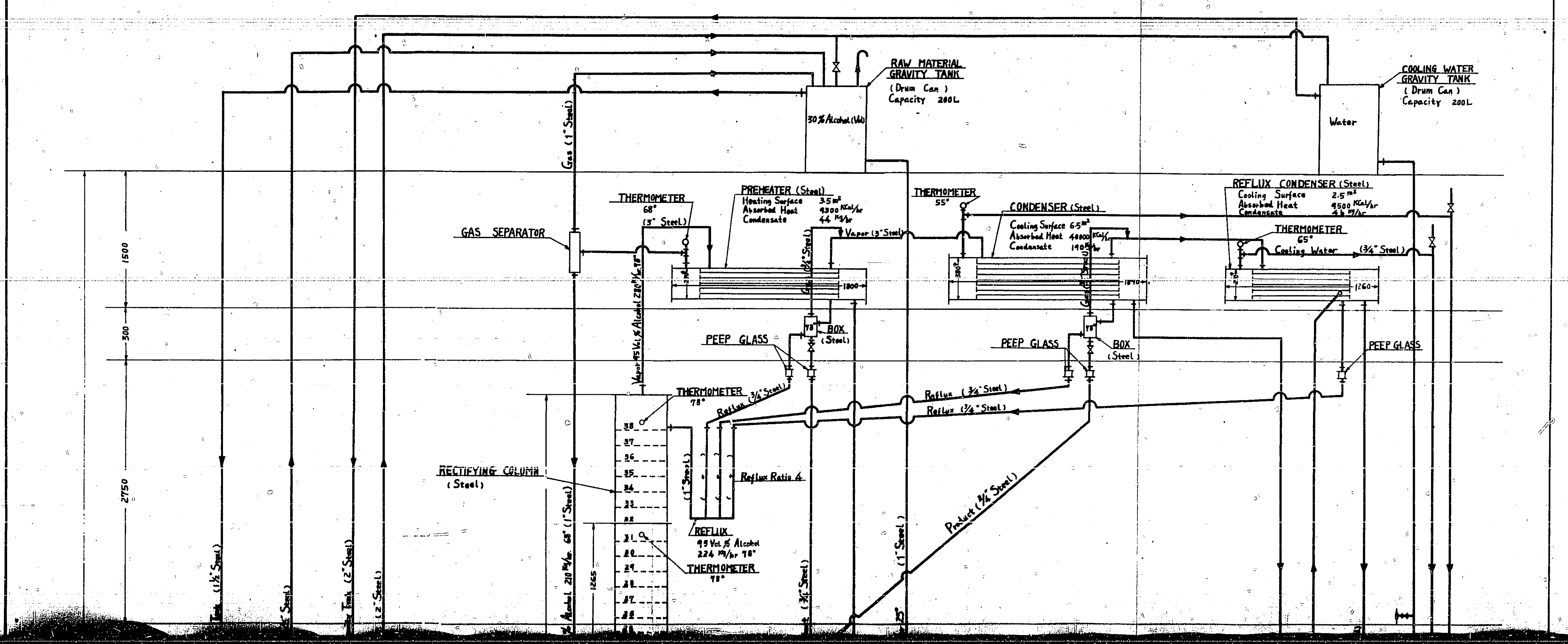


Figure 1 (B)6
ALCOHOL DISTILLATION TOWER DIAGRAM



RAW MATERIAL GRAVITY TANK
(Drum Can)
Capacity 200L
30% Alcohol (Vol)
COOLING WATER GRAVITY TANK
(Drum Can)
Capacity 200L
Water
Gas (1" Steel)
GAS SEPARATOR
THERMOMETER
68°
(3" Steel)
PREHEATER (Steel)
Heating Surface 3.5 m²
Absorbed Heat 9300 KCal/hr
Condensate 44 Kg/hr
Vapor (3" Steel)
Gas (3/4" Steel)
1800
THERMOMETER
55°
CONDENSER (Steel)
Cooling Surface 6.5 m²
Absorbed Heat 48000 KCal/hr
Condensate 190 Kg/hr
380
1840
REFLUX CONDENSER (Steel)
Cooling Surface 2.5 m²
Absorbed Heat 9500 KCal/hr
Condensate 4 Kg/hr
THERMOMETER
65°
Cooling Water (3/4" Steel)
1260
78°
BOX (Steel)
PEEP GLASS
BOX (Steel)
PEEP GLASS
PEEP GLASS
1500
300
2750
1265
Vapor 95 Vol.% Alcohol 280 Kg/hr 78°
THERMOMETER
78°
Reflux (3/4" Steel)
Reflux (3/4" Steel)
Reflux (3/4" Steel)
38
37
36
35
34
33
32
31
30
29
28
27
26
RECTIFYING COLUMN
(Steel)
(1" Steel)
Reflux Ratio 4
REFLUX
95 Vol.% Alcohol
224 Kg/hr 78°
THERMOMETER
78°
Product (3/4" Steel)
(1" Steel)
(3/4" Steel)
Alcohol 210 Kg/hr. 68° (1" Steel)
Tank (1½" Steel)
Steel)
Tank (2" Steel)
(2" Steel)

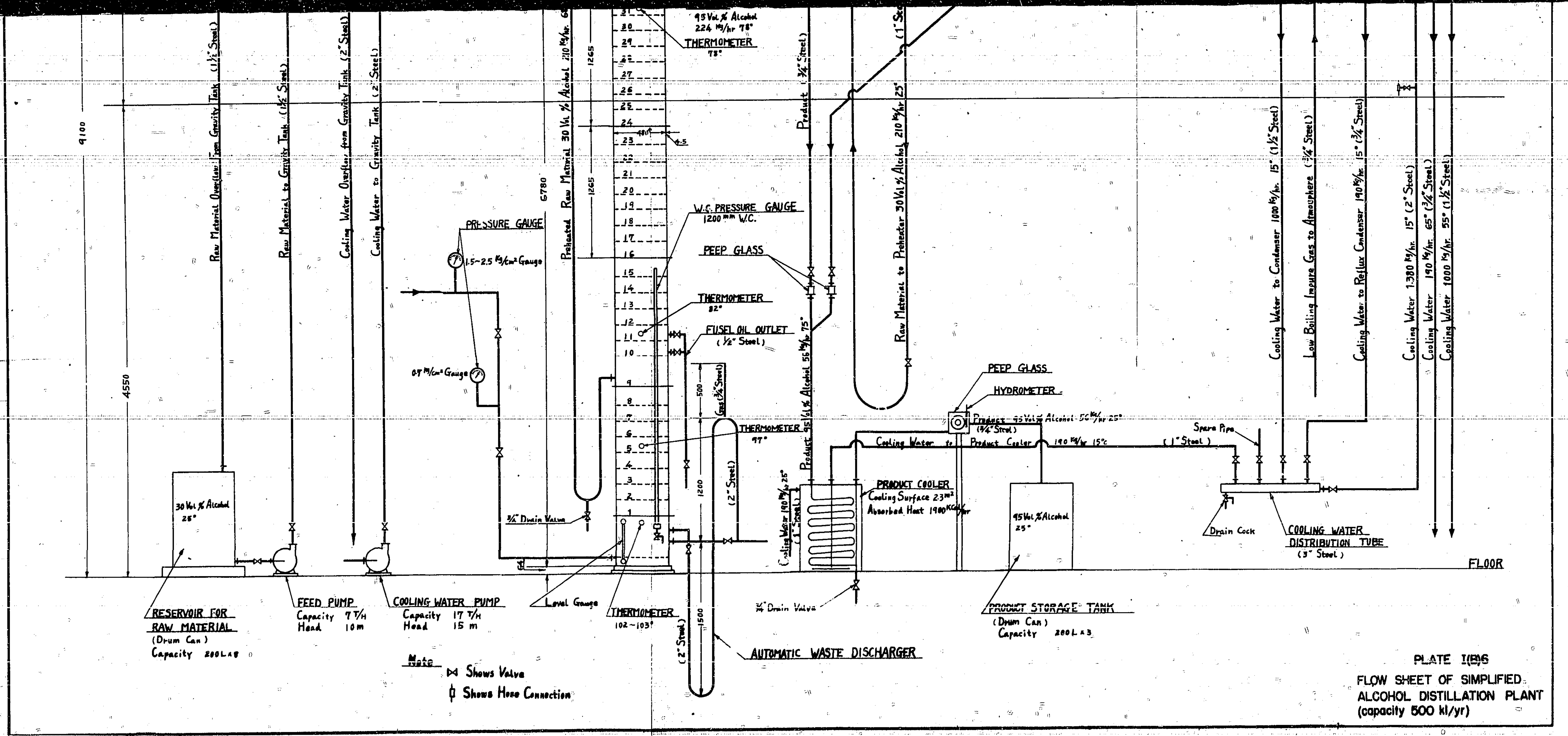


PLATE I(B)6

FLOW SHEET OF SIMPLIFIED ALCOHOL DISTILLATION PLANT (capacity 500 kl/yr)

ENCLOSURE (B)6

Table II(B)6
TEST RESULTS OF SIMPLIFIED ALCOHOL DISTILLATION APPARATUS*

		Temperature**										Pressure			Quantity				Alcoholic Content (vol.%)	
		Rectifying Column					Cooling Water										Cooling Water			
Time (A.M.)	Raw Material Preheater Outlet	T_1	T_2	T_3	T_4	T_5	Condenser Outlet	Reflux Condenser Outlet	Product Cooler Outlet	Product Storage Tank	Boiler Pressure (psi gage)	Rectifying Column Inlet Pressure (kg/cm^2 gage)	Bottom of Column P_2 (mm water column)	Product lit/min & kl/yr	Raw Material lit/min kl/yr	Condenser (kg/min)	Reflux Condenser (kg/min)	Raw Material	Product
9:00	68	102.5	100	82	78.5	78	52	19	17.5	22	15	0.75	1050	1.07 463.7	3.98 1721	21.4	8.5	30	95.2
9:30	68	102.5	100	82	78.5	78	49	19	17.5	22	19	0.6	1050	1.03 447.1	3.833 1660	18.5	8.5	30	95.2
10:00	68	102.0	98	83	78	77.5	52	20	18	22	20	1.15	1050	1.34 586.8	4.99 2175.4	15.4	1.7	29.7	93.95
10:30	55	102.5	93	82	78.5	78	52	19	20	21	40	0.9	1130	1.48 640	5.51 2380.3	38.3	1.4	29.8	94.9
11:00	56	103.0	97	82	78	77.5	49	18	19	21	37	0.8	1070	1.56 676.8	5.82 2514.2	38	1.2	29.8	95.0
11:30	58	103.0	98	83	78.5	78	49	18	23	22	38	0.7	1100	1.56 676.8	5.81 2513.5	41.2	2.4	29.9	95.1
12:00	59	103.0	97	82	78.5	78	50	25	25	22	40	0.8	1230	1.6 693.4	5.97 2579.04	41.7	2.8	30	95.1
Mean of Normal State#	57	102.9	96.2	82.25	78.37	77.87	50	20	21.75	21.5	38.75	0.8	1132.5	1.55 671.75	5.77 2492.64	39.8	1.95	29.87	95.0

*Capacity: 500kl/yr (300 days operation)
Date July 31, 1945
**Raw material reservoir temperature constant at 24°
Cooling water inlet temperature constant at 17°

#Normal state was from 10:30 to 12:00

ENCLOSURE (B) 7

SYNTHESIS OF METHANOL

(In Two Parts)

by

CHEM. ENG. LIEUT. S. ENDO

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)7

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)7

PART I

by

CHEMICAL ENGINEERING LIEUT.
S. ENDO

Research Period: 1943-1944

SUMMARY

Some experiments were made to find a good catalyst and conditions for the synthesis of CH_3OH from CO_2 and H_2, for utilization of the waste gas in the butanol fermentation industry. The catalyst to be used for the industry was Zn-Cu-chromite (atomic ratio of Zn:Cu:Cr = 8:3.2:2) or Zn+Cu+aluminate (atomic ratio of Zn:Cu:Al = 7:2:1). The duration of catalytic activity is 400 hours and 260 hours, respectively. The experimental conditions which afford good results, are: pressure 200 kg/cm^2, temperature 250 - 270°C, for the chromite catalyst; and pressure 150 kg/cm^2, temperature 250 - 270°C, for the aluminate catalyst. The space time yield of pure methanol under these conditions is 0.4 - 0.5.

I. INTRODUCTION

A. History of Project

It is well known that in the n-butanol fermentation of starchy materials, a large quantity of CO_2 and H_2 is produced. For utilizing the waste gas of this fermentation industry, the present experiments to study the fundamental conditions of the methanol synthesis were undertaken from April, 1943 to March, 1944. A larger scale pilot plant was established in the Depot in May, 1944. But the project was discontinued after March, 1944; therefore, there is no data of a larger scale experiment. A flow sheet for this pilot plant is shown in Figure 4(B)7. The important references for the methanol synthesis from CO_2 and H_2 are mentioned in the following literature:

J. C. Woodruff, Ind. Eng. Chem., 19, 1147 (1927)
J. C. Woodruff, U.S.P. 1695447
B. N. Dolgow, Chem. Zentr., 105, 2653 (1934)
B. N. Dolgow, Chem. Abs., 28, 5805
A. Z. Karpov, Chem. Abs., 34, 5047 (1940)
E. M. Bocharova, Chem. Abs., 32, 4518 (1938)
FUJII, J. P. 154358

B. Key Research Personnel

Chem. Eng. Lieut. Comdr. A. YAMAOKA
Chem. Eng. Lieut. M. YOSHIDA
Chem. Eng. Lieut. S. ENDO
Engineer INOUE

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

The flow sheet of the pilot plant is shown in Figure I(B)7.

B. Description of Test Procedures

1. Preparation of Catalysts. Solutions of 0.5 N $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Cr(NO_3)_3$ or $Al(NO_3)_3$ were mixed in definite proportions and heated to 80°C. The solution was poured into an equivalent amount of 0.5 N.NaOH, and the precipitate formed was washed with hot water and filtered. It was dried at 350°C, powdered in a ball-mill, and made into tablets.

2. The Raw Material Gases. CO_2 from market and H_2 produced in the Depot were mixed in a ratio of 1:3.

3. Procedure of the Operation. To the reaction vessel, which contained 50cc of catalyst, the mixed gas was passed at a rate of 4lit/hr and heated slowly to 200°C during 7 hours. Maintaining the reaction vessel at a definite temperature and pressure, the reaction products were obtained and their composition determined. The gas composition was determined by the Hempel method and the composition of liquid product, being composed of CH_3OH and H_2O, was determined by the specific gravity. From these data, the volume of the charged gas, specific velocity in the reaction vessel, and space time yield of CH_3OH were calculated by the following formula:

The volume of charged gas = The equivalent gas volume of the liquid products + The volume of waste gas.

$$\text{Space velocity (SV)} = \frac{\text{The volume of charged gas (lit/hr)}}{\text{The volume of the catalyst (lit)}}$$

$$\text{Space time yield of } CH_3OH \text{ (S.T.Y.)} = \frac{\text{The quantity of produced } CH_3OH \text{ per one hour (gm)}}{\text{The volume of the catalyst (cc)}}$$

C. Experimental Results

The effect of temperature and the chemical composition of the catalyst on the yield of methanol is shown in Table I(B)7 and Figure 2(B)7. The duration of catalyst activity was investigated by determining the temperature necessary to maintain the S.T.Y. of CH_3OH at 0.4 - 0.6. The results were shown in Table II(B)7 and Figure 3(B)7.

III. CONCLUSIONS

The atomic ratio of a good mixed catalyst is as follows:

Zn : Cu : Cr = 8 : 3.2 : 2
Zn : Cu : Al = 7 : 2 : 1

Using these catalysts the following S.T.Y. of CH_3OH were obtained at the indicated temperature.

Cat.	Temp.	S.T.Y.
Zn:Cu:Cr = 8:3.2:2	250 - 320°C	1.3 - 1.4
Zn:Cu:Al = 7:2:1	300 - 325°C	1.2 - 1.3.

ENCLOSURE (B)7

The activity of the catalyst depends largely on the Cu-content. As Cu-content increases, the catalyst becomes more active at low temperatures.

The conditions under which these catalysts show durability in regard to catalyst activity are:

	Zn:Cu:Cr	Zn:Cu:Cr	Zn:Cu:Al
Catalyst composition	8:3.2:2	8:3.2:2	7:2:1
Reaction pressure	150 kg/cm^2	200	150
Reaction temperature	275-400°C	260-355	250-310
Space velocity	15000-16000	15000-16000	15000-16000
S.T.Y. of CH_3OH	0.4-0.5	0.4-0.6	0.4-0.5
Life of catalyst	150 hrs	400	260.

ENCLOSURE (B)7

Table I(B)7-a
CATALYST ACTIVITY IN SYNTHESIS OF CH_3OH

Exp.No.	Condition*			Product		STY
	Temp. (°C)	SV	Total (gm)	% of CH_3OH (%)	CH_3OH (gm)	of CH_3OH
No. 1	230	14650	13	40	5	0.05
	250	14860	27	39	11	0.11
	275	14035	44	30	13	0.13
	300	15350	80	39	31	0.31
	325	15800	105	39	41	0.41
	350	16190	118	39	46	0.46
	375	16248	151	38	51	0.51
	400	16340	181	36	65	0.65
	425	16355	178	30	53	0.53
No. 3	225	14380	27	32	9	0.09
	250	14745	45	48	22	0.22
	275	15160	89	51	45	0.45
	300	15760	120	49	59	0.59
	325	15870	143	47	66	0.66
	350	16900	143	40	57	0.57
	375	16270	142	37	53	0.53
	400	15890	129	33	42	0.42
No. 4	230	14800	58	38	20	0.20
	250	15400	85	44	37	0.37
	275	16700	162	46	75	0.75
	300	16710	200	51	102	1.02
	325	17230	192	43	84	0.84
	350	16210	192	42	81	0.81
	375	18860	201	38	76	0.76
	400	16920	177	31	55	0.55

* In all cases: pressure was 200 Kg/cm^2, time was 2 hours. The catalyst was 50cc of Zn:Cu:Cr in the following ratios: Experiment No. 1 7:1:3, Experiment No. 3 7:5:3, Experiment No. 4 7:6:3.

ENCLOSURE (B)7

Table I(B)7-b
CATALYST ACTIVITY IN SYNTHESIS OF CH_3OH

Exp.No.	Catalyst Zn:Cu:Cr	Condition*			Product		STY
		Temp. (°C)	SV	Total (gm)	% of CH_3OH (%)	CH_3OH (gm)	of CH_3OH
No. 7	7:9:3	230	15470	100	47	47	0.47
	50cc	250	16830	151	51	77	0.77
		275	17003	203	51	104	1.04
		300	18235	248	51	126	1.26
		325	16290	197	49	96.5	0.97
		350	16830	195	44	85.8	0.86
		375	16214	159	38	60	0.60
		400	16430	176	32	56	0.56
No.11	Zn:Cu:Cr	225	15810	108.7	57.7	62.7	0.68
	8:32:2	250	17657	229	61	139.7	1.40
	50cc	275	18335	236	55	130	1.30
		300	18750	260.5	51.5	134	1.34
		325	17501	248	46	114	1.14
		350	16805	223	46	103	1.03
		375	16895	194	42	81	0.81
No.13	Zn:Cu:Al	225	15240	64	49	31	0.31
	7:2:1	250	15220	87	44	38	0.38
	50cc	275	17030	154	46	71	0.71
		300	18700	242	50	121	1.21
		325	18330	272	47	128	1.28
		350	17260	246	41	101	1.01
		375	17380	217	32	69	0.69
		400	16390	181	20	36	0.36

* In all cases: pressure was 200 Kg/cm^2, time was 2 hours.

ENCLOSURE (B)7

Table II(B)7-a
THE RESULTS OF THE DURATION TEST

Duration Time (hr)	Condition*			Product		S. T. Y. of CH_3CH
	Temp (°C)	S.V.	Total (gm)	% of CH_3OH (gm)	CH_3OH (gm)	
14	250-270	15650	103	39	40	0.40
34	270	15440	115	40	46	0.46
54	270	15430	104	39	40	0.40
64	270	15380	99	38	37	0.37
74	280	15540	119	40	48	0.48
94	280	15490	109	36	39	0.39
104	280	15610	106	38	40	0.40
124	290	15830	126	38	47	0.47
148	290	15570	120	41	49	0.49
160	300	15970	131	44	58	0.58
180	300	15680	124	38	47	0.47
200	300	16050	127	38	49	0.49
220	300	15510	124	36	44	0.44
234	300	15780	118	37	44	0.44
258	310	15640	124	36	45	0.45
268	310	15860	123	39	48	0.48

* Pressure: 150 kg/cm^2;
Time: 2 hrs.
Catalyst: Zn:Cu:Al::7:2:1; 50^{cc}

ENCLOSURE (B)7

Table II(B)7-b
THE RESULTS OF THE DURATION TEST

Duration Time (hr)	Condition*		Product			S. T. Y. of CH_3CH
	Temp.	S.V.	Total (gm)	% of CH_3OH	CH_3OH (gm)	
10	230°C 275	15420	65	35	22	0.22
14	275	15480	94	40	38	0.38
40	300	16108	137	40	55	0.55
60	300	15860	125	48	60	0.60
80	300	15637	107	49	53	0.53
100	300	15637	118	45	54	0.54
126	300	15283	79	51	41	0.41
146	310	15320	90	49	44	0.44
160	310	16520	100	39	39	0.39
180	320 340	15230	82	43	35	0.35
190	340 360	15660	74	37	27	0.27
208	360 400	15100	73	25	19	0.19

* Pressure: 150 kg/cm^2
Time: 2 hrs.
Catalyst: Zn:Cu:Cr::8:3.2:2; 50cc

ENCLOSURE (B)7

Table II(B)7-c
THE RESULTS OF THE DURATION TEST

Duration Time (hr)	Condition*		Product			S. T. Y. of CH_3OH
	Temp. (°C)	S.V.	Total (gm)	% of CH_3OH	CH_3OH (gm)	
4	230	14680	56	42	23	0.23
14	250	14730	78	49	38	0.38
28	260	15350	105	50	53	0.53
46	270	15740	115	49	56	0.56
66	270	15770	118	50	59	0.59
82	270	15810	100	51	51	0.51
90	275	15790	120	51	61	0.61
110	280	16230	129	49	63	0.63
124	280	16000	98	49	48	0.48
144	285	16460	145	49	71	0.71
164	285	15930	117	51	60	0.60
184	285	15620	109	46	50	0.50
192	285	15760	110	43	47	0.47
196	290	16185	111	45	50	0.50
216	300	15340	98	46	45	0.45
222	300	15380	85	45	38	0.38
230	305	15375	93	46	43	0.43
250	310	15660	107	45	48	0.48
268	310	15570	99	46	46	0.46
274	315	15270	84	44	37	0.37
276	320	15030	99	45	45	0.45
298	325	15670	107	42	45	0.45
318	330	15840	123	43	53	0.53
338	330	15250	140	27	38	0.38
346	330	15280	91	40	36	0.36
352	335	14980	90	42	38	0.38
364	340	15090	91	39	35	0.35
370	345	14950	97	40	39	0.39
378	350	15625	102	39	40	0.40
396	355	15320	115	38	44	0.44
400	355	12615	102	30	30	0.30

* Pressure: 200 kg/cm^2
Time: 2 hrs.
Catalyst: Zn:Cu:Cr::8:3.2:2 ; 50cc

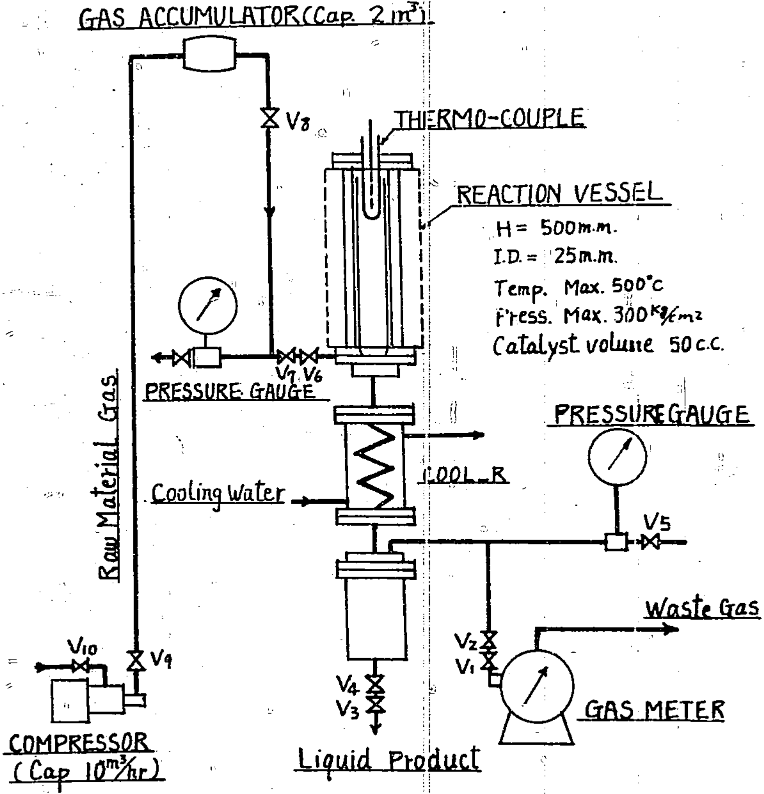


Figure 1 (B)7
FLOW SHEET OF THE PILOT PLANT FOR METHANOL SYNTHESIS

ENCLOSURE (B)7

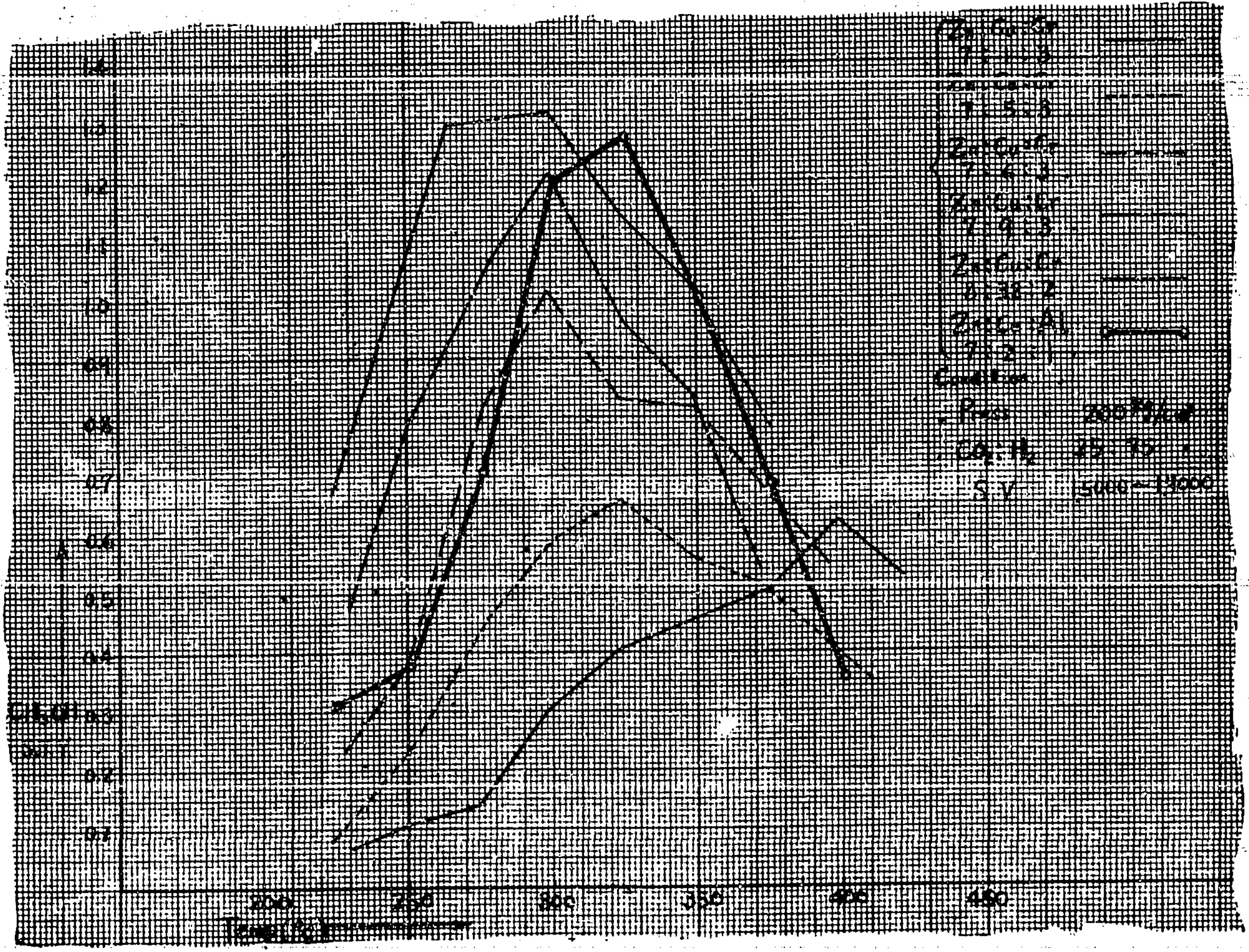


Figure 2 (B)7

CATALYST ACTIVITY IN SYNTHESIS OF CH3OH

ENCLOSURE (B)7

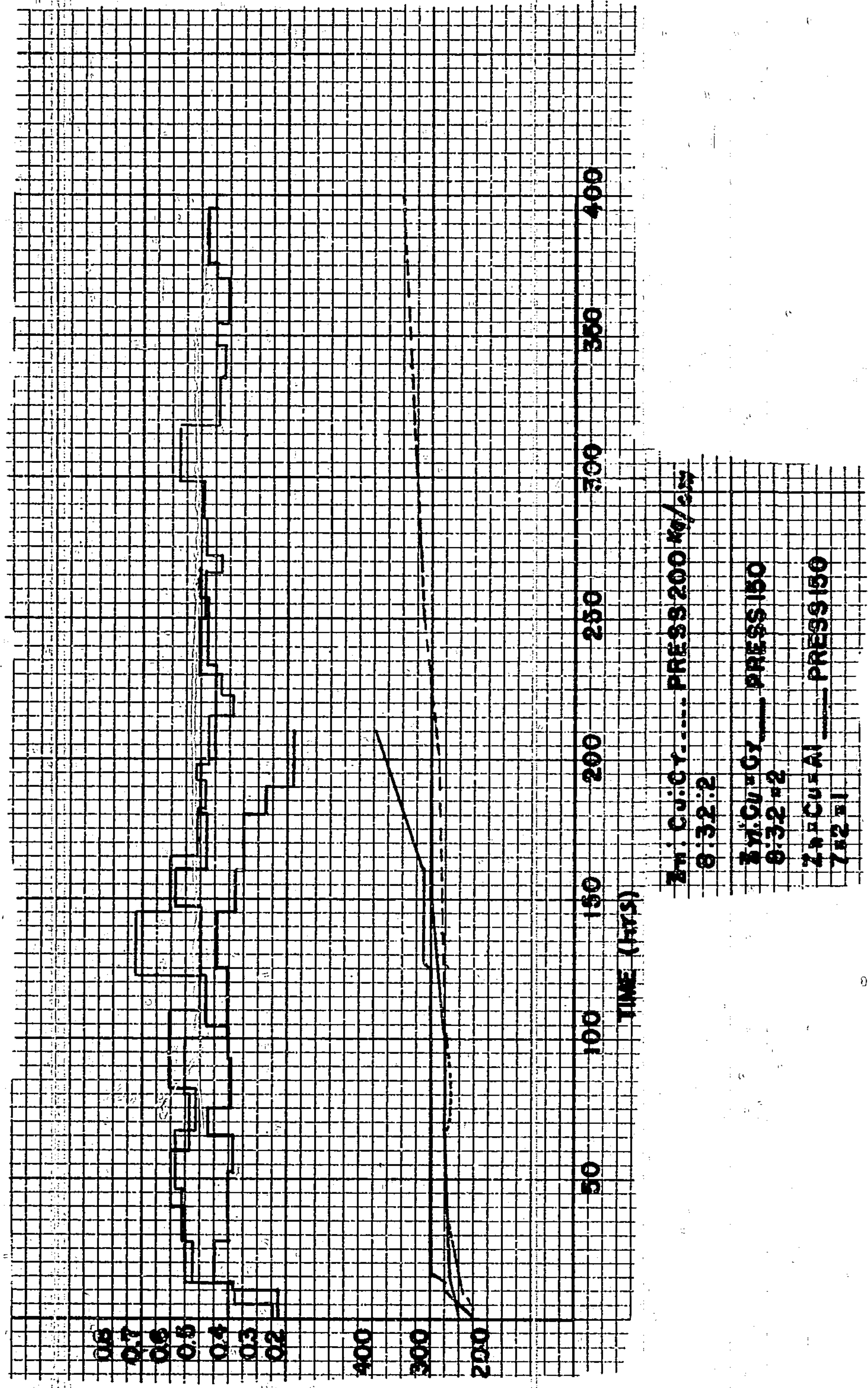
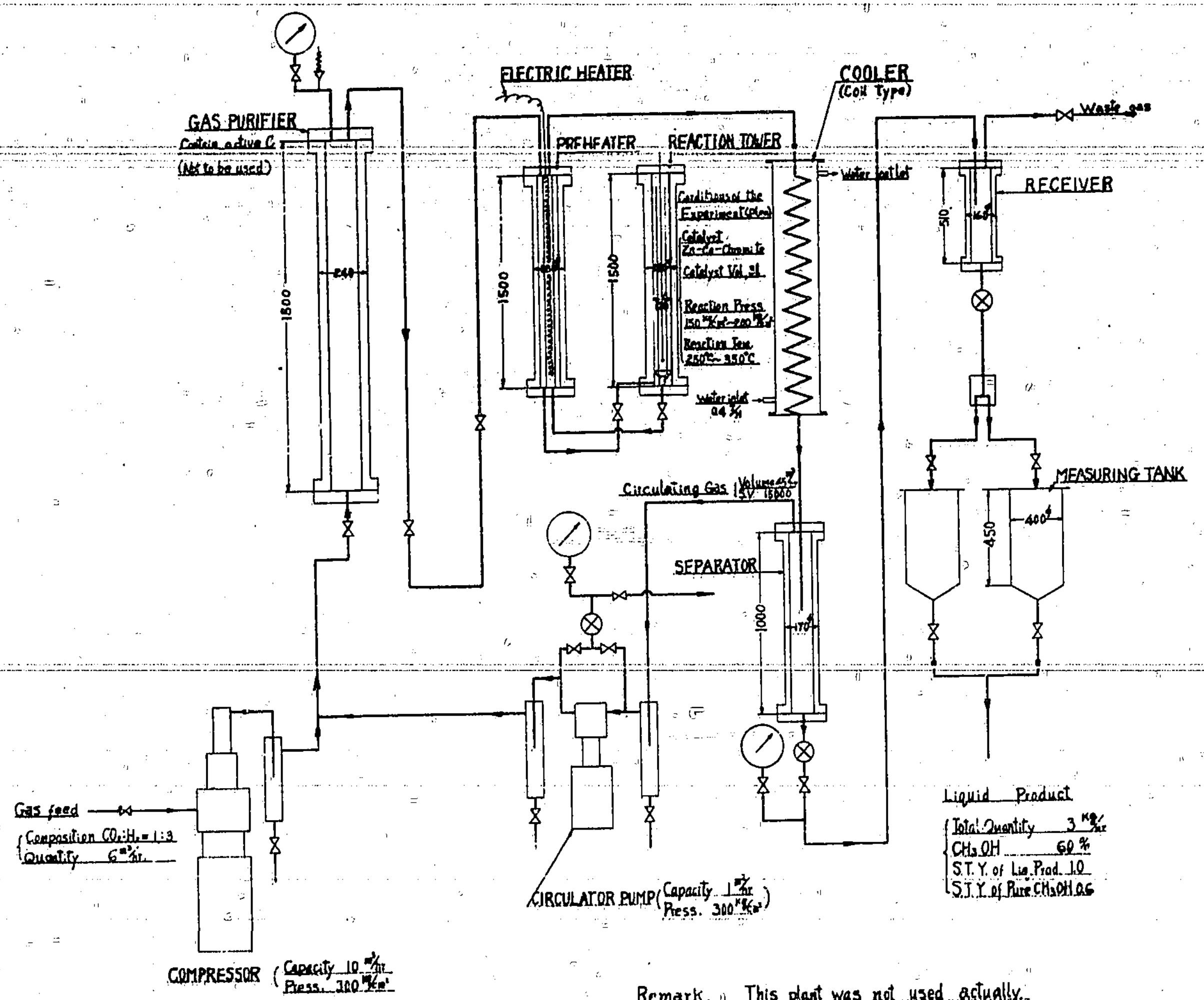


Figure 3 (B)7
THE RESULTS OF THE DURATION TEST

ENCLOSURE (B)7



Remark. This plant was not used actually.

Figure 4 (B)7
FLOW SHEET OF THE PILOT PLANT
FOR CH_3OH SYNTHESIS FROM CO_2 AND H_2

Figure 5 (B)7
PILOT PLANT FOR SYNTHESIS
OF METHANOL FROM WATER GASES

ENCLOSURE (B)7

PART II

by

CHEMICAL ENGINEERING LIEUT.
S. ENDO

Research Period: 1943-1944

SUMMARY

This study was made to find a new catalyst for the methanol synthesis from water gas. The result of the experiments was as follows:

The Zn-Cu-chromite catalyst, having the composition Zn:Cu:Cr = 8:3.2:2, was found to be a good one. Its catalytic activity was kept for 20 days under the following conditions:

Reaction temperature ....250-350°C
Reaction pressure ....150 kg/cm^2
S.V. 10,000-15,000
S.T.Y. ....0.5-1.0.

I. INTRODUCTION

A. History of Project

Previously, a Cu-uranium catalyst was used in the methanol synthesis plant because of its strong activity at low temperatures and low pressures. However, its activity was impaired by overheating and the poisonous action of sulfur in the gas. The Zn-Cu-chromite catalyst, mentioned in Part I, was therefore studied.

B. Key Research Personnel

Chem. Eng. Lt. Comdr. A. YAMAOKA
Chem. Eng. Lt. S. ENDO
Chem. Eng. T. INOUE

II. DETAILED DESCRIPTION

The gas used for this experiment was a mixture of 1 mol of CO and 2 mols of H_2. CO was prepared by burning charcoal and the CO_2 was removed with caustic. The details of the experiment and the apparatus used are the same as those described in Part I.

The experimental results: Using the previously studied Zn-Cu-chromite catalyst, similar results for the experiments made in Part I were obtained.① The Zn-Cu-chromite catalyst, having the composition Zn:Cu:Cr= 8:3.2:2, was found to be a good one. Its catalytic activity was kept for 20 days under the following conditions:

ENCLOSURE (B)7

Reaction temperature	250-350°C
Reaction pressure	150 kg/cm^2
S.V.	10,000-15,000
S.T.Y.	0.5-1.0.

ENCLOSURE (B) 8

STUDIES ON THE PRODUCTION OF HIGHER ALCOHOLS FROM CRACKED PETROLEUM GASES

by

NAVAL ENGINEER
T. ITAKURA, PH.D

Research Period: 1938-1940

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)8

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)8

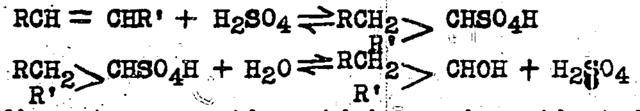
SUMMARY

This investigation was undertaken to produce higher alcohols, such as isopropyl and secondary butyl alcohols, from C_3H_6 and C_4H_8 in cracked petroleum gases. It was recognized that 52% dil. H_2SO_4 was active in the direct hydration reaction of C_3H_6(g.)-H_2O(Vap.) at 110°C. This work was conducted from September, 1938, to April, 1940.

I. INTRODUCTION

It is well known that Berthelot assumed that gaseous olefines react with concentrated sulphuric acid (corresponding to $H_2SO_4(0\text{-}1)H_2O$) and change into alkyl sulphuric acid at normal temperatures and pressures. He also confirmed that the alkyl esters of sulphuric acid were readily hydrolysed to corresponding alcohols and sulphuric acid.

Though the mechanism of these changes is obscure and Berthelot only assumed the formation of alkyl esters in explaining these phenomena, many investigators (Kolbe, Senderens, Williamson, Brooks, Humphrey, Ipatieff and many others) have generally accepted the formation of the intermediate product as probable. Thus, the following reversible reactions are now generally accepted:



$$\mathrm{RCH{=}CHR' + H_2SO_4 \rightleftharpoons \substack{RCH_2\\R'}\!>CHSO_4H}$$

$$\mathrm{\substack{RCH_2\\R'}\!>CHSO_4H + H_2O \rightleftharpoons \substack{RCH_2\\R'}\!>CHOH + H_2SO_4}$$

In the gaseous olefine-steam reaction which was investigated, mainly at 110°C and normal pressure by a streaming method, the dilute sulphuric acid (about 52% H_2SO_4, corresponding to $H_2SO_4 \cdot 5H_2O$) seems to act differently than described above. Accordingly, experiments were carried out under various conditions by the author, in order to study the new phenomena from both the theoretical and practical points of view.

II. DETAILED DESCRIPTION

A. Apparatus

The apparatus used is shown in Figure 1(B)8 and 2(B)8.

B. Test Procedures

The gaseous olefine passes through a gas meter, is introduced into a steam evaporator, and mixed with steam at different ratios. The gas enters the bottom of a convertor which is filled with pumice pieces and is heated to 110°C electrically. Varying concentrations of H_2SO_4 flow down over the pumice surfaces and mix with the ascending gaseous olefine-steam mixture in a countercurrent. Thus, the gas is hydrated into the corresponding alcohol by the direct catalytic action of dilute sulphuric acid. The alcohols thus formed are distilled out of the convertor to be cooled in a condenser.

Other experiments were also tried in the same steaming apparatus, employing various solid catalysts (tablets 2mm x 1mm) instead of pumice pieces. Other experimental conditions and procedures were the same as the previously mentioned. This study on the direct hydration of gaseous olefines in the presence of solid catalysts was attempted as a comparison to the dilute sulphuric acid catalyst. These results of the solid catalyst hydration of propylene are given in Table I(B)8. The experimental results of the dilute sulphuric acid hydration of propylene and butylene at

110°C are given in Table II(B)8 and Table III(B)8 respectively.

C. Summary of Experimental Results

1. In the above experiments, as much as 15% of the charged olefine was changed directly to the corresponding alcohols. Conditions of the reaction were varied by changing the concentration of dil H_2SO_4 catalyst, the ratio of steam to charged olefines, and the temperatures of the reaction.

2. The most favorable conditions for the formation of isopropanol from propylene at 110°C were found to be as follows:

Conc. of H_2SO_4 catalyst	52%
Mol. ratio steam to charged olefines	3
Yield	15%

3. The most favorable conditions for the formation of secondary butyl alcohol from n-butene at a steam-olefine ratio of 3:1 were found to be as follows:

Conc. of H_2SO_4 catalyst	50%
Yield	18%

4. Some data were obtained as to the effect of temperature upon yield of product. It appeared that variations in temperatures exerted no appreciable effect on the yield of product. A temperature of 110°C was the most convenient experimentally.

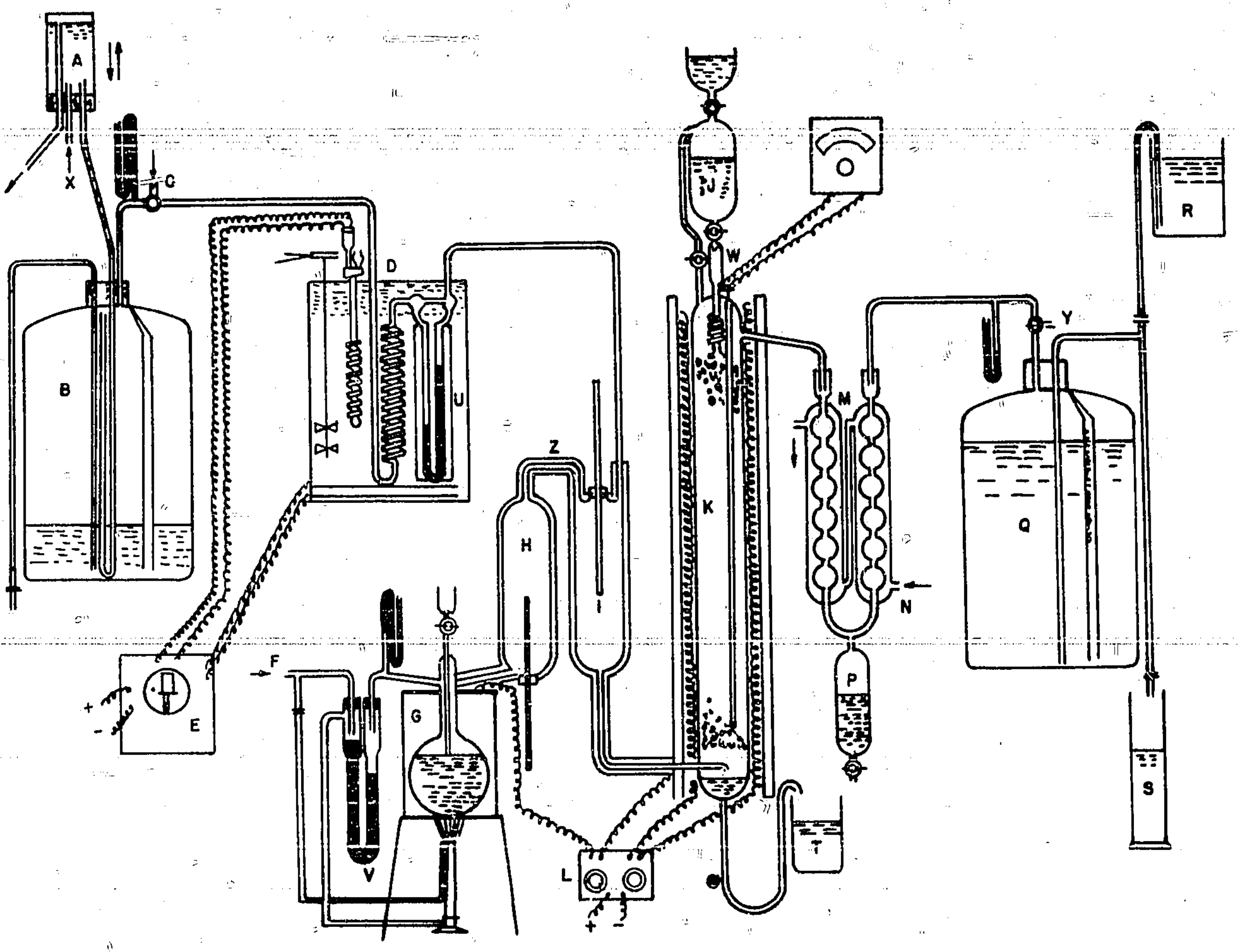
5. The concentration of alcohols in the aqueous product was no greater than 4% by volume.

III. CONCLUSIONS

By a streaming method employed in the laboratory, gaseous olefines can be converted to corresponding alcohols continuously, under the influence of the catalytic hydration action of dil. H_2SO_4. Yields of isopropanol and secondary butanol varying from 10-18% were obtained at 110°C in the presence of 50-52% H_2SO_4, using a charged gas composed of 3 mols of steam to 1 mol of olefine.

It is considered, however, that it would be difficult to apply these experimental results on a commercial scale, since the concentration of alcohols thus formed is too small to recover economically by distillation.

ENCLOSURE (B)8



(A) CONSTANT LEVEL
(B) PROPYLENE RESERVOIR
(C) PROPYLENE INLET
(D) THERMOSTAT
(E) RELAY
(F) COAL GAS INLET
(G) STEAM PRODUCER
(H) PREHEATOR
(I) MIXER
(J) DIL. SULPHURIC
(K) CONVERTOR
(L) RELAY
(M) CONDENSER
(N) ICE WATER
(P) RECEIVER
(Q) PROPYLENE
(R) WATER TANK
(S) CYLINDER
(T) SULPHURIC ACID RECEIVER
(U) FLOW WATER
(V) GAS REGULATOR
(W) THERMOCOUPLE
(X) PROPYLENE INLET
(V) PROPYLENE INLET
(Z) CAPILLARY

Figure 1(B)8
EXPERIMENTAL APPARATUS FOR PREPARATION OF ALCOHOLS FROM OLEFINES

ENCLOSURE (B)8

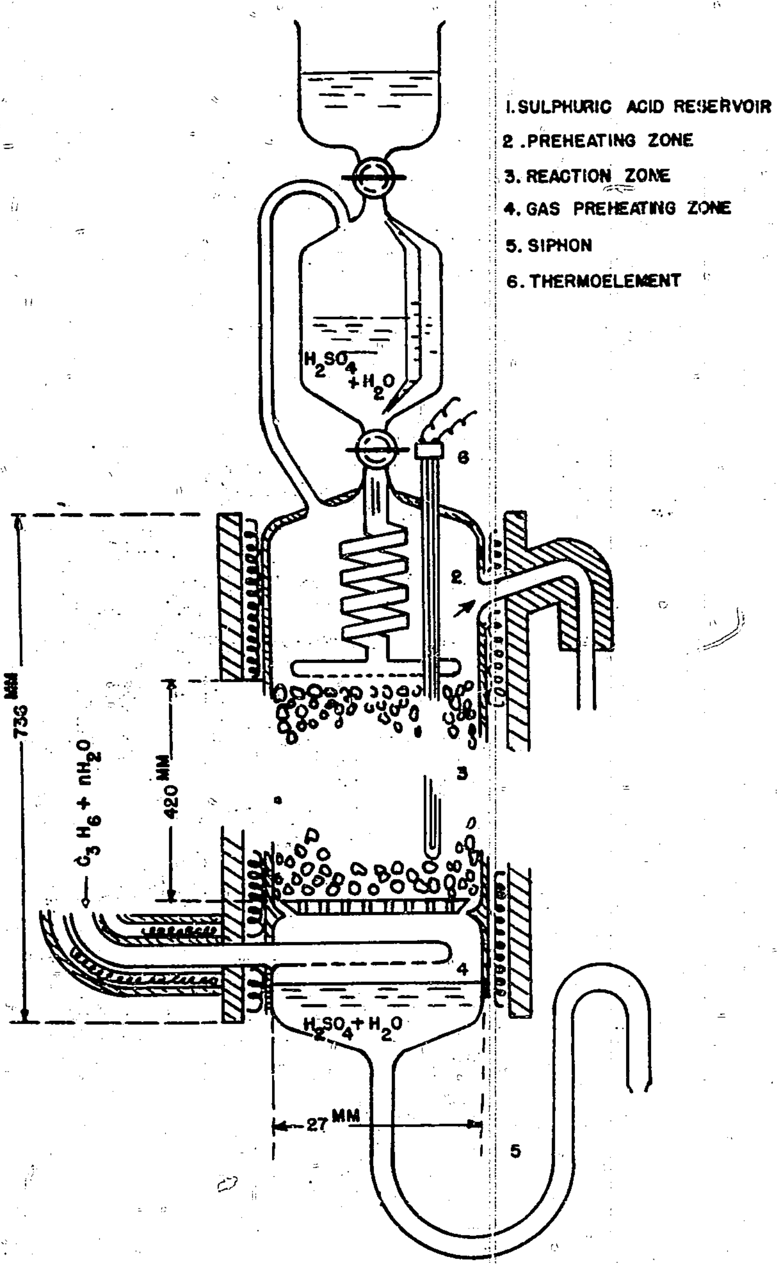


Figure 2(B)8
DETAILS OF REACTION TOWER

ENCLOSURE (B)8

Table I(B)8
SOLID CATALYST HYDRATION OF PROPYLENE

Exp. No.	Experimental Conditions				Products*
	Catalysts (Kinds and Compositions)	Reaction Temp. (°C)	Gas Space Velocity per hr	Steam Ratio $\frac{H_2O}{C_3H_6}$ (mol.)	Conv. % Calculated from Gas Consumption
6	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	120	278	1	2.2
7	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	140	278	1	2.2
8	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	160	278	1	10.0
9	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	170	278	1	6.3
5	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	180	278	1	5.5
4	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	190	278	1	4.1
3	$Ba_3(PO_4)_2 + H_3PO_4$ (Molar Ratio)	200	278	1	2.7
10	CdO + H_3PO_4 (Molar Ratio)	160	276	1	5.6
15	CdO + H_3PO_4 (Molar Ratio)	170	276	1	2.7
14	CdO + H_3PO_4 (Molar Ratio)	180	276	1	4.0
13	CdO + H_3PO_4 (Molar Ratio)	190	276	1	4.5
12	CdO + H_3PO_4 (Molar Ratio)	200	276	1	3.6
16	CdO + H_3PO_4 (Molar Ratio)	170	1670	1	5.4
17	CdO + H_3PO_4 (Molar Ratio)	170	786	1	4.3
18	CdO + H_3PO_4 (Molar Ratio)	170	706	1	6.0
19	$AlPO_4$+Acid Clay (1=1 wt)	180	302	3	6.4
20	$AlPO_4$+ Acid Clay (1=1 wt)	780	698	3	3.9
21	Mg-Borate + Acid Clay (1=1 wt)	180	205	3	5.5
22	Hg-Borate + Acid Clay (1=1 wt)	180	906	3	5.0
23	Hg-Borate + Acid Clay (1=1 wt)	180	806	3	6.0
24	Hg-Borate + Acid Clay (1=1 wt)	180	524	3	3.9
25	Al_2O_3 + Acid Clay (1=1 wt)	180	464	3	4.1
26	Al_2O_3 + Acid Clay (1=1 wt)	180	916	3	5.7
23	Al_2O_3 + Acid Clay (1=1 wt)	180	516	3	3.9
29	Acid Clay	180	490	3	4.8
30	Al-Borate +Acid Clay (1=1 wt)	180	504	3	4.0
31	Cu-Borate +Acid Clay (1=1 wt)	180	547	3	3.7
33	Cd-Borate +Acid Clay (1=1 wt)	180	150	3	3.7
34	H_3PO_4 adsorbed on Pumices	180	162	3	12.5
35	B-Borate + H_3PO_4(1=1 mol)	180	35.3	3	5.9
35	H_3PO_4+ Acid Clay (1=1 wt)	180	15.4	3	3.9
37	Co-Borate+H_3PO_4+Acid Clay(1 1 1wt)	180	30.0	3	6.8
38	Mn-Borate + Acid Clay	180	28.0	3	4.2
44	H_3PO_4 adsorbed on Silica Gel	180	13.7	10	2.0
45	Ag_2SO_4+ H_3PO_4 (1=1 mol)	150	17.6	9	6.8
50	Ag_2SO_4+ H_3PO_4 (1=1 mol)	180	16.2	25	7.1
51	$Cd_3(PO_4)_2$+H_3PO_4(5=4 wt)	150-160	15.8	3	13.0
52	$Ag_2(SO_4)$+H_2SO_4(96=4 wt)	170-180	13.3	3	8.1
53	$Zn_3(PO_4)_2$+H_3PO_4(5=3 wt)	170-180	26.1	3	2.7
56	$Ba_3(PO_4)_2$+H_3PO_4(5=3 wt)	150	26.3	3	8.1
58	3% $CuSO_4$+45%H_2SO_4(1=1 wt)	150	15.0	3	7.4
60	3% Na-stearate+45%H_2SO_4(1=1 wt)	150	12.5	3	11.3
61	3% $C_6H_5SO_3K$+45%H_2SO_4 (1=1 wt)	180	150	3	7.4
62	3%Na_2SO_4+45%H_2SO_4 (1=1 wt)	180	150	3	8.9

*All products contained a trace of polymers

ENCLOSURE (B)8

Table II(B)8
DILUTE SULPHURIC ACID HYDRATION OF PROPYLENE

Exp. Conditions		Raw Gas Compositions* (%)					Unconverted Gas Compositions* (%)					Distillates		Conversion Percent
dil-H_2SO_4 Concentrations (%)	Steam Ratio $\frac{H_2O}{C_3H_6}$ (mol)	C_3H_6	CO_2	O_2	CO	H_2	C_3H_6	CO_2	O_2	CO	H_2	Grams	Specific Gravity (15/4°C)	
0	3	95.6	0.2	1.2	0.4	0.1	94.6	0.2	0.8	0.2	0.0	54.0	1.0000	0.1
25	3	93.2	0.5	1.3	0.0	1.1	90.6	0.0	1.6	0.0	1.6	56.0	0.9993	8.3
30	3	91.6	0.0	1.2	0.4	0.5	87.4	0.0	3.7	0.1	1.0	14.4	0.9977	9.1
32	3	96.3	0.4	0.7	0.0	1.1	94.8	0.2	0.6	0.2	0.1	15.4	0.9984	7.4
34	3	96.3	0.4	0.7	0.0	1.1	93.7	0.0	0.9	0.5	0.4	17.0	0.9971	12.0
35	3	93.6	0.0	1.4	0.1	1.8	90.3	0.5	1.7	0.0	2.8	22.0	0.9935	9.8
38	3	94.6	0.0	1.0	0.3	2.0	90.8	0.0	2.0	0.0	2.6	19.6	0.9934	12.7
40	3	93.6	0.0	1.0	0.4	0.0	85.9	0.0	2.5	0.2	1.3	50.0	0.9990	9.3
42	3	96.3	0.4	0.7	0.0	1.1	83.9	0.2	2.2	1.3	0.1	46.0	0.9992	10.6
45	3	96.0	0.0	0.8	0.4	1.3	90.7	0.2	1.5	0.2	1.3	42.0	0.9986	12.5
46	3	99.0	0.0	0.0	0.0	0.0	96.4	0.2	1.0	0.2	0.1	31.0	0.9984	15.0
48	3	94.6	0,0	1.0	0.3	2.0	89.0	0.0	2.4	0.1	1.7	18.4	0.9970	13.7
50	3	96.0	0.0	0.8	0.4	1.7	82.1	0.2	3.0	0.1	0.9	12.4	0.9957	13.8
50	3	93.2	0.8	0.4	0.4	1.1	88.0	0.2	2.4	0.8	0.6	16.4	0.9969	12.2
52	3	92.5	0.0	1.6	0.0	2.2	81.2	0.2	4.4	0.6	2.1	27.0	0.9968	21.1
53	3	90.1	0.0	1.4	0.3	2.4	82.8	0.0	2.6	0.0	3.2	——	——	21.3
54	3	92.6	0.0	0.6	0.4	0.4	78.8	0.0	1.2	0.2	0.8	22.0	0.9962	20.5
55	3	93.8	0.0	0.8	0 2	0.7	88.8	0.0	1.4	0.1	1.3	48.4	——	20.2
57	3	94.6	0.6	0.2	0.4	2.2	88.0	0.0	1.6	0.2	2.4	14.8	0.9959	16.0
58	3	85.4	0.0	2.8	0.0	0.4	75.4	0.0	4.2	0.1	1.4	50.0	——	13.0
59	3	93.8	0.0	3.6	0.0	1.4	88.9	0.2	5.4	0.0	0.3	22.0	0.9983	12.2
62	3	91.6	0.0	1.2	0.4	1.5	87.0	0.2	1.8	0.2	0.2	16.0	0.9970	11.9
0	1	95.6	0.2	1.2	0.4	0.1	94.6	0.2	1.2	0.2	0,0	None	0.9937	9.8
25	1	73.8	0.0	3.6	0.0	0.9	65.6	0.0	7.8	0.0	0.2	None	0.9994	8.8
25	1	83.1	0.0	1.5	0.2	1.1	82.2	0.0	2.6	0.4	0.8	None	0.9984	8.9
28	1	94.1	0.0	0.4	0.3	0.7	91.7	0.4	1.3	0.2	0.2	None	0.9969	10.7
30	1	83.8	0.0	1.5	0.2	1.1	80.0	0.0	2.4	0.2	2.8	None	None	10.2
30	1	95.6	0.2	0.2	0.2	0.2	94.6	0.1	0.5	0.2	0.2	None	None	9.3
38	1	96.0	0.0	1.8	0.2	0.8	89.0	0.8	1.8	0.0	1.2	None	0.9981	7.8
42	1	94.6	0.6	0.2	0.4	2.2	93.0	0.0	0.8	0.0	2.2	None	0.9998	11.3
44	1	94.6	0.6	0.2	0.4	2.2	90.9	0.3	1.1	0.6	2.2	None	0.9964	11.4
48	1	95.6	0.2	0.2	0.2	1.2	95.1	0.2	0.3	0.2	0.5	None	0.9977	13.5
52	1	92.7	0.1	1.6	0.4	1.4	87.4	0.1	2.3	0.3	1.5	None	0.9972	14.4
55	1	99.0	0.0	0.0	0.0	0.0	97.5	0.0	0.4	0.2	0.0	None	0.9987	13.0
60	1	96.0	0.0	0.8	0.4	0.0	86.8	0.0	2.4	0.0	1.5	None	None	11.4
42	6	99.0	0.0	0.0	0.0	0.0	96.9	0.0	1.3	0.0	0.0	None	0.9977	8.9
48	6	99.0	0.0	0.0	0.0	0.0	96.6	0.0	0.4	0.2	0.2	None	0.9963	9.4
50	6	94.1	0.0	0.4	0.3	0.7	83.4	0.0	2.8	0.1	0.9	None	0.9986	14.0
52	6	92.5	0.0	1.6	0.0	0.4	81.2	0.2	4.4	0.1	1.4	None	0.9968	14.1
54	6	94.1	0.0	0.4	0.3	0.7	92.9	0.2	1.0	0.1	0.7	None	0.9961	11.0
55	6	99.0	0.0	0.0	0.0	0.0	96.8	0.0	0.6	0.2	0.0	None	0.9984	11.1
58	6	94.6	0.6	0.2	0.4	2.2	92.2	0.0	0.9	0.2	0.0	None	0.9985	10.2

*No C_mH_n homologue were contained

ENCLOSURE (B)8

Table III(B)8
DILUTE SULPHURIC ACID HYDRATION OF BUTYLENE

Exp. Conditions			Raw Gas Compositions* (%)				Unconverted Gas Compositions* (%)				Conversion (%)
dil-H_2SO_4 Concentration (%)	React. Temp. (°C)	Steam Ratio $\frac{H_2O}{C_4H_8}$ (mol)	C_4H_8	CO_2	O_2	CO	C_4H_8	CO_2	O_2	CO	
40	110	3	94.6	0.0	0.8	0.1	91.4	0.0	1.1	0.0	12.4
42	110	3	87.3	0.4	2.1	0.6	83.7	0.0	2.8	1.6	12.1
44	110	3	92.9	0.3	1.5	0.1	87.2	0.0	2.2	0.0	15.5
46	110	3	91.0	0.0	1.6	0.0	87.5	0.0	2.8	0.0	16.2
48	110	3	94.9	0.0	0.8	0.3	91.8	0.0	1.9	0.2	16.8
50	110	3	84.1	0.0	2.5	0.0	75.1	0.0	4.5	0.0	18.7
52	110	3	91.7	0.1	1.2	0.4	83.1	0.0	2.6	0.2	16.6
54	110	3	92.2	0.0	1.9	0.2	88.8	0.0	2.4	0.2	13.3
54	110	3	93.9	0.0	1.0	0.3	88.4	0.0	1.7	0.3	13.3
56	110	3	90.6	0.0	1.4	0.3	81.5	0.0	3.5	0.3	19.9
58	110	3	87.7	0.0	2.3	0.1	81.0	0.0	3.7	0.1	20.5
52	100	3	97.8	0.0	0.0	0.1	89.8	0.1	1.7	0.3	16.3
52	105	3	91.7	0.1	1.2	0.4	83.1	0.3	2.6	0.2	16.6
52	105	3	85.9	0.6	2.5	0.2	78.8	0.6	3.1	0.1	17.4
52	108	3	96.6	0.0	0.4	0.0	91.0	0.0	1.6	0.0	13.3
52	110	3	90.7	0.9	2.1	0.0	85.8	0.3	2.5	0.0	14.8
52	112	3	96.0	0.0	0.4	0.2	87.1	0.4	2.6	0.1	16.5
52	113	3	90.3	0.0	0.7	0.0	81.2	0.2	2.8	0.0	14.0
52	118	3	96.1	0.0	0.4	0.2	91.3	0.0	1.2	0.2	13.5
52	120	3	94.0	0.0	0.1	0.1	87.5	0.0	1.5	0.7	15.2
52	125	3	91.8	0.0	1.4	0.0	86.2	0.0	2.1	0.7	18.3
52	130	3	96.7	0.0	0.3	0.3	89.0	0.0	2.0	0.3	20.4

*No C_mH_n or H_2 present

ENCLOSURE (B) 9

STUDIES ON ETHYL ALCOHOL

(In Two Parts)

by

ENGINEER O. MIYATA

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)9

LIST OF TABLES AND ILLUSTRATIONS

PART I

PART II

ENCLOSURE (B)9

PART I

PREPARATION OF ETHER FROM ETHYL ALCOHOL

by

ENGINEER O. MIYATA

Research Period: 1944-1945

SUMMARY

Ethyl alcohol fuel is mixed with ether for good starting qualities; hence, large amounts of ether are necessary as blending fuel.

The sulfuric acid process for production of ether is used, but for mass production of ether, this is not satisfactory. Using activated acid clay, the solid catalytic process of preparing ether has been studied.

As the results of this study, the yield of ether to the alcohol consumed is shown to be 60.2% at 200°C and at 0.33 space velocity. This yield corresponds to 92.5% of the theoretical. (cf, Table II(B)9.) The life of the catalyst appears to be longer than 155 hours.

Date of the beginning	Oct. 1944
Date of the finish	Feb. 1945

I. INTRODUCTION

K. KOBAYASHI observed that ether is produced from ethyl alcohol in the presence of acid clay at about 250°C, but the yield is low due to the formation of ethylene as a side reation, and the life of this catalyst is very short.

This study was projected to confirm these facts.

II. DETAILED DESCRIPTION

The preparation of ether from ethyl alcohol was carried out in the apparatus shown in Figure 1(B)9.

Ethyl alcohol, contained in the calibrated glass cylinder, was run into the reaction tube at constant velocity by adjusting the stopcock. The silica reaction tube was 18mm i.d. and 1200mm long, and was placed in a tubular electric heater that was 1000mm long, and heated to reaction temperature (180°-230°C). The middle of the reaction tube was filled with the catalyst of active clay; and a Ni-Cr thermocouple, enclosed in a sheath of 5mm i.d. silica tubing, was imbedded in the center of the catalyst mass. Reaction products leaving the reaction tube were conducted through two condensers.

ENCLOSURE (B)9

The condensate was collected in the receivers and gas was collected in a gas bottle.

The composition of this condensate, mainly ether, unreacted alcohol, and water, was determined by distillation. The composition of gas (mainly ethylene) was determined by Hempel's gas analysis apparatus.

Samples: Concentrations of alcohol used in this study were 99.3% and 94.5%

Catalyst: Catalyst used in this study was activated acid clay obtained from Toyo Active Clay Co.

Experimental Result. The types of dehydration of ethyl alcohol may be represented as follows:

$$2\ C_2H_5OH \qquad (C_2H_5)_2O \qquad H_2O \ \dots\dots\dots\dots \ (1)$$

$$C_2H_5OH \qquad C_2H_4 \qquad H_2O \ \dots\dots\dots\dots \ (2)$$

Generally, reaction (1) occurs at temperatures below 300°C, and reaction (2) at temperatures above 300°C.

At first a study was carried out to clarify the effect of reation temperature and of space velocity. Results are shown in Table I(B)9.

It was found that lower yields of ether and higher gas formation were obtained at higher reaction temperatures. At the higher space velocity, the yield of both ether and ethylene was decreased. Concentrations of alcohol lower than 99.3% are not effective in this reaction. Consequently, it was found that the most effective reation conditions are 200°C and 0.33 space velocity.

The life of this catalyst was tested by the same method using 94.5% alcohol at 200°C and a space velocity of 0.33. Condensate was removed from the separator every two or three hours and tested by distillation.

Table II(B)9 tabulates typical data only, and the mean value in this table is the mean of the total data obtained throughout the experiment (155 hours).

These results show that during the first part of the reaction the catalyst activity is low, but the activity soon increases and remains constant during 155 hours of the experiment. Therefore, it appears that this catalyst is satisfactory for the preparation of ether from alcohol.

ENCLOSURE (B)9

Table I(B)9
PREPARATION OF ETHER BY THE DEHYDRATION OF ALCOHOL IN THE PRESENCE OF ACTIVE CLAY

Expt. no.	1	2	3	4	5
Alcohol Conc. (% by vol.)	99.3	99.3	99.3	99.3	94.5
Reaction Temp. (°C)	180	200	230	230	200
Space Velocity*	0.33	0.33	0.33	0.5	0.33
Condensate Yield (% by vol.)	95.2	92.8	82.8	88.0	92.8
Condensate Comp. (% by vol.)					
Ether fraction, (%)	37.0	57.0	59.0	46.8	57.3
Alcohol fraction, (%)	61.5	38.5	30.5	50.8	34.1
Vol. ethylene gasified (lit/100cc of charge)	1.69	2.07	6.14	3.84	0.81
Yield of ether (Vol. % of charged alcohol)	35.3	53.2	52.1	42.1	56.2
or (Vol. % of reacted alcohol).	88.6	90.5	70.8	82.2	92.0
<u>Material Balance</u>					
Vol. of alcohol converted to ether, (%)	39.6	59.6	53.5	46.6	63.2
Vol. of alcohol converted to ethylene, (%)	4.4	5.4	16.1	10.1	2.2
Vol. of alcohol unreacted, (%)	54.8	33.5	23.6	42.5	31.2
Loss of alcohol (%)	1.2	1.5	6.8	0.8	3.4
Total =	100.0	100.0	100.0	100.0	100.0

Notes: The material balance of this reaction was calculated by following explanation.

(1) Content of ethyl alcohol in the above fraction was analyzed to be 93%.

(2) Amount of ethylene gas is calculated on the basis of 0.38 of C_2H_4 from 1cc of ethyl alcohol.

(3) Ether is formed at rate of 89 per 100 of alcohol.

*Feed Vol./Cat. Vol./hr.

ENCLOSURE (B)9

Table II(B)9
LIFE TEST OF CATALYST

Test Time, (hrs)	3	39	155	mean
Yield of condensate, (%)	83.3	93.3	99.0	96.9
Composition of condensate:				
Ether fraction, (%)	53.0	69.0	58.9	58.5
Alcohol fraction, (%)	28.9	20.2	27.7	28.1
Yield of ether to used alc., (%)	46.5	68.0	61.7	60.2
Yield of ether to theoretical (%)	69.0	94.0	95.5	92.5

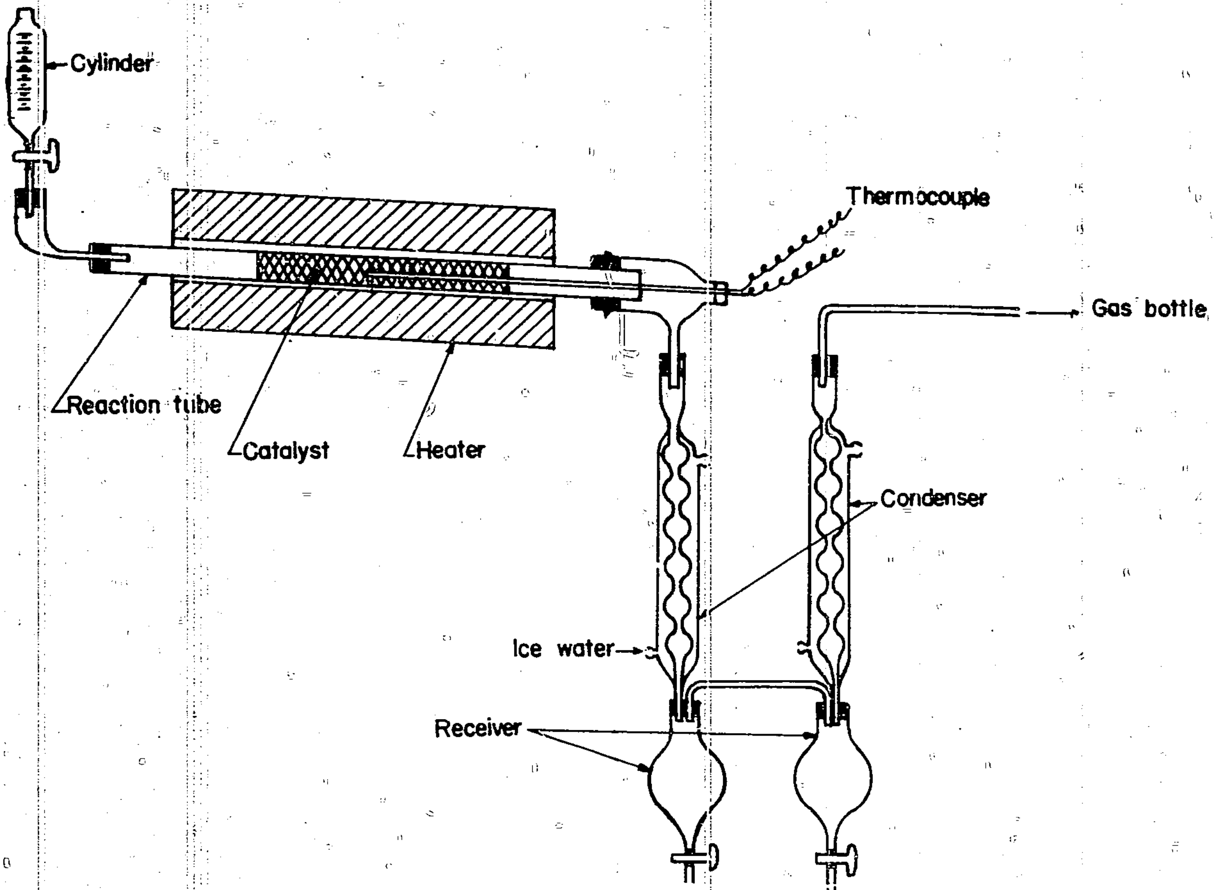


Figure 1 (B)9
EXPERIMENTAL APPARATUS OF THE PREPARATION OF ETHER

ENCLOSURE (B)9

PART II

PREPARATION OF ACETONE FROM ETHYL ALCOHOL

by

ENGINEER O. MIYATA

Research Period: 1944-1945

SUMMARY

The object of our research is to produce acetone from ethyl alcohol catalytically, since acetone mixed with ethyl alcohol gives better results in combustion engines than ethyl alcohol alone.

This study was begun in April, 1945, and not finished. At present, it has been found that the yield of acetone from ethyl alcohol is 56%, using a mixed catalyst of Zn-Fe oxides at 430°C.

I. INTRODUCTION

Demand of ethyl alcohol as an aviation fuel has increased with the scarcity of gasoline in Japan. Since acetone improves the quality of alcohol by blending, the demand of acetone has increased.

Acetone is at present prepared by the fermentation method and by the condensation of acetaldehyde.

There was a demand for other preparation methods such as the ethyl alcohol conversion to acetone by catalytic reation. This study was concerned with the most effective catalyst and most suitable reaction temperature for this reaction. Since the presence of water is necessary as indicated in the following equation,

$$2\ C_2H_5OH + H_2O = CH_3COCH_3 + CO_2 + 4H_2$$

The effect of water must be clarified.

II. DETAILED DESCRIPTION

Experimental apparatus of the preparation of acetone is shown in Fig. 1(B)9. This apparatus and experimental method is the same as was used in preparing ether from alcohol.

Samples: Samples used for this study were prepared by mixing water and ethyl alcohol in the following proportions: 5:5, 8:2, and 84:16 (by volume ratio).

ENCLOSURE (B)9

Catalyst: Catalysts used in this study were ZnO and Fe_2O_3 and their mixtures, prepared by precipitation from corresponding metallic nitrate solutions with sodium carbonate and subsequent ignition to the oxides. The weight ratios of ZnO to Fe_2O_3 used were: 1:9, 3:7, and 5:5.

Results: The experimental results are shown in Tables III(B)9, IV(B)9, and V(B)9.

III. CONCLUSIONS

Increasing concentration of charged alcohol resulted in increasing formation of gaseous products such as CO_2, H_2, aldehydes, etc. Consequently, it appears that the most suitable concentration of alcohol for use in this reaction is under 16 per cent.

Catalytic action of a mixture of Zn-Fe oxide is superior to that of either by itself. The desirable mixing ratios of ZnO to Fe_2O_3 appears to be from 3:7 to 5:5.

The lower the reaction temperature, the less the decomposition or alcohol, and the more the quantity of unreacted alcohol. The yield of acetone decreases with the decreasing reaction temperature.

On the contrary, at higher temperatures, the greater is the decomposition and loss of alcohol. Consequently, it appears that the suitable reaction temperature in the presence of this mixed catalyst is about 430°C.

No study was made of the effect of varying space velocity on the yield of acetone, since the investigation was not completed. It was also intended to investigate further the use of other catalysts in this reaction.

ENCLOSURE (B)9

Table III(B)9
PREPARATION OF ACETONE IN PRESENCE OF ZnO

		Experiment No.			
		1	2	3	4
Alcohol Concentration (% by vol.)		50	20	16	16
Reaction Temperature (°C)		450	450	450	430
Space Velocity*		0.5	0.5	0.5	0.5
Condensate Yield (% by vol.)		67	72	84	88
Condensate Composition (% by vol.)	Acetone Content	8.4	8.8	8.3	6.6
	Alcohol Content	38.0	5.8	1.6	2.6
Yield of Acetone to used Alcohol (% by vol.)		11.2	31.7	43.5	36.5
Unreacted Alcohol; (% by vol.)		50.8	19.2	8.6	23.7
Loss of Alcohol; (% by vol.)		31.4	30.6	22.2	18.3

* Feed vol/cat.vol/hr

Table IV(B)9
ACETONE PREPARATION IN PRESENCE OF Fe_2O_3

		Experiment No.			
		1	2	3	4
Alcohol Concentration (% by vol.)		50	20	16	16
Reaction Temperature (°C)		450	450	450	430
Space Velocity		0.5	0.5	0.5	0.5
Condensate Yield (% by vol.)		64.5	75.0	82.5	86.0
Condensate Composition (% by vol.)	Acetone Content	7.5	8.7	8.1	6.5
	Alcohol Content	42.1	5.7	2.1	4.6
Yield of Acetone to used Alcohol (% by vol.)		9.7	32.4	41.7	35.0
Unreacted Alcohol; (% by vol.)		54.0	21.3	10.8	24.7
Loss of Alcohol; (% by vol.)		30.3	27.1	22.9	19.6

Table V(B)9

PREPARATION OF ACETONE IN PRESENCE OF MIXTURES OF ZnO & Fe_2O_3

		Experiment No.						
		1	2	3	4	5	6	7
Alcohol Concentration (% by vol.)		16	16	16	20	50	16	16
Ratio of ZnO to Fe_2O_3 (by wt)		5:5	5:5	5:5	5:5	5:5	3:7	1:9
Reaction Temperature (°C)		450	430	400	430	430	430	430
Space Velocity		0.5	0.5	0.5	0.5	0.5	0.5	0.5
Condensate Yield (% by vol.)		85.0	90.0	93.0	76.0	70.0	86.8	84.6
Condensate Composition (% by vol.)	Acetone Content	9.4	9.9	8.0	10.8	9.7	8.5	1.0
	Alcohol Content		7.0	3.5	2.0	33.7	2.3	4.2
Yield of Acetone to used Alcohol (% by vol.)		50.0	55.7	46.5	41.0	13.6	46.0	37.0
Unreacted Alcohol (% of used Alcohol)			5.6	20.3	7.6	47.2	12.5	22.2
Loss of Alcohol (% of used Alcohol)		20.4	5.8	5.7	27.2	31.2	14.3	19.2

ENCLOSURE (B) 10

SYNTHESIS OF ISOBUTANOL FROM WATER GAS

by

CHEM. ENG. LIEUT.
S. ENDO

ENGINEER
T. INOUE

Research Period: 1943-1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)10

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)10

SUMMARY

Some experiments were made to study the synthesis of i-butanol from water gas with Zn-Cr-alkali catalysts. The composition of the best catalyst was Zn : Cr = 7 : 3 (atomic ratio).

I. INTRODUCTION

A. History of Project

In Japan, commercial isooctane was prepared from n-butanol, but its octane number was comparatively low. To increase the octane value, a purer isooctane was required and, in this connection, the present study was undertaken to find a good catalyst for synthesis of i-butanol from water gas. The results of these experiments are incomplete because the project was discontinued.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr.	A. YAMAOKA
Chem. Eng. Lieut.	S. ENDO
Chem. Engineer	T. INOUE

II. DETAILED DESCRIPTION

A. Apparatus and Test Procedure

The apparatus and operating procedure used in this study were the same as described in a previous report on the methanol synthesis. Zn-chromite catalysts were used which were prepared in the same manner as those described in the methanol synthesis, except for the fact that no copper was included.

The powder catalysts were each mixed with 30% by weight of K_2CO_3 and air dried. The feed gas consisted of a mixture of one volume of CO and two volumes of H_2.

The liquid reaction product contained i-butanol, methanol, other alcohols, and water. Determination of the content of i-butanol and methanol was made by the distillation of the product.

B. Experimental Results

1. The relation between the composition of the catalyst and the yield of i-butanol is shown in Table I(B)10.

2. Results of an activity life test of the catalyst (Zn : Cr = 7 : 3), using a gas of CO : H_2 = 1 : 1, are shown in Table II(B)10.

III. CONCLUSIONS

A. When water gas of the composition CO : H_2 = 1 : 1 was passed over Zn-chromite catalyst heated to 450-475°C, under 250kg/cm^2 pressure, and space velocity 5000, the space time yield of liquid product was 0.25~0.35. The contents of i-butanol and methanol were each about 25%.

B. The most effective catalyst studied had an atomic ratio Zn : Cr of 7 : 3. This catalyst maintained its activity for 200 hours.

ENCLOSURE (B)10

Table I(B)10

SYNTHESIS OF ISO-BUTANOL FROM WATER GAS

Catalyst (Zn:Cr)	S.T.Y. of Liquid Product (gm/cc/hr)	Content of i-Butanol (wt%)
10:0	0.10	10
7:3	0.20	15
5:5	0.14	12
3:7	0.10	8
0:10	0.09	7

Reaction pressure.....................200kg/cm^2
Reaction temperature..................450-475°C
S.V. 5000

Table II(B)10

LIFE OF CATALYST IN SYNTHESIS OF I-BUTANOL FROM WATER GAS

Duration (hr)	S.T.Y. of Liquid Product (gm/cc/hr)	Content of i-Butanol (wt%)	Content of CH_3OH (wt%)
20	0.25	27	30
80	0.25	23	35
120	0.30	22	30
160	0.35	25	25
200	0.25	25	25

Reaction pressure.....................250kg/cm^2
Reaction temperature..................450-475°C
S.V. 5000

ENCLOSURE (B) 11

ENGINE TEST OF ALCOHCL AS AVIATION FUEL

(In Two Parts)

by

CHEM. ENG. LIEUT. K. TSUNODA

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)11

LIST OF TABLES AND ILLUSTRATIONS

PART I

PART II

ENCLOSURE (B)11

PART I

by

CHEMICAL ENGINEERING LIEUT.
K. TSUNODA

Research Period: 1944-1945

SUMMARY

Objective of Project The object of this test was to find the fundamental engine performance of ethyl alcohol as aviation gasoline by the single cylinder testing machine, proceeding to the full scale engine test.

Significant Results Ethyl alcohol has very high anti-knock properties as compared with usual aviation gasoline. In apite of its octane number being only about 92, its maximum allowable boost is over (+) 600mm Hg in single-cylinder Kinsei 4 type aircooled test engine.

It is apt to cause autoignition even at lower boost which easily changes to preignition. We get the diagram (drawn from memory) of the limit of the autoignition as shown in Figure I(B)11.

According to Figure I(B)11:

1. Autoignition does not occur at any air-fuel ratio below (+)0 boost.

2. Autoignition begins to occur between (+)0 and (+) 100 boost, and the HP is somewhat higher in the area of autiognition.

3. The area limited by autiognition on the lean side and the rapid decrease in the HP on the rich side becomes much narrower above (+)400mm boost.

4. There is no safe combustible area at (+)600mm boost.

Autoignition begins at definite temperature which is just 200°C in this test. This temperature is supposed to have some relation to slow oxidation of alcohol.

I. INTRODUCTION

A. History of Project

Since April, 1944, we began to use ethyl alcohol as an aviation fuel. At first we blended it into gasoline only about 10% by volume and tested the engine performance carefully. However, with the increasing shortage of aviation gasoline, its blending ratio was increased rapidly to 30, 50 and 75% for experimental purpose, and finally, in October, we began to test pure ethyl alcohol as the fuel for the training airplane (50% blend of ethyl alcohol was the highest ratio actually used in training plane.). Above experiments by full scale engines were done mainly at the First Naval Technical Depot at YOKOSUKA. The following experiments were done particularly on the single cylinder engine performance of pure ethyl alcohol from October, 1944 to March, 1945.

B. Key Research Personnel Working on Project

Eng. Comdr. K. NAKATA
Eng. Lieut. Comdr. T. NAKAYAMA

II. DETAILED DESCRIPTION

A. Description of test apparatus

Single cylinder testing machine

"Kinsei" 4 type air cooled cylinder
Cylinder diameter 140mm
stroke 150mm
Compression ratio 66(variable compression)
Maker: Ishikawajima Aircraft Company Ltd.
Engine Counterbalanced and maximum Engine Speed 3000 R.P.M.

B. Test Procedures

1. Physical and chemical properties of used ethyl alcohol We used ethyl alcohol whose various properties were established as "1 alcohol" in the Naval Fuel Specifications.

General The alcohol may be added as specified to gasoline.

1. Purity: 99 wt % min.
2. Specific gravity (15°/4°C);0.797 max.
3. Distillation:
   distillate at 78-80°C. 95% min.
4. Reaction neutral
5. Solubility in water

This alcohol shall be mixed at any temperature and be a clear solution.

C. Methods of Tests

We made three tests of engine performances in order to find the anti-knock properties of pure ethyl alcohol:

1. The first test series was the boost-up method; namely, we elevated the intake air pressure from (-) 100mm Hg for each 100mm boost, and found when the fuel began to detonate, as judged by exhaust flame color. We called this point "the maximum boost of the fuel."

2. The second test consisted of changing the air-fuel ratio; at every boost we changed the air-fuel ratio from the rich side to the lean side by regulating the fuel supply, and measured the change of the HP accompanied with the air-fuel ratio.

3. The engine's ignition was switched off at every air-fuel ratio and it was determined whether the engine continued to run; that is, whether ethyl alcohol already began autoignition or not. We called this point the limit of autoignition; that is, the boost at which autoignition began. As a rule, when the rear spark plug temperature exceeded 200°C, autoignition occurred.

D. Results

By above mentioned method the engine performance diagram (Figure 1(B)11) of pure ethyl alcohol was obtained which had the brake horsepower as ordinate and the air-fuel ratio as abscissa.

III. CONCLUSIONS

A. On the Anti-knock Properties

By these single cylinder engine tests, ethyl alcohol proved itself to be very high anti-knock fuel. For example, normal aviation gasoline which had 91 octane number began to detonate at about (+) 200mm boost, regardless of air-fuel ratio, but pure ethyl alcohol did not detonate even at (+)600mm boost if mixture was rich enough. From this point of view, the anti-knock property of pure ethyl alcohol seems to be no problem, but it has other various weak points as an aviation fuel, such as volatility. Even if an excess of ethyl alcohol is supplied into the intake for the purpose of increasing its vapor pressure, the amount of vapor evolved does not increase, since ethyl alcohol has a fixed boiling point. In the case of the full scale engine, therefore, the distribution of fuel to every cylinder becomes very bad, which causes the detonation. We cannot conclude that ethyl alcohol has very high anti-knock property from the single cylinder engine test alone. It actually has high anti-knock property by single cylinder engine test, but often it proves to be low anti-knock value by full scale engine tests.

B. Autoignition of Ethyl Alcohol

Another weak point of ethyl alcohol as an aviation fuel is its autoignition property. Ethyl alcohol has the property of beginning autoignition under high pressure and temperature. Autoignition induces preignition, which is not desirable. If the area limited by the beginning point of autoignition of the lean side, and the point of rapid fall of the HP on the rich side, is called "the safe combustible area," it becomes very narrow at (+) 300mm boost as shown in the diagram.

ENCLOSURE (B)11

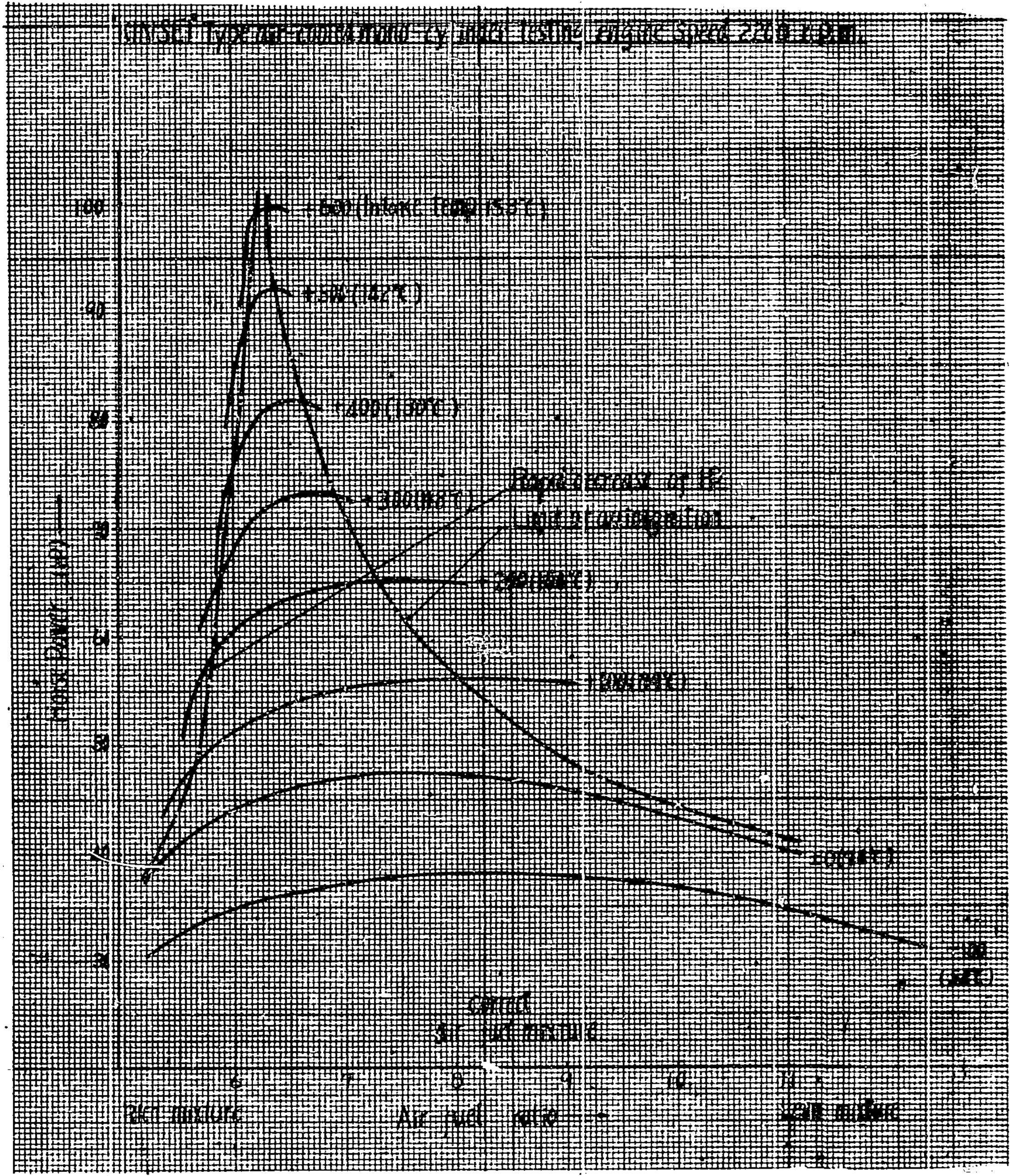


Figure 1 (B)11
ENGINE PERFORMANCE DIAGRAM OF ETHYL ALCOHOL

ENCLOSURE (B)11

PART II

by

CHEM. ENG. LT. COMDR.
T. NAKAYAMA

Research Period: 1944-1945

SUMMARY

To examine the practical value of alcohol as an aviation fuel, especially to improve its volatility, the author examined the effect of blending ethyl ether, acetone, and gasoline with ethyl alcohol.

The effect of the latter two was satisfactory, but the former was not satisfactory because of its knocking tendency.

I. INTRODUCTION

A. The Characteristics of Alcohol

1. Heat of combustion of alcohol is less than that of gasoline, thus fuel consumption of alcohol is increased.

2. Latent heat of vaporization of alcohol is very large; thus its volatility is very poor, and the difficulties of starting, acceleration and cylinder distribution of the fuel arise, but its anti-knock property is improved by the cooling effect of alcohol.

3. Corrosive Action on Aluminum Alloys and Steel. Because of these properties, the setting of carburetor fuel flow must be changed, and the addition of arsenic soda (sodium arsenite) (5mg/100cc of alcohol) is necessary to prevent corrosion. In this way, for the training planes of 1000 to 1500 hp class, alcohol can be used for limited performance, but for first class planes, alcohol cannot be used as fuel because it limits the performance of engines.

B. Key Research Personnel Working on Project

CHEM. ENG. LT. COMDR. T. NAKAYAMA

II. DETAILED DESCRIPTION

A. Description of the Test Apparatus

The aircraft engine "Kinsei" 5 type was used for testing these fuels. Its characteristics were:

14 cylinders and double-row radial air-cooled,
Compression ratio, 7.0
Carburetor type,
Cylinder bore 140mm, stroke 150mm,
Maximum output power 1300 hp at 2550 r.p.m. and
+350mm Hg (aviation gasoline with octane rating 91 was used).

Water brake type dynamometer was used.

B. Test Procedure

The mixtures of alcohol with ethyl ether, acetone or gasoline were tested by "Kinsei" 5 type engine. The test was made at every boost (±)0, (+)100, (+)200mm Hg, etc., and the minimum fuel consumption of each mixture, temperatures of cylinders, and exhaust gas were recorded. Thus, the volatility performance characteristics of each mixture were observed.

C. Experimental Results

The mixtures of alcohol and blending fuels had the properties and performance results as shown in Table I(B)11.

III. CONCLUSIONS

Ethyl ether has high volatility, but it causes detonation. Therefore, its allowable concentration is very small, and consequently, it cannot be blended in sufficient quantity to affect the volatility of the mixture.

Acetone has good volatility and anti-knock properties, and its blended fuel showed the best performance. The more acetone added, the better the resulting fuel.

Gasoline had a higher heat of combustion than the other blending agents, so that the fuel consumption of the gasoline alcohol blend was lowest. However, the effect of the gasoline on anti-knock properties and volatility was not as great as that of acetone.

Table I(B)11
PROPERTIES AND ENGINE PERFORMANCE CHARACTERISTICS OF ALCOHOL BLENDS

		Octane Number	Vapor Pressure	Distillation Temperature (°C)					Engine Performance **		
				First	10%	50%	90%	97%	Max.boost (mm Hg)	Max. hp	Fuel Consumption (lit/hr)
Alcohol	100%	92	0.19		78	78	78	78	+250	1210	610
Alcohol Ethyl Ether	95% 5%	90	0.28	65	78	78	78	78	+200	1324	537
	90% 10%#	89	0.31	60	76	76	78	78	+200	1130	590
	80% 20%	89	0.51	48	78	78	78	78	+150	1087	533
Alcohol Acetone	90% 10%	91	0.31	60	76	76	78	78	+300	1202	
	90% 10%#	90	0.31	60	76	76	78	78	+350	1290	670–770*
	80% 20%	91	0.38	58	76	76	78	78	+350	1325	625–775*
Alcohol Water	95% 5%	92							± 0	878	Fuel consumption is the same rate as for aviation gasoline.
Aviation Gasoline	100%	87							+150	1010	
Alcohol iso-Octane	80% 20%	90	0.25	67	73	76	78	79	+100	951	
Alcohol Benzene	80% 20%	87		67	70	75	78	86	+100	971	
Alcohol Toluene	80% 20%	89	0.21	71	76	76	77	79	+100	971	
Alcohol iso-Propyl-ether	80% 20%	90	0.27	65	70	76	79	79	+100	979	
Alcohol Pine root oil	80% 20%	85		75	77	78	167	181	+ 50	909	
Alcohol A92G	80% 20%	85		59	72	77	138	179	+100	984	

0.15% Leaded *Allowable range of change of fuel consumption **At 2500 RPM

ENCLOSURE (B) 12

STUDIES ON THE UTILIZATION OF ALCOHOL FOR AVIATION FUEL

by

CHEM. ENG. LIEUT. COMDR.
T. YAMAMOTO

Research Period: 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)12

SUMMARY

In order to eliminate the shortcomings of alcohol for aviation fuel; namely, the corrosive action on metals, the low antiknocking property, and the low volatility of alcohol, the experiments described herein were carried out. Since the research was stopped with the war's end, scarcely any of the results obtained were applied in practical service.

I. INTRODUCTION

In 1944, the third year of the war, in view of the scarcity of aviation fuel, it was decided to utilize alcohol for aviation fuel, since it could be produced in Japan.

Many difficulties were found in the utilization of alcohol for aviation fuel (even for training planes) due to the difference (compared with gasoline) in fuel-air ratio for the complete combustion, the low volatility due to its high latent heat of vaporization, the corrosive action on metals, the dissolving action on paints, etc. As a result of the low volatility, the distribution of the fuel to each cylinder of a full scale aviation engine was not uniform. Consequently, detonation or pre-ignition was likely to occur in the cylinder supplied with too weak a mixture, and irregular firing in the cylinder supplied with too rich a mixture, even when the operation was made at a proper overall mixture ratio. Although experiments were made by the author to eliminate these defects of alcohol, only one finding was given practical application. So the use of alcohol was developed for each particular engine mainly by the experiments made at the First Naval Technical Depot and Yokosuka Air Corps. All of the detailed data of the experiments made by the author were lost. Therefore, this report was written from memory.

II. DETAILED DESCRIPTION

A. On the Anticorrosive Additives of Alcohol

The accessories of the engine made of light alloy castings, especially the inner surface of the carburettor body which was made of aluminium alloyed with a small amount of copper, were corroded by the use of alcohol. Moreover, the parts made of brass and steel were also stained, although this corrosion was not as severe as that of the aluminium alloy. There were two types of corrosion of the aluminium alloys, one of which was the formation of a gelatinous deposit on the metals, and the other, the formation of pinholes. Steel and brass were stained but not corroded. Although the reasons for this corrosion were not fully understood when these experiments were made, anticorrosive additives for alcohol were sought.

The experiments made were as follows: Test pieces were cut from engine accessories and were polished by sand paper until they exhibited a glassy luster.

They were then submerged in glass bottles containing the samples of alcohol and held thermostatically at a temperature of 60°C. After 50 hr had elapsed, the test pieces were taken out, and washed by reagents to eliminate the deposit, then dried and weighed. The washing reagents were 5% cold nitric acid for aluminium alloy, 5% cold sulphuric acid for brass, and 10% solution of ammonium ferric citrate for steel. Although many kinds of additives were tested by measuring the decrease in weight per cm^2 of the test pieces under the above conditions, aliphatic amines such as ethyl amine, diethyl amine, dibutyl amine, cyclohexyl amine, etc., showed good results on all of the metals tested, especially dibutyl amine, which was the best. In regard to the quantity to be added to alcohol, the addition of 0.3% by wt. decreased the corrosion considerably and 0.5% addition gave perfect results.

In connection with this work, it is of interest that Yokosuka First Technical Depot developed sodium arsenite for this purpose, and this compound was selected for practical use in view of availability, although dibutyl amine was superior.

B. On the Prevention of Detonation

Anhydrous alcohol showed a performance nearly the same as the 87 octane aviation gasoline when used by carburettor engines having less than 1,000 horse power out-put. The octane number of pure ethyl alcohol cannot be measured by the ordinary C.F.R. motor method due to the fact that the air-fuel ratio showing the maximum knocking rate is out of the range of mixture regulation by the carburettor. The octane number, as actually determined using a carburettor nozzle having a large diameter to obtain the air-fuel ratio for maximum knock, was 91-92. The difference in the antiknocking properties indicated by the C.F.R. engine and the practical engine was mainly due to the non-uniform distribution of fuel to each cylinder caused by its low volatility. The cylinders which were supplied a weak mixture were more likely to give what was later found to be auto-ignition with a high boost pressure than when an aviation gasoline was used; that is to say, the possible limit of safe operation for alcohol, relative to the mixture ratio and the boost pressure, was narrower than that of gasoline.

Although one method to extend this allowance is to increase the antiknocking properties of the fuel, tetraethyl lead lowers rather than raises the antiknocking property of alcohol. Therefore, more than one hundred kinds of additives to increase the octane rating of alcohol were tested. Among these, iron-pentacarbonyl and diethyl selenide were effective. Although the octane rating of alcohol with 0.3% of iron-pentacarbonyl added was approximately 100, this fuel could not be used practically on account of misfiring with continued operation of the engine. This was due to the deposition of iron oxide (formed by combustion) on the insulator of the spark plugs. The use of additives to expel the combustion residue of the antidetonant, such as the use of ethylene bromide in ethyl fluid, was not at all successful.

Dimethyl selenide had an antiknock effect for alcohol one-half as great as iron carbonyl, and gave no cylinder or spark plug deposits. While this compound showed promise as a satisfactory antidetonant for alcohol, the experiments were not pursued, in view of the shortage of selenium.

C. On Increasing the Volatility of Alcohol

The greatest short-coming of alcohol as an aviation fuel is its low volatility. In spite of the fact that alcohol has a boiling point lower than that of the mean value of gasoline, its volatility is extremely low, owing to its high latent heat of vaporization. In general, the fuel is evaporated partly in the carburetor and the remainder is introduced in in the liquid state. The fuel which does not evaporate is apt to flow along the walls of the suction pipes and the super charger casing, and then flow down to the lower part of the engine. Hence, there are differences in the air-fuel mixture ratio on the upper part and the lower part of a radial type engine. This phenomenon is more pronounced with alcohol than gasoline due to alcohol's low volatility. In order to increase the volatility of alcohol, blending fuels suitable for this purpose were tested. The experiments carried out were as follows:

Measured volumes of the fuel and air at a constant temperature were introduced into a spiral glass tube which was insulated from the heat of the atmosphere by a Dewar's flask. The evaporated fuel escaped with air, and the part of the fuel which was not evaporated flowed down into a measuring graduate. The tests were made by varying the air-fuel ratio, and the relationship between the amount of the fuel evaporated and the air-fuel ratio was obtained. The volatilities of fuels having different latent heats of vaporization were compared by the curves which combined latent heat and volatility (boiling point) effects.

The effects of the blended fuels are summarized as follows:

1. Alcohol blended with 20% by volume of ethyl ether showed nearly the same volatility as ordinary aviation gasoline.

2. Alcohol blended with 30% of acetone or isopropyl ether was also about the same as the mixture described above in (1).

3. Methanol had scarcely any effect on the volatility of alcohol.

4. Water included in alcohol seriously suppressed the evaporation of alcohol.

5. The mixture of 75% of aviation gasoline and 25% of alcohol showed the maximum point on the volatility-mixing ratio curve. This maximum point seemed to be caused by the formation of an azeotropic mixture. The maximum point could be moved from 10% to 30% of alcohol depending on the properties of the gasoline.

Although the primary training planes having a 300 horse power engine could not stop and restart in the air during the cold season using alcohol alone, the difficulty was eliminated by the use of 3% ethyl ether blended with alcohol, the application of asbestos insulation between the cooling fins, and by heating the intake gases by means of the exhaust. This scheme was used at temperatures of +20°C and below.

ENCLOSURE (B) 13

THE SPECTROSCOPIC INVESTIGATION ON THE MECHANISM OF THE COMBUSTION OF ALCOHOL

by

CHEM. ENG. LIEUT. COMDR.
Y. MOMOTARI

CHEM. ENG. LIEUT.
Y. KAKIUCHI

Research Period: 1944

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)13

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)13

SUMMARY

The more excessive the air-ratio,* the more remarkably intense is the observed spectrum of the lead-oxide band in the flame spectrum of the leaded alcohol. On the other hand, when leaded commercial iso-octane is used for combustion, not only the intensity is generally weaker than that of alcohol but a certain maximum point appears.

This experiment was started in Nov., 1944, but was not finished.

I. INTRODUCTION

Organic lead compounds are the excellent anti-knocks for gasoline, but, on the other hand, they rather promote knocking when employed for alcohol. With this in mind, the spectroscopic investigation on the difference of their conditions for combustion was carried out.

II. DETAILED DESCRIPTION

Each definite quantity (0.2% vol. %) of tetramethyl-lead was added to ethanol and commercial iso-octane, and spectroscopic photographs were taken of their inner flame as they were burnt under different conditions of air-ratio. The intensity of each spectrum was measured by a microphotometer. See **Figure 2(B)13.**

The results were as follows:- When leaded alcohol is used for combustion, the more the air-ratio, the more remarkably intense is the spectrum of the lead-oxide band ($\lambda\lambda$5678) in the flame spectrum.

On the other hand, when leaded commercial iso-octane is used for combustion, not only the intensity is generally weaker than that of alcohol but a maximum point (about 88% air-ratio) appears. **See Figure 1(B)13.**

Table I(B)13
SPECTRUM INTENSITIES

Alcohol	Air-Ratio	62%	75%	88%	105%
	Rel. Int. of PbO-Band*	1.1	1.4	4.1	11.2
Isooctane	Air-Ratio	71%	82%	93%	95%
	Rel. Int. of PbO-Band*	0.7	1.7	1.5	1.0

* This is the relative intensity of the PbO-band ($\lambda\lambda$ 5678) against that of the Pb line spectrum (λ 3672).

---

* The "air-ratio" is defined as follows: Air actually supplied at combustion theoretical air volume at complete combustion.

ENCLOSURE (B)13

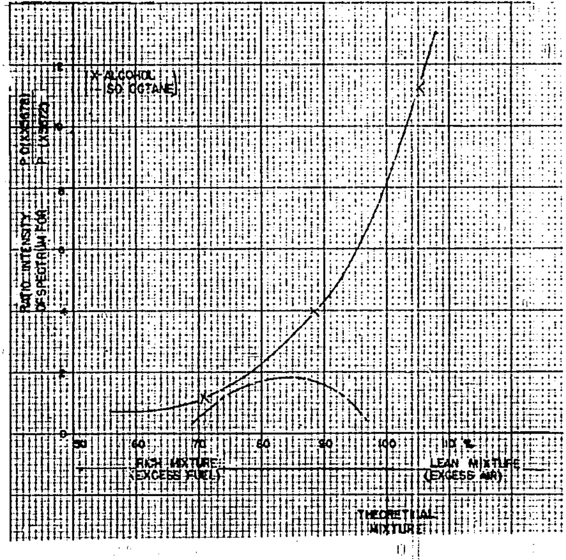
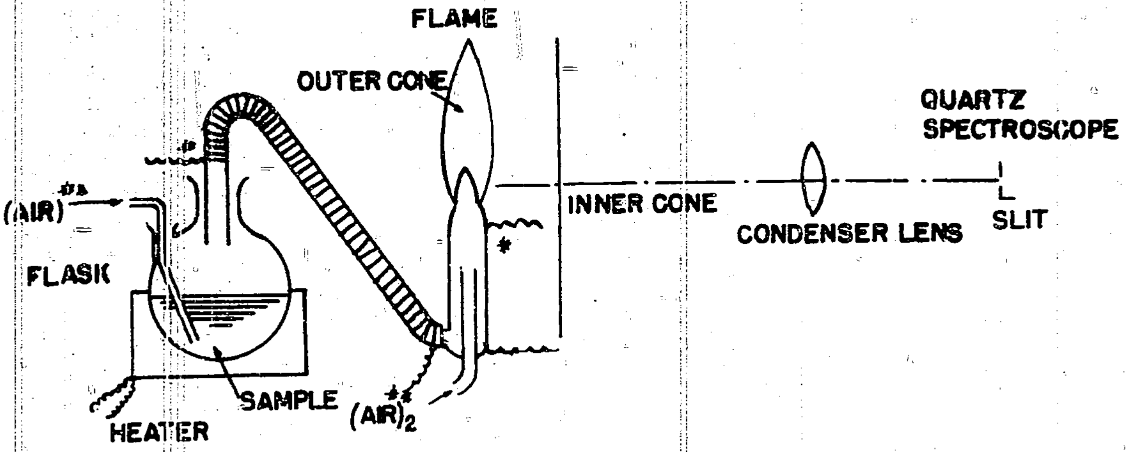


Figure 1 (B)13

RADIO INTENSITY OF SPECTRUM FOR : $\frac{Pb0(\lambda\lambda 5678)}{Pb\ (\lambda 3672)}$



* The temperature of the passage way though which the sample air mixture passes is properly heated electrically.

** The "air ratio" defined previously is $\frac{(air)1+(air)2}{\text{theoretical air volume for complete combustion}}$

Figure 2 (B)13

SKETCH OF THE APPARATUS FOR COMBUSTION FLAME

ENCLOSURE (B) 14

STUDIES ON THE CORROSIVE PROPERTIES OF ALCOHOL FUELS

by

CHEM. ENG. LIEUT. COMDR.
Y. MOMOTARI

NAVAL PROF.
K. HIROMOTO

Research Period: 1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B) 14

SUMMARY

The traces of copper-ion and chlorine-ion in ethanol definitely possess corrosive properties and the corrosion seems to be accelerated by the co-operative reaction of copper-ion and chlorine-ion.

I. INTRODUCTION

The aliphatic alcohols are much more corrosive to the metals commonly employed in automobile construction than normal hydrocarbon fuels ~~and~~ much trouble has occurred. The trouble most generally encountered was the corrosion of brass and aluminum in carburetors, due to the ready attack of the aluminium by alcohol.

II. DETAILED DESCRIPTION

The ethanol, which attacked the aluminium metal violently, was distilled into two separate parts. The distillate (pure alcohol) did not attack the aluminium metal at all, but the residue part attacked the aluminium metal violently. When the residue part was analyzed by means of chemical and spectroscopic methods, NaCl, Fe, Pb, Mg, Ca, Br and gasoline, etc., were found to be present. Of these impurities, chlorine-ions and copper-ions were found by laboratory test to be the active components of the corrosive substance in ethanol.

The test conditions were as follows:

Test piece.......................aluminium metal (1cm x 5cm)
Test temperature....................................50°C
Tested time...24 hrs.

The aluminium test piece was immersed in ethanol at a temperature of 50°C maintained by means of thermostat for 24 hrs. The appearance of the attacked test piece was of two types: one state consisted of pin-hole black spots on the surface of the test piece; the other, a gelatinous substance which covered the surface of the test piece. We found that former was caused by the copper-ion, the latter by the chlorine-ion.

Accordingly, it was possible to evaluate the corrosion visually.

The copper-ion or the chlorine-ion alone is not markedly corrosive when present in ethanol. For example, even when one of these classes of ion exists (0.02 mg per liter of ethanol), corrosion scarcely appears. When ethanol contains both ions, the corrosive action of ethanol becomes very noticeable.

It would be deduced from these experiments that the maximum allowable content of copper-ion is 0.02 mg, and chlorine-ion is 1 mg per liter of ethanol, when aluminium metal contacts both.

In the case of alloy of aluminum and copper, because it contains copper-metal, the alloy is attacked by ethanol containing the chlorine-ion only, but unattacked when copper-ion only exists.

III. CONCLUSIONS

The maximum allowable content of copper-ion is 0.02 mg and chlorine-ion is one mg per liter of ethanol, if the corrosion of aluminium metal by ethanol is to be prevented.

ENCLOSURE (B)14

This problem occurred when the chlorine-ion was mixed in ethanol that had been transported by a ship-tank which previously transported gasoline, and its bottom was filled with sea-water. The copper-ion in ethenol entered when the ethanol was distilled by copper column on a commercial scale. As the anti-corrosion dope of such ethanol, it is supposed that aliphatic amines may be suitable for the copper-ion, because these form the complex salt of copper and amines.

To prevent trouble from the chlorine-ion in transporting at sea, only clean drums, but not ship tanks, should be used.

ENCLOSURE (B) 15

STUDIES ON THE PREVENTION OF CORROSION OF METALLIC MAGNESIUM AND MAGNESIUM ALLOY BY METHANOL

by

CHEM. ENG. LIEUT.
S. ENDO

Research Period: 1941-1942

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)15

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)15

SUMMARY

Studying the action of pure methanol on metallic magnesium ribbon from Kahlbaum, the following conclusions were reached:

1. The corrosive action of pure methanol is prevented by addition of water, especially when potassium chromate is added.

2. A precipitate is formed by the reaction of potassium chromate and methanol which can be removed by addition of very small quantity of alkali.

3. Methanol of 99.0% purity and of sp.gr.0.769-0.799, when 5% of 0.1% potassium chromate solution and 5% of 0.1% caustic potash solution are added may be kept for 50 days in a magnesium vessel without any precipitation or corrosive action.

4. The anti-corrosive action of an alkaline solution of potassium chromate is also effective for 40% methanol solutions.

I. INTRODUCTION

A. History of Project

The purpose for which this research was made was to examine a method of preventing the corrosion of magnesium by methanol and to find whether or not methanol could be used for aviation fuel. There are several methods for rendering magnesium alloys anti-corrosive, such as the fluoridation method, Sutton method, and Bengaugh method. These methods are effective against air and sea water, but are not effective in the presence of methanol. Therefore, the present experiment was undertaken with metallic magnesium ribbon and a magnesium alloy.

B. Key Research Personnel

Chem.Eng. Lt. Comdr., A. YAMAOKA
Chem.Eng. Lt., M. YOSHIDA
Chem.Eng. Lt., S. ENDO

II. DETAILED DESCRIPTION

A. Materials

Materials which were used in this experiment are:

Mg - metallic ribbon from Kahlbaum.
Mg-alloy - contains Mn 0.1 - 0.5%, Al 5 - 7%, Zn 1.5%
CH_3OH - CH_3OH from market, d. 0.796, purity 99.0% by wt.

Methanol was purified by removing acetone by Bate's* method, aldehyde by Dunlop** & Lenz's*** method, and acids and esters by distillation with

---

*Bates, J. Chem. Soc. 123, 401 (1933)
**Dunlop, J. Am. Chem. Soc., 28, 395 (1906)
***Lenz, A. Anlyt. Chem., 52, 96 (1933)

caustic potash, dehydrating with magnesium according to Bjerrum's method and finally rectifying with a rectifier of 100cm length and 6mm diameter. At 64.5°C., 99.5% was distilled. From the density of 0.7865, the purity was estimated to be 99.99% by the method of Bjerrum.

B. Method of Experiment

In this experiment, the metal was dipped into the liquid to be examined and kept at room temperature for a definite time. Observations were made and recorded.

III. EXPERIMENTAL RESULTS

A. Experiments with Mg-ribbon

Pure methanol reacts violently on Mg-ribbon with the evolution of hydrogen. The corrosive action of commercial methanol on magnesium and its alloys was therefore attributed to the chemical property of the methanol and not to impurities. Influences of water and other substances on the corrosive action of methanol were studied.

1. Influence of water. The results of the experiment are shown in Table I(B)15. The corrosive action of CH_3OH on Mg-ribbon decreases as the water concentration is increased. With less than 2% water present, this corrosive action is excessive.

2. Influences of Inorganic Substances. When 2% of 0.1 molar aqueous solutions of various inorganic compounds were added, some comparatively effective inhibitors were found, and the results are recorded in Table II(B)15.

3. Influences of Organic Substances. Aniline, pyridine, quinoline, hydroxylamine, ether, acetone, acetaldehyde, ethyl, propyl and butyl alcohols, lecitine, and soap were tried as inhibitors. The corrosive action of methanol on metallic magnesium was prevented by the presence of soap.

B. Experiments with magnesium alloy

The alloy was polished with emery-paper, washed with petroleum ether, and then immersed in methanol.

1. Pure methanol acts on the alloy and the original shape of the alloy is lost after 5-6 hrs.

2. The corrosive action of the methanol is diminished by the addition of water. With methanol containing 4% water, apparent corrosion does not take place for 2-3 days.

3. Potassium Bichromate. The anti-corrosive action of the addition of potassium bichromate solution to methanol is stronger than that of water. The results of experiments using potassium bichromate solution are shown in Table III(B)15.

4. Potassium Chromate. The results using potassium chromate as an inhibitor are shown in Tables IV & V(B)15. It was found that a precipitate appeared when K_2CrO_4 was used as an inhibitor. The formation of this precipitate could be delayed by adding a small concentration of alkali as shown in Table VI(B)15.

IV. CONCLUSIONS

When Mg-ribbon is immersed at room temperature in pure methanol, hydrogen and magnesium methylate are formed. The latter is soluble in methanol, and thus the corrosive action of methanol on the metal and alloy will proceed. However the corrosive action is prevented by the addition of water, since the methylate is decomposed by the action of water and is converted to magnesium hydroxide, which is deposited on the metallic surface. Thus, the water serves to inhibit the corrosive action of the methanol. Potassium chromate was also found to be a useful corrosion inhibitor.

Table I(B)15
INFLUENCE OF WATER UPON THE CORROSION OF Mg BY CH_3OH

Time (hr)	Amount of H_2O (%)						
	0.1	0.5	1.0	2.0	5.0	10.0	30.0
1	1 b	1 b	2 c	3 c	4 f	5 f	5 f
2	a	b	2 b	3 b	4 f	4 f	5 f
4			b	3 b	cf	df	df
24					cf	cf	df
120					ce	cf	cf
240					b	be	cf
1200					b	b	ce

Key to the Meaning of Symbols

1. Violent evolution of H_2
2. Rapid evolution of H_2
3. Moderate evolution of H_2
4. Slow evolution of H_2
5. Very slow evolution of H_2

a. Original form destroyed.
b. Entire surface corroded.
c. Some surface corrosion.
d. Little surface corrosion.
e. Original gloss destroyed.
f. Original gloss maintained.

ENCLOSURE (B)15

Table II(B)15
INFLUENCES OF INORGANIC SUBSTANCES UPON THE CORROSION OF MG BY CH_3OH

Inorganic Substances	Appearance of Mg & CH_3OH	Degree of Corrosion
Potassium ferrocyanate	The surface of Mg loses its gloss	slight
$K_2Cr_2O_7$	Brownish precipitate formed	very slight
Borax	The surface of Mg blackened	slight
NH_3	The gloss is lost	slight
$(NH_4)_2CO_3$	The surface of Mg blackened	slight
Sodium acid phosphate	The gloss is maintained	slight
$NaHCO_3$	The gloss is maintained	slight
$KClO_3$	The gloss is maintained	slight
NH_4 CH_3COO	The precipitate is formed	slight

Table III(B)15
INFLUENCE OF $K_2Cr_2O_7$ UPON THE CORROSION OF Mg BY CH_3OH

Exp. No.	$K_2Cr_2O_7$		Time of Exposure (days)								Precipitant Remarks
	Amount of Aqueous Solution Used	Concentration of Aqueous Solution Used	1	3	5	10	20	30	50	70	
K_1	(Vol % of CH_2OH) 1	(%) 0.1	-	-	-	-	-	#	###	###	slight
K_2	5	0.1	-	-	-	-	-	-	#	##	slight
K_3	1	1.0	-	-	-	-	-	-	--	#	slight
K_4	1	2.5	-	-	-	-	-	-	--	#	slight
K_5	5	1.0	-	-	-	-	-	-	-	-	Excessive
K_6	5	2.5	-	-	-	-	-	-	-	-	Excessive

Key

The degree of corrosion is shown as follows:

(-) no corrosion of Mg.
(#) less than 3 corroded spots.
(##) Mg slightly corroded.
(###) Mg excessively corroded.

ENCLOSURE (B)15

Table IV(B)15
INFLUENCE OF K_2CrO_4 UPON THE CORROSION OF Mg ALLOY BY CH_3OH

	K_2CrO_4		Time of Exposure (Days)							
Exp. No.	Amount of Aqueous Solution Used (Vol % of CH_3OH)	Concentration of Aqueous Solution Used (%)	1	3	5	10	15	20	30	40
K_1	2	0.1	-	-	# P	#	#	#	##	##
K_2	5	0.1	-	-	- P	-	-	-	#	#
K_3	10	0.1	-	-	- P	-	-	-	-	-
K_4	15	0.1	-	-	-	-	-	-	-	-
K_5	20	0.1	-	-	- P	-	-	-	-	-
K_6	1	1.0	-	-	- P	-	-	-	#	#
K_7	5	1.0	-	-	- P	-	-	-	-	-
K_8	10	1.0	-- PP.	-	-	-	-	-	-	-
K_9	1	2.5	-- PP.	-	-	-	-	-	-	-
K_{10}	5	2.5	-- PP.	-	-	-	-	-	-	-
K_{11}	1	5	-- PP.	-	-	-	-	-	-	-

Key

The degree of corrosion is shown as follows:

p.	slight precipitate
pp.	excessive precipitate
-.	no Mg corrosion
#.	less than 3 corroded spots
##.	Mg slightly corroded

ENCLOSURE (B)15

Table V(B)15
INFLUENCE OF ADDITION OF $K_2Cr\ O_4$ AND H_2O UPON THE CORROSION OF Mg-ALLOY BY CH_3OH

Exp. No.	Amount of Aqueous Solution Used (Vol % of CH_3OH)	K_2CrO_4 Concentration of Aqueous Solution Used (%)	The Amount of H_2O (Vol %)	Time of Exposure (days) 1	3	5	10	15	20	30	40
46	5	0.1	5	-	-	-	-	-	-	-	-
82	10	0.1	10	-	-	-	-	-			-
71	20	0.1	20	-	-	$\bar{P}$	-				#
73	5	0.1	5	-	-	P	-				-
74	10	0.1	10	-	-	$\bar{P}$	-				-
51	K_2CrO_4 wt. % CH_3OH 0.01		10	-	-	$\bar{P}$	-				-
52	0.01		20	-	-	$\bar{P}$	-				-
53	0.01		40	-	-	$\bar{P}$	-				-
	$K_2Cr_2O_7$ wt. % CH_3OH										
48	0.06		10	$\bar{P}$.$\bar{P}$-		-	-				-
49	0.06		20	$\bar{P}$	-	-	-				-
50	0.06		40	$\bar{P}$	-	-	-				-

Key

The degree of corrosion is shown as follows:

p.	slight precipitate
pp.	excessive precipitate
-.	no Mg corrosion
#.	less than 3 corroded spots
##.	Mg slightly corroded

ENCLOSURE (B)15

Table VI(B)15
INFLUENCE OF ADDITION OF K_2CrO_4 AND ALKALI UPON THE CORROSION OF Mg-ALLOY BY CH_3OH

	K_2CrO_4		Alkali		Time of Exposure (days)							
Exp. No.	Amount of Aq. Soln. Used Vol. % of CH_3OH	Concentration of Aq. Soln. Used (%)	Amount of Aq. Soln. Used $NaHCO_3$ Vol % of CH_3OH	Concentration of Aq. Soln. Used (%)	1	3	5	10	15	20	30	40
32	2	0.1	1	0.1	-	-	- P	-	-	#	##	#
23	5	0.1	1	5	-	- P	-	-	-	-	-	-
24	10	0.1	1	2.5	-	- P	-	-	-	-	-	-
25	10	0.1	1	5	-	-	- P	-	-	-	-	-
35	2	0.1	NaOH 1	0.1	-	-	-	#	#	#	#	#
36	2	0.1	5	0.1	-	-	-	-	# PP	#	#	#
38	2	0.1	10	0.1	-	-	-	-	# P	#	#	#
42	5	0.1	1	0.1	-	-	-	-	# P	#	#	#
43	5	0.1	5	0.1	-	-	-	-	- P	-	-	-
37	2	0.1	NH_4OH 5	0.1	-	-	-	- P	-	-	-	-
39	2	0.1	10	0.1	-	-	-	-	- P	-	#	#
44	5	0.1	5	0.1	-	-	-	- P	-	-	-	-
45	5	0.1	10	0.1	-	-	-	- P	-	#		#

Key

The degree of corrosion is shown as follows:

p.	slight precipitate
pp.	excessive precipitate
-.	no Mg corrosion
#.	less than 3 corroded spots
##.	Mg slightly corroded

ENCLOSURE (B) 16

STUDIES ON ALCOHOL-PROOF PAINTS

by

CHEM. ENG. LIEUT.
M. OKAZAKI

Research Period: 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B) 16

SUMMARY

Investigation of a suitable paint, lacquer, or varnish for the protection of rusting and corroding of the inside of drum-cans by ethyl alcohol was undertaken.

Synthetic resin varnishes of vegetable oil base have the best qualities, and are especially resistant to ethyl-alcohol.

Other paints or lacquers are not suitable for the above purpose, even though they are not attacked by alcohol, since the drying temperature is so high that it is necessary to use a large scale drying apparatus in industrial practice.

I. INTRODUCTION

A. History of Project

The object of this investigation was to find a suitable varnish or paint for the inside of drum-cans which would prevent corroding of the can and contamination of contents when filled with ethyl-alcohol.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. M. OKAZAKI

II. DETAILED DESCRIPTION

A. The only apparatus used in the test was an air bath and a large scale drying apparatus.

B. Test Procedure

1. Seven paints, selected from the twelve previously examined oil-proof paints and considered to be resistant to ethyl-alcohol, were examined in the same manner as in the previous studies on oil-proof paints.

2. The three varnishes which showed good qualities for use with ethyl-alcohol were painted on the inside of drum-cans which had been used once. After drying at 150°-160°C. in a large-scale air bath, the cans were filled with ethyl-alcohol and allowed to stand in the open air for 40 days. At the end of this period, the condition of the varnish and contamination of the alcohol was observed.

C. Experimental Results

1. The three materials observed to be the best were varnishes composed chiefly of vegetable oils, such as linseed oil or paulownia oil, and synthetic resins. Although these varnishes had the best qualities in regard to resistance to ethyl-alcohol, the drying temperature is high.

2. These varnishes must be dried at high temperature to get good qualities. They can be dried at lower temperatures but the qualities are not satisfactory under these drying conditions.

3. Lacquers composed of cellulose acetate or nitrate and paints were unsatisfactory.

III. CONCLUSIONS

Varnishes composed of vegetable oils and synthetic resins were found to be the most suitable materials for protecting the inside of drum-cans against rusting and corroding by ethyl alcohol.

The supply of raw materials for these varnishes is not scarce, but their drying offers difficulties in industrial practice, since they should be dried at 150° - 160°C. It would be necessary to prepare a large scale drying apparatus of large capacity.

Practical application of this project is not easy now, since there are many problems to be investigated, such as the components of the varnishes and the method of drying.

ENCLOSURE (B) 17

ALCOHOL FUEL UTILITY TEST
AS AEROENGINE FUEL

by

ENG. CAPT.
T. KONDO

ENG. LT. COMDR.
S. SOMA

Research Period: 1944-1945

Prepared for and Reviewed with Authors
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)17

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)17

SUMMARY

Alcohol (99%) could be used for small power engines; that is, 300 to 500 hp aero-engines with full power rating. For large power engines it could be used only with reduced power.

Alcohol (94%) had many troubles when used in carburettor engines, but could be used in injection engines at reduced power.

Alcohol-gasoline fuel [Alcohol(99%) 50% + Aviation gasoline 50% (by vol.)] with the same octane number as the base gasoline could be used for low power range.

It was necessary to increase the fuel consumption by 20-40% for alcohol fuels.

In winter, it was necessary to cover engine heads to prevent the misfiring of spark plugs.

Aluminium material was corroded by alcohol fuel. Anodic oxidation of aluminium and addition of sodium arsenite in fuel were necessary.

I. INTRODUCTION

A. History of Project

Owing to the shortage of aviation gasoline, tests with alcohol as aviation fuel were started in May, 1944, in compliance with the request of the First Naval Fuel Depot, and after about one year the test was finished and the above-mentioned conclusions were obtained.

B. Key Research Personnel Working on Project

Eng. Comdr.	K. NAKATA
Eng. Comdr.	K. HOSHIMIYA
Eng. Comdr.	T. NAKAYAMA
Eng. Capt.	T. KONDO
Eng. Comdr.	S. SOMA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

Various practical aviation engines were used for bench tests.

Various practical aeroplanes were used for flight tests.

B. Test Procedure and Experimental Results

1. Alcohol-gasoline mixed fuel testing. First, aviation gasoline and alcohol were mixed in the following proportion.

Aviation gaso. 87 octane 50% & alcohol(purity 99%) 50% (spec. 87 Hoi)
Aviation gaso. 85 octane 50% & alcohol(purity 99%) 50% (spec. 85 Hoi)
Aviation gaso. 80 octane 50% & alcohol(purity 99%) 50% (spec. 80 Hoi)
Aviation gaso. 70 octane 50% & alcohol(purity 99%) 50% (spec. 70 Hoi)

ENCLOSURE (B) 17

Several practical aero-engines were operated with these fuels

Tempuu 10 type 9 cyls.single row aircooled 300hp max.boost -50mm Hg.
Tempuu 20 type 9 cyls.single row aircooled 500hp max.boost+130mm Hg.
Kotobuki2 type 9 cyls.single row aircooled 500hp max.boost+150mm Hg.
Sakae 10 type 14 cyls.double row aircooled 940hp max.boost+250mm Hg.
Kinsei 40 type14 cyls.double row aircooled1000hp max.boost+200mm Hg.

It was found that the engines could be operated under the following conditions. (See Table I(B)17)

These performances were confirmed by flight tests with the following aeroplanes; that is,

93 type medium training plane(with Tempuu 10 type engine)
Shiragiku(training plane with tempuu 20 type engine)
90 type training plane(with Kotobuki 2 type engine)
Zero-fighter (with Sakae 10 type engine)
96 type torpedo-bombing aeroplane(with Kinsei 40 type engine)

Increasing the fuel consumption in these tests was performed by enlarging the fuel nozzle area of the engine carburettor. The power to boost pressure was the same as gasoline. During the tests, corrosion of aluminium materials in the fuel pass was discovered, and 0.005 gm/liter of sodium-arsenite was added to the mixed fuel to prevent corrosion by orders of the First Naval Fuel Depot.

2. Alcohol Fuel Testing. Immediately after the engine test with the alcohol-gasoline mixed fuel was finished, the fuel was changed to a 94% alcohol (spec. No. 2 alcohol) alone, and experiments made with the following engines.

Homare 20 type 18 cyls.double row aircooled 2000hp max.boost+500mmHg.
Kasei 20 type 14 cyls. double row aircooled 1750hp max.boost+450mmHg.
Atsuta 30 type 12 cyls.inverted Vee watercooled1400hp max." +325mmHg.
Sakae 30 type 14 cyls. double row aircooled 1150hp max.boost+300mmHg.
Tempuu 10 type
Tempuu 20 type
Kotobuki 2 type } same as before
Sakae 10 type
Kinsei 40 type

Using No. 2 alcohol, trouble occurred in acceleration in all engines except Kasei, 20 type and the Atsuta 30 type (solid injection), when the power was varied from dead slow to medium power. Then 99% alcohol (No. 1 alcohol) was applied to the above carburettor engines, and it was found that the engines could be operated under the following conditions: (See Table II(B)17)

(These performances were confirmed by flight tests using the following aeroplanes.)

93 type training plane (with Tempuu 10 type engines)
Shiragiku (training plane with Tempuu 20 type engine)
90 type training plane (with Kotobuki 2 type engine)
Zero fighter (with Sakae 10 type engine)
96 type torpedo-bombing aeroplane(with Kinsei 40 type engine)
Shiden (fighter with Homare 20 type engine)
Raiden (fighter with Kasei 20 type engine)
Suisei (diving bomber with Atsuta 30 type engine)
Zero fighter (with Sakae 30 type engine)

ENCLOSURE (B)17

In these tests, fuel consumption was increased by enlarging the fuel nozzle area of the engine carburettor.

To prevent the corrosion of aluminium materials in the fuel pass, sodium arsenite was added to the alcohol, but the effect was not sufficient, so the materials were coated with an electric oxidation oxide film.

When high power flights were made, vibration occurred, but there was no time to investigate these troubles. Moreover, when a relatively lean mixture ratio was taken to avoid this vibration, because of the bad distribution of alcohol to each cylinder, (this was thought to be one of the chief reasons causing the vibration), a very high exhaust gas temperature was reached; that is, over 800°C. This tendency was very severe in flight tests, because of the use of long exhaust passes, Zero fighters with Sakae 30 type engine and also with 10 type engine could not fly with a boost over zero mm Hg.

Other marked troubles caused by alcohol were bad starting and bad acceleration. It was thought that these were caused by the high latent heat of alcohol as well as bad distribution. Normal aviation gasoline was used only for starting, and was contained in one of the gasoline tanks or a special starting gasoline tank of 5 liters. No good counter-measure was devised to prevent bad acceleration, but adjustment of slow nozzle or slow vernier nozzle was somewhat effective. Moreover, careful attention was necessary during quick acceleration. Even in small power engines, such as Tempuu 10 type, 20 type, and Kotobuki 2 type, starting and acceleration were not satisfactory, so that 3% of ethyl ether was added to No. 1 alcohol with good results.

In winter, misfire of ignition plugs in these low power engines occurred, and as a counter-measure the cylinder heads were covered with asbestos cords.

III. CONCLUSIONS

This test was started only about a year before the war ended. Alcohol was used in training the air corp, only about two or three months before the war ended. The research period was too short to obtain good conclusions. Moreover, even a sufficient amount of alcohol for these tests could not be obtained.

ENCLOSURE (B)17

Table I(B)17
OPERATIONAL CONDITIONS FOR AEROENGINES

Engines	Fuel	Consumption increase (by vol.)	Allowable max. boost with alcohol-gasoline mixed fuel	Allowable max. boost with the ordinary gasoline	Power rate
Tempuu 10 type	70 Hoi	nothing	-50mm Hg	-50mm Hg	full power
Tampuu 20 type	85 Hoi	25%	130mm Hg	130mm Hg	full power
Kotobuki 2 type	80 Hoi	10%	150mm Hg	150mm Hg	full power
Sakae 10 type	87 Hoi	30%	50mm Hg	250mm Hg	80% power
Kinsei 10 type	87 Hoi	30%	60mm Hg	200mm Hg	85% power

Table II(B)17
ALCOHOL FUEL UTILITY TEST DATA

Engines	Alcohol	Consumption Increase	Allowable max. boost with the Alcohol	Allowable max. boost with the Ordinary Gasoline	Power Rate
Homare 20 type	No. 1	65 %	150 mm Hg (over +90 mm with supplementary fuel)	500 mm Hg (over +125mm with supplementary fuel)	70% power
Kasei 20 type	No. 2	70 %	200 mm Hg (over +50 mm Hg with supplementary fuel)	450 mm Hg (over +160 mm Hg with supplementary fuel	85% power
Atsuta 30 type	No. 2	70 %	250 mm Hg	325 mm Hg	95% power
Sakae 30 type	No. 1	65 %	120 mm Hg	300 mm Hg	85% power
Tenpuu 10 type	No. 1	70 %	— 50 mm Hg	50 mm Hg	full power
Tenpuu 20 type	No. 1	70 %	130 mm Hg	130 mm Hg	full power
Kotobuki 20 type	No. 1	70 %	150 mm Hg	150 mm Hg	full power
Sakae 10 type	No. 1	70 %	50 mm Hg	250 mm Hg	80% power
Kinsei 40 type	No. 1	70 %	60 mm Hg	200 mm Hg	85% power

ENCLOSURE (C)

ENCLOSURE (C)

REPORT ON KYUSHU REGIONAL FUEL DEPARTMENT ALCOHOL PLANT SHIMABARA, KYUSHU

ENCLOSURE (C)

I. INTRODUCTION

KYUSHU CHIHO SOKANFU KOJO is a government-owned alcohol plant manufacturing alcohol from sweet potatoes and is located in SHIMABARA, Kyushu. The plant is under the jurisdiction of the Regional Fuel Department for Kyushu. It was visited by the Petroleum Team of NavTechJap on 18 October, 1945. In the absence of the Factory Manager, the Chief Engineer, Mr. B. **YOSHII**, was interviewed and assisted in gathering the information presented herewith.

II. HISTORY AND ORGANIZATION

The Shimabara Alcohol Plant was built in 1938 and production of ethanol from sweet potatoes started in 1939. The plant has not been in operation since 18 August, 1945, but production is being resumed in the immediate future. Originally the alcohol was used in the manufacture of medicinals and beverages but recently most of the production has been sent to Sasebo Naval Station for use as fuel.

The names of the Department Heads are listed below:

Position	Name
Head of Factory	N. SAGARA
Chief Engineer	B. YOSHII
Head of Dept. Of General Affairs	S. NODA
Chief of Operations	M. ODE
Head of Dept. of Raw Materials	T. HAGIHARA
Head of Machinery Dept.	M. YABE
Head of Distillation Dept.	J. OGATA
Head of Testing Dept.	Y. TSUKAHARA

III. DESCRIPTION OF PROCESS

The sweet potatoes used as a raw material are obtained in two different forms: (1) whole or (2) sliced and dried. The whole potatoes are first washed and then sliced before the raw material is introduced by a bucket conveyor into two 45 kl kettles for cooking. The potatoes are steamed at atmospheric pressure and then the mash is transferred to the fermentation vats. There are twenty fermentation vats each of 90 kl capacity. Evolved carbon dioxide is not recovered.

There are two rectifying columns for the final distillation process. The columns are approximately three feet in diameter and each has eight plates with 12 bubble caps each. Although some of the caps were made of copper, most of them were of wood and were held in place by copper wire.

IV. PRODUCTION CAPACITY

There is tabulated below a summary of the annual alcohol production since the plant started operation in 1939:

Year	Alcohol Produced (Kiloliters)
1939	1,378
1940	3,056
1941	3,325
1942	2,884
1943	2,817
1944	3,840
1945 (to Sept. 1st)	952

ENCLOSURE (C)

V. CONCLUSION

The Shimabara Alcohol Factory is typical of many similar units which have been set up by the Japanese Government for the production of alcohol from sweet potatoes. As such it is of interest, since it indicates the acute need for any material which could be utilized as fuel.

RESTRICTED

ENCLOSURE (D)

ENCLOSURE (D)

LIST OF JAPANESE RESEARCH REPORTS PERTAINING TO ALCOHOLS FROM THE FIRST NAVAL FUEL DEPOT, OFUNA

(Forwarded through ATIS to the Washington Document Center
Refer to ATIS No. 4577 and NavTechJap Document No. listed below)

NavTechJap No.	Title	Author	Year
ND26-0006.1	On Alcohol.	S. KOMATSU	Aug. 1926.
6.2	Studies on Denaturing of Alcohol.	T. EGUCHI N. MATSUO	Oct. 1928.
6.3	Studies on the Ignition Delay Time of Liquid Fuel by Droppint Method. Part I, Alcohols.	N. ISOGAI Y. NISIDA	Nov. 1933.
6.4	Synthesis of Methanol.	T. EGUCHI	Nov. 1935.
6.5	Studies on the Methanol Synthesis.	T. EGUCHI	Mar. 1936.
	I. Decomposition of Methanol in the Presence of Various Catalysts.		
	II. Selection of Catalysts.		
	III. Equilibrium of CO-H_2-CH_3OH System at High Pressure.		
	IV. Synthetic Conditions at High Temperature and Pressure.		
6.6	Studies on the Methanol Synthesis.	T. EGUCHI	Mar. 1936.
	V. On the Promoter of Catalysts.		
	VI. Action of Poisons on the Catalyst.		
	VII. Theoretical Consideration of Catalyst.		
6.7	Test Reports on the Alcohol Blended Motor Benzol.	M. AKITA N. ISOGAI T. WADA H. KONISI	July, 1937
6.8	Studies on the Synthesis of Propyl-Alcohol from Propylene.	T. ITAKURA	Nov. 1939.
	I. Concentrated Sulfuric Acid as Catalyst.		
	II. Diluted Sulfuric Acid as Catalyst.		
	III. Mechanism of Catalytic Action of $H_2SO_45H_2O$.		

ENCLOSURE (D)

NavTechJap No.	Title	Author	Year
	IV. On the Tranformation between $H_2SO_45H_2O$ and $H_2SO_43H_2O$, Boiling Temperature and its Chemical Energy.		
	V. Chemical Equilibrium in the Hydrolysis of Propylene.		
ND26-0006.9	Synthesis of Ethyl and Butyl Alcohol from Ethylene and Butylene.	T. ITAKURA	Aug. 1940.
6.10	Sugar Chemistry.	S. KOMATSU	Apr. 1944.