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MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 2
NAVAL RESEARCH ON AVIATION GASOLINE

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

18 February 1946

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

Subject: Target Report - Japanese Fuels and Lubricants, Article 2 - Naval Research on Aviation Gasoline.

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

1. Subject report, dealing with aviation gasoline research by the Japanese Navy 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, assisted by Lt. Comdr. C.S. Goddin, USNR, Lieut. W.H. Millett, USNR, and Ens. E.R. Dalbey, USNR, interpreter and translator.

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Captain, USN

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U.S. Naval technical mission to Japan.

JAPANESE FUELS AND LUBRICANTS - ARTICLE 2

NAVAL RESEARCH ON AVIATION GASOLINE

"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 2
NAVAL RESEARCH ON AVIATION GASOLINE

The Japanese fleet air arm utilized a combat aviation gasoline of 91 or 92 CFR-M octane number except during the last months of the war when concessions in quality became necessary to maintain supply. Aviation fuel of 100 octane number was made only in experimental quantities.

Considerable research attention was concentrated by the First Naval Fuel Depot, OFUNA, on developing a wide variety of processes, including alkylation, isomerization polymerization, hydrogenation, catalytic reforming and catalytic cracking, for manufacturing iso-octane and other high octane blending stocks. Commercial scale installations were made of all these processes, with the exception of isomerization and catalytic reforming. Particular ingenuity was demonstrated in the development of a large commercial plant for synthesis of iso-octane from acetylene derived from calcium carbide. The research and development work of the Japanese Navy played a leading part in the growth of the growth of the aviation industry in Japan.

Complete facilities were installed at the First Naval Fuel Depot, OFUNA, for the service testing of aviation fuels and lubricants, including full-scale aircraft engine test stands and an elaborate high-altitude low-temperature cold room. Numerous special fuel blends, dopes and anti-detonants were tested, and fundamantal combustion studies were made.

Although in the last year of the war frantic efforts were made to utilize various substitute aviation fuel sources, expecially alcohol and pine root oil, none of these materials, and no dopes or anti-detonants other than tetra-ethyl fluid were actually used in combat aviation fuels; however, ethyl alcohol was used for training purposes.

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REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA, Kanagawa Prefecture.
First Naval Technical Depot, YOKOSUKA.
Third Naval Fuel Depot, TOKUYAMA.
Army Fuel Research Institute, FUCHU.
Kyushu Imperial University, FUKUOKA, Kyushu.

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Y. YAMAMOTO, Engineering Lieutenant-Commander, IJN, Head of Hydrogenation and Gasoline Blending Section of the First Naval Fuel Depot.
H. HOSHIMIYA, Engineering Lieutenant-Commander, IJN, Research Chemist of the First Naval Fuel Depot, specializing in aviation fuels.
K. SONE, Engineering Lieutenant, IJN, Research Chemist of the First Naval Fuel Depot, specializing in hydrocracking.
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I. WATANABE, Engineering Rear-Admiral, IJN, Superintendent of the Third Naval Fuel Depot.
I. MOTOYOSHI, Engineering Captain, IJN, Chief Engineer of the Third Naval Fuel Depot.
KIROSHIMA, Ph.D., Professor of Chemistry, Kyushu Imperial University, Specialist in the Chemistry of Rubber.
N. NAKAHARA, President of Toa Nenryo K.K. (East Asia Fuel Co.), closely associated with the development of catalytic cracking in Japan.
S. NOMURA, The Nomura Office, TOKYO, one of the foremost petroleum executives in Japan.
Research Assistants of the First Naval Fuel Depot, whose names are included in individual Japanese reports submitted as Enclosure (B).

Referenced Japanese Reports:

"Technical Notes on Research Work", Army Fuel Research Institute, FUCHU.
"Development of Catalytic Cracking in Japan" by N. NAKAHARA. Submitted as Enclosure C of NavTechJap Report, "Japanese Fuels and Lubricants, Article 10 - Miscellaneous Oil Technology and Refining Installations", Index No. X-38(N)-10.

INTRODUCTION

One of the most pressing problems confronting the Japanese throughout the war was that of maintaining an adequate supply of aviation gasoline in the face of insufficient resources and equipment.

This report summarizes the findings of the Petroleum Section of the U. S. Naval Technical Mission to Japan relative to aviation gasoline research conducted by the Japanese Navy at the First Naval Fuel Depot, OFUNA, supplemented by pertinent information obtained from other laboratories, commercial plants and naval installations. There is included in the report a discussion of the methods used in manufacturing aviation gasoline base stocks from non-petroleum sources, the development of aviation gasoline blends and dopes, and the service testing of products in aircraft engines. Changes in aviation gasoline specifications necessitated by the decreasing supply of raw material are described. There is also included a discussion of the fundamental engine combustion research conducted by the Japanese Navy.

Detailed reports of the aviation gasoline research projects investigated at the First Naval Fuel Depot have been prepared in English by the technical personnel of the Depot and are included in this report as Enclosures (B)1 to (B)38, inclusive. A summary of thirty-four of these reports has been prepared in English by Chemical Engineering Lt. Commander H. HOSHIMIYA of the Japanese Navy and is submitted herewith as Enclosure (A).

Since all of the research files of the First Naval Fuel Depot were burned in August 1945, by order of the Superintendent of the Depot, it was necessary to recall the Japanese personnel to reassemble this information from laboratory notebooks and available records. The preparation of reports and drawings continued for a period of nearly three months, during which time each Japanese author was frequently interrogated and assisted in the organization and translation of his reports by the Petroleum Section of the U. S. Naval Technical Mission to Japan. The material, which is submitted as Enclosures (A) and (B), constitutes an integral part of this report, and although it may include minor errors in construction introduced in the translation by the authors, it does serve as an accurate indication of the quality and extent of the aviation gasoline research conducted by the Japanese Navy.

THE REPORT

Part I
MANUFACTURING METHODS

A. MANUFACTURE OF AVIATION BASE STOCKS FROM PETROLEUM SOURCES

1. Distillation of Crudes

The standard military combat aviation gasolines up to 1944 were 87-92 CFR-M octane fuels containing a maximum of 0.1 volume per cent of tetra-ethyl lead (see Table 4 for a list of Navy combat aviation gasoline specifications). These fuels were made from light naphtha cuts from selected crudes, or by blends of straight run naphthas with iso-octane and hydrocracked naphthas.

Prior to the war substantial quantities of aviation gasoline, aviation blending stocks and selected crudes containing aviation grade naphtha were imported from foreign sources, especially the United States. It has been estimated that some 7,000,000 barrels of aviation gasoline and the equivalent of 14,000,000 barrels of aviation naphtha contained in crude oils, were imported during the period 1937-1941. Kettleman Hills was the crude imported in greatest volume. After Pearl Harbor, aviation base crudes were obtained from Borneo and North and South Sumatra, including such fields as SERIA, SANGA SANGA, MIRI, ABABU, TALANG AKAR, and DJAMBI.

Japan's domestic production of crudes containing high octane aviation naphtha was very limited. One such crude is known to be Omonogawa, from the AKITA field, which contains some 17% of naphtha of 76 octane number (92 with 0.1% T.E.L.).

As the supplies of high quality crudes dwindles in the latter stages of the war, Japan was forced to shift emphasis from the preparation of aviation gasoline by simple distillation of crudes, to more complicated processes for converting gases, gas oils, and low octane naphthas into suitable high octane blending stocks.

2. Catalytic Cracking and Reforming

Although catalytic cracking studies were initiated by the Tokyo Imperial University in 1934, not much attention was given to the process until after announcement of the Houdry Process in America. Attempts to purchase licensing rights to the Houdry and Universal Oil Products Co. catalytic cracking processes in 1939 failed due to the Moral Embargo, and strenuous efforts were made thereafter to develop a satisfactory process in Japan.

A catalytic cracking pilot plant of 25 barrels per day charge capacity was completed by the Navy at OFUNA in September, 1942. This unit was based, at least in part, on the Universal Oil Products Company's design, and utilized a Japanese activated acid clay catalyst which was found to be superior to the U.O.P. synthetic catalyst as manufactured by the Nippon Oil Company. Adiabatic reactors were employed and the catalyst was regenerated by circulating flue gas with oxygen content controlled to 2-6%. Cracking tests on East Indies crudes were continued until January 1945, when tests were started on pine root oil fractions (NavTechJap Report, "Japanese Fuels and Lubricants, Article 4 - Pine Root Oil Program," Index No. X-38(N)-4; Enclosure (B)5). On the basis of pilot plant data, the Navy started construction of four 2,000 barrel per day catalytic cracking units, two at YOKKAICHI and two in FORMOSA. Of the Units at YOKKAICHI, one unit was completed and produced 10,000 kiloliters of aviation gasoline in 1944; the second unit, although completed in 1945. was never operated,

due to lack of gas oil charging stock. The two units at FORMOSA were not completed by the end of the war. The Japanese Army constructed a 3,000 barrel per day unit and also unsuccessfully attempted modification of a thermal cracking unit at its MARIFU refinery. The Toa Nenryo Oil Company also began, but did not complete, construction of a 3,000 barrel per day unit at WAKAYAMA. In addition to these larger units, the Nippon Oil Company and Showa Oil Company were reported to have converted a total of three thermal cracking units to catalytic cracking. These units were small, about 150 barrels per day charge capacity, and it was reported that operations were not highly successful.

In connection with the pine root oil program, it was planned, in 1945, to erect some 21 small catalytic cracking units each having a charging capacity of 10kl to 30kl per day of pine root oil fraction, yielding about 35 per cent of 90-92 octane, (0.15 vol. % T.E.L.) aviation gasoline. None of these units were completed, however.

No evidence of research studies or industrial application of the fluid catalyst cracking process was encountered.

Some catalytic reforming investigations were made by the Toa Oil Company, but no industrial applications were reported. The Japanese Navy at OFUNA made extensive studies in 1945 of small simplified catalytic reforming units to process pine root gasoline of 185°C. end point, yielding 50-60% of 92-94 octane (0.15% of T.E.L.) aviation gasoline (NavTechJap Report, Index No. X-38(N)-4, Enclosures (B)5, (B)6). Japanese acid clay was used as the catalyst in these units.

In summary, the Japanese catalytic cracking and reforming processes were late in their commercial application, and no significant amount of aviation gasoline was produced by these methods.

3. Hydrocracking

The Japanese Navy initiated autoclave tests in 1935 on the high pressure hydrocracking of mineral oils, in conjunction with the coal liquefaction program. In 1940, continuous pilot plant studies were undertaken with emphasis on producing 92 octane (0.1 vol. % T.E.L.) aviation gasoline from high and low temperature tar and from East Indian crudes. In 1945, the hydrocracking of substitute oils from pine roots, soya beans and rubber were investigated. Typical pilot plant results are given in Table I.

Details of the above experiments are given in Enclosure (B)16 (Parts 1-6), (B)18, and (B)19 of this report, also NavTechJap Report, Index No. X-38(N)-4, Enclosures (B)7, (B)8.

A number of commercial scale hydrocracking plants were installed in the Japanese Empire. A tentative list of such plants, based mainly on information secured from the Teikoku Nenryo Company in TOKYO, is given in Table II. All of these plants were based primarily on the Navy process using NiO-MoO_3 catalyst and operating at 200 atmospheres and 400-450°C., with a space velocity of 0.5-1.0.

A related process successfully operated for production of aviation gasolines was the hydrogenation of cracked gasoline, accomplished at 100 atmospheres, and 330-350°C., using a NiO-acid clay (50:50), or a NiO-MoO_3-MgO (14:43:43) catalyst. A plant of this type was first installed at TOKUYAMA about 1937 (NavTechJap Report, Index No. X-38(N)-10, Enclosure F).

Although firm production figures were not obtained, it is fairly evident that hydrocracking of oil and hydrogenation of gasoline were the most successful processes in Japan for producing high octane aviation stocks (exclusive of simple distillation of crudes), insofar as actual volume of

production during the war was concerned. Catalytic cracking was considered to be a more economical process, but was late in getting started.

Table I
TYPICAL PILOT PLANT HYDROCRACKING TEST RESULTS

Stock	Catalyst	Reaction Temperature (°C.)	Reaction Pressure (Atms.)	Yield of AvGas (%)	CFR-M Octane With 0.1% T.E.L.
High Temperature Tar	MoS_3	470	200	25	92
Low Temperature Tar	MoS_3	430	200	50	89
Sumatra Kerosene	$NiO-MoO_3$	420	200	70	87
Omonogawa Gas Oil	$NiO-MoO_3$	430	200	73	89
Oha Gas Oil	$NiO-MoO_3$	410	200	70	92
Soya Bean Oil	MoS_3	450	200	40	85*
Pine Root Oil	$NiO-MoO_3$	430	200	50	95*
Oil From Rubber	$NiO-MoO_3$	460	200	42	92*

*Includes 0.15 vol. % of T.E.L.

Table II
OIL HYDROGENATION AND HYDROCRACKING PLANTS IN JAPAN

Operated By	Location	No. of Units	Process	AvGas Capacity (kl/year)
JAPANESE NAVY				
Second Naval Fuel Depot	YOKKAICHI, Honshu	2	Kerosene hydrocracking	2x20,000
		2	Cracked gasoline hydrogenation	2x20,000
Third Naval Fuel Depot	TOKUYAMA, Honshu	1	Kerosene hydrocracking	10,000
		1	Cracked gasoline hydrogenation	10,000
JAPANESE ARMY				
Iwakuni Refinery	IWAKUNI, Honshu	1	Kerosene hydrocracking	20,000
Shiheigai Refinery	SHIHEIGAI (Ssu-p'ing-kai) Manchuria	1	Kerosene or gas oil hydrocracking	unfinished
CIVILIAN				
Toa Nenryo Co. Wakayama Works	WAKAYAMA, Honshu	1	Cracked gasoline hydrogenation	-
Toho Kagaku Kogyo Co.	NAGOYA, Honshu	1	Kerosene or gas oil hydrocracking	10,000
Teikoku Nenryo Kogyo Ube Works	UBE, Honshu	1	Low temperature tar hydrocracking	10,000
Nippon Yuka Kogyo Co. Kawasaki Works	KAWASAKI, Honshu	1	Low temperature tar hydrocracking	10,000
Chosen Jinzo Sekiyu Co. Agochi Works	AGOCHI, Korea	1	Low temperature tar or kerosene hydrocracking	-
Manshu Jinzo Sekiyu Co. Fushun Works	FUSHUN, Manchuria	1	Low temperature tar or kerosene hydrocracking	5,000

4. Isomerization

The Japanese Navy conducted research experiments at OFUNA on the production of iso-paraffins, starting about 1937. At this time a program was initiated for the preparation of iso-butane from n-butane, for use in alkylation (Enclosure (B)6). A pilot plant of 10 liters per hour butane charge capacity was operated at OFUNA from 1942-1944. This unit was based at least in part, on observations of a Dutch plant in PALEMBANG, and utilized $AlCl_3$ catalyst supported on acid clay with operating conditions of 110°C. and 15-20 atmospheres. A research study also was made of the production of iso-butane by cracking Fischer-Tropsch condensate oil in the presence of $AlCl_3$ (Enclosure (B)3).

The synthesis of high octane isomeric hexanes from pinacone and pinacoline, and by isomerization of n-hexane were studied (Enclosures (B)4 and (B)5). In this connection the manufacture of acetone from acetylene was investigated as a source of pinacone and pinacoline (Enclosure (B)12). Synthesis of iso-dodecane as a high octane safety fuel was also studied (Enclosure (B)4, Part 2).

No evidence of the industrial application of isomerization or synthesis of any high octane isomeric compounds, other than iso-octane, was obtained.

B. MANUFACTURE OF ISO-OCTANE

1. Synthesis From C_4 Hydrocarbons

The synthesis of iso-octane in Japan was accomplished by two processes, alkylation with iso-butane, and polymerization of butenes plus hydrogenation of the dimer. Research on polymerization of butylenes was carried on at OFUNA during the period 1937-1945 (Enclosures (B)2 and (B)10). As the result of this work a catalyst composed of $BaSO_4$, acid clay and H_3PO_4 in the ratio of 80:5:15 was developed and used at TOKUYAMA and other plant installations in JAPAN for polymerization of butylenes at 150-170°C. and 40 atmospheres (NavTechJap Report, Index No. X-38(N)-10, Enclosure F). It was claimed that this type of catalyst had better activity and selectivity than standard U.O.P. catalyst.

Some studies were also made on catalysts and optimum conditions for hydrogenation of the butylene polymer (Enclosure (B)10, pages 41-50). The hydrogenation step, as performed in the TOKUYAMA plant, utilized a nickel oxide catalyst at 200°C. and five atmospheres pressure.
Research studies on the alkylation of iso-butylene with propylene and n-butylene in the presence of concentrated H_2SO_4 were made at OFUNA during the period 1939-1942 (Enclosure (B)8). A pilot plant based on this process was also constructed.

A shortage of C_4 hydrocarbons caused by the small crude throughputs and limited cracking capacity of Japanese refineries, prevented wide scale application of iso-octane synthesis plants. Alternative sources were sought and successful processes were developed for the synthesis of butylene from butanol and actylene. Available data indicate that only one alkylation plant was built in JAPAN, -- a 2,000kl per year unit installed at YOKKAICHI in 1942. Installations of butylene polymerization-hydrogenation plants were more numerous. The largest plant was installed by the Korean Nitrogen Fertilizer Company at KONAN, Korea, with a rated capacity of 30,000kl per year of iso-octane, operating on butylenes from acetylene. Actual output was substantially less than this, probably around 10,000kl per year. The next largest plant, located at YOKKAICHI, was designed to produce 10,000kl per year, operating on butylenes from butanol. Actual output of this plant was reported as negligible, however, due to shortages in the supply of butanol obtained from Formosa. A large installation, for producing iso-octane from acetylene (derived from natural gas by the arc

process) and from butanol was also under construction at the sixth Naval Fuel Depot at SHINCHIKU in [illegible].

The remainder of the plants in Japan were much smaller, in the range of 200kl to 2,000kl per year, all of which operated on butylenes in refinery cracked gases. These smaller plants reported to be in existence included one unit each at TOKUYAMA, MARIFU, TSURUMI and KAWASAKI, as well as an additional small unit at YOKKAICHI.

There is evidence that the actual total production of iso-octane in the Empire did not exceed 12,000kl per year. In any event, the amount produced was insufficient to permit production of 100 octane gasoline in any more than experimental quantities. The large bulk of the iso-octane, both imported and of Japanese manufacture, was used in the blending of 91 and 92 octane aviation fuels.

2. Production of Butylenes

Several alternate sources for the production of butylenes to be used as the raw material for iso-octane manufacture were investigated, and some of these sources were applied commercially. The dehydrogenation of n-butane using an aluminum oxide-chromic acid catalyst was studied briefly at the First Naval Fuel Depot but was discontinued because of the scarcity of cracked gas (Enclosure (B)1).

Before the war, elaborate plans were formulated for producing butylenes from n-butanol. Fermentation plants for the production of butanol from sugar molasses and sweet potatoes were erected throughout Japan. These plants were intended to provide sufficient butanol for the production of 100,000kl per year of iso-octane, but by 1944 they had all been converted to the production of ethyl alcohol because of the serious shortage of aviation gasoline and the higher yields obtained in the ethyl alcohol fermentation process. Details of this alcohol program and the related research projects studied by the Japanese Navy are described in the NavTechJap Report, "Japanese Fuels and Lubricants, Article 3 - Naval Research On Alcohol Fuel", Index No. X-38(N)-3.

It is of particular interest that the largest iso-octane plant in the Japanese Empire utilized butylenes synthesized from acetylene. Construction of this plant was begun in 1937 by the Chosen Chisso Hiryo K.K. (Korean Nitrogen Fertilizer Company) at KONAN, Korea, and had a design capacity of 30,000kl per year of iso-octane. The acetylene was obtained from calcium carbide, a method particularly attractive to the Japanese in view of abundant supplies of coal and hydro-electric power. Research pertaining to this process was continued by the Navy, in cooperation with the Korean Nitrogen Fertilizer Company throughout the war.

Construction of another iso-octane plant utilizing acetylene was started at the Second Naval Fuel Depot, YOKKAICHI, but was never fully completed. The acetylene was to be prepared by the cracking of refinery gas using an electric arc process, details of which are given in Enclosures (B)14 and (B)15.

The synthesis of iso-butene from acetylene proceeded through the following steps:

(a) The preparation of acetaldehyde from acetylene using a dilute sulfuric acid solution of mercuric sulfate as catalyst.

(b) The preparation of crotonaldehyde from acetaldehyde using the aldol condensation method and subsequent distillation.

(c) The preparation of butanol from crotonaldehyde using a mixed NiO-CuO catalyst supported on diatomaceous earth (Ni:Cu=1:3).

(d) The dehydration of n-butanol to n-butene using an activated Japanese acid clay catalyst.

(e) Isomerization of n-butene to iso-butene at 350°-400°C. using a phosphoric acid catalyst supported on charcoal.

The research conducted by the Japanese Navy relative to each of the above steps is described in detail in Enclosure (B)10. One of the major drawbacks encountered in the commercial application of the process was attributed to the loss of mercury catalyst in converting acetylene to acetaldehyde, especially in view of the scarcity of mercury in Japan. To circumvent this difficulty, other methods for effecting the conversion were studied (Enclosure (B)13). Of particular interest in this connection are the pilot plant studies relative to the methylation of acetylene and subsequent hydrolysis of the vinyl methyl ether thus formed.

The preparation of n-butene from acetylene by catalytic polymerization to vinyl acetylene followed by partial hydrogenation was also studied but was not considered suitable for commercial application (Enclosure (B)11).

C. THE MANUFACTURE OF AVIATION BASE STOCKS FROM NON-PETROLEUM SOURCES

The acute shortage of aviation gasoline base stock during the latter part of 1944 necessitated the consideration of many non-petroleum sources for this type of fuel. Although the study of most of these substitutes never advanced beyond the laboratory or pilot plant scale, yet there were two sources for which large scale production programs were initiated. These two programs involved the use of ethyl alcohol and pine root oil previously discussed in this report and described in detail in the two NavTechJap Reports, "Japanese Fuels and Lubricants, Article 3 - Naval Research on Alcohol Fuel", Index No. X-38(N)-3, "Japanese Fuels and Lubricants, Article 4 - Pine Root Oil Program", Index No. X-38(N)-4.

Investigations of the application of additional non-petroleum sources to the preparation of substitute aviation fuels are described below:

1. Soya Bean Oil

The preparation of gasoline from soya bean oil by cracking in the presence of activated Japanese acid clay had been investigated in Japanese research laboratories, but the quality of the fuel thus formed was unsatisfactory for aircraft use. In 1944 the First Naval Fuel Depot initiated autoclave studies on the preparation of aviation gasoline by the thermal cracking of soya bean oil. A 20 per cent yield of gasoline having an octane number of 89 (0.15% lead by volume) was obtained. Complete data are presented in Enclosure (B)17.

In 1945 laboratory and pilot plant studies of the catalytic hydrocracking of soya bean oil were undertaken. Gasoline having an octane number of 85 (0.15% lead by volume) was prepared in 40 per cent yield using a molybdenum trisulfide catalyst at 200 atmospheres and 420-450°C. Subsequent autoclave tests indicated that titanium dioxide was a more effective catalyst, but no pilot plant data were obtained. Details of the catalytic hydrocracking of soya bean oil are given in Enclosure (B)18.

2. Rubber

In 1942 Japan's supply of natural rubber was more than adequate for her needs, and, in consequence, this raw material was considered as a source of hydrocarbons for aviation gasoline. Although gasoline was never prepared from rubber commercially, many laboratories investigated the problem

during the war period.

In pilot plant studies at the First Naval Fuel Depot, rubber was decomposed in a pipe still, cracked, and fractionated in a continuous unit (Enclosure (B)19). Hydrocracking of the product yielded a gasoline with an octane number of 73 (unleaded), or 92.4 (0.15% lead by volume). This product consisted mainly of naphthenes (41.2%) and paraffines (46%) and appeared to be suitable as an aviation gasoline, although service testing of the fuel was never undertaken in view of the scarcity of rubber by 1944.

Similar pilot plant studies were conducted at the Army Fuel Research Institute, FUCHU. The procedures used in each of two processes studied are described as follows:

(a) Crude rubber was depolymerized and liquefied at 280°C., under steam pressure. The oil product was hydrocracked in the liquid phase using a slurry catalyst, and the middle oil thus obtained was hydrogenated in the vapor phase to aviation gasoline. The gasoline thus prepared had an octane number of 91 with 0.15 per cent lead by volume.

(b) The rubber was depolymerized as in method (a), thermally cracked at 420-450°C., and the middle oil thus obtained was hydrogenated in the vapor phase using a molybdenum catalyst. The product had an octane number of 95 with 0.15 per cent lead by volume.

Professor KIROSHIMA of Kyushu Imperial University, who has specialized in the chemistry of rubber for many years, also studied the possibility of obtaining a high octane aviation fuel from rubber. A summary of the several different methods investigated in his laboratory and the characteristics of the resulting gasolines is presented in Table III. Detailed reports (in Japanese) of these studies were obtained and are listed in Enclosure (C).

Table III
AVIATION GASOLINE FROM RUBBER

(Data obtained from Kyushu Imperial University)

Method	Yield (Wt. %)	Analysis			Octane Number	
		Olefines	Aromatics	Naphthenes and Paraffine	Clear	Leaded 0.15% by vol.
Dry Distillation	36	42	30	28	75	77
Dry Distillation followed by catalytic cracking with acid clay	31	12	27	61	80	85
Dry Distillation in presence of $AlCl_3$	25	14	24	62	75	88
Dry Distillation in presence of $AlCl_3$ followed by catalytic cracking with acid clay	45	3	86	11	90	94
Hydrogenation using NiO catalyst at 450°C. and 100 atmospheres	48	2.4	37.3	59.3	81	96

3. Other Sources

During 1945, the Army Fuel Research Institute tested several other materials as possible sources of aviation gasoline. Although these were only laboratory studies, it is of interest that such substances as camphor, camphor oil, birch bark, pine needles, and orange peel were considered.

Part II
SERVICE TESTS

A. ENGINE TEST FACILITIES AT THE FIRST NAVAL FUEL DEPOT, OFUNA

1. Single Cylinder and Full-Scale Aircraft Engine Tests

Engine test facilities were installed at the First Naval Fuel Depot in 1942 in order to examine the service performance characteristics of aviation fuels and lubricants. Up until this time, the service testing had been carried out at the First Naval Technical Depot, YOKOSUKA, and the new installations at OFUNA were added to provide a more convenient means for the study of aviation fuels and lubricants in connection with research on manufacture. The test equipment comprised one laboratory equipped with several single-cylinder aircraft engines, and two separate test installations for full scale multi-cylinder engine work. The engine tests were supported by two other laboratories, one equipped to carry on analytical tests of lubricants, and the other for the chemical testing of fuel, and C.F.R. Motor Method octane number determinations. There was no evidence in the Japanese Navy's research of any routine testing in C.F.R. type engines of anti-knock properties of fuels under rich-mixture conditions.

The single-cylinder and multi-cylinder full scale test installations are described in Enclosure (B)33, and the test operating methods are discussed. These full scale stands were well laid out, soundproofed, and seemed to be comparable to American standards. Details of the single-cylinder and multi-cylinder engine installations are shown in Figures 1 to 11. Special attention is called to Figure 4, which shows the design features of the "KINSEI", No. 4 type, single-cylinder, variable-compression ratio, counter-balanced aircraft test engine manufacture by the Ishikawajima Aircraft Company, Ltd.

In detonation tests in aircraft engines, the maximum allowable boost and corresponding horsepowers were determined over the useful range of air-fuel ratio, using cylinder head temperature and exhaust flame color to indicate limits due to detonation.

2. Low-Temperature and Low-Pressure Experimental Laboratory

An elaborate high-altitude, low-temperature cold room installation was constructed to conduct research on fuels, lubricating oils and hydraulic oils under conditions up to 20,000 meters altitude and temperatures as low as -55°C. This unit was designed by the Ebave Company, Ltd. The cost of the installation was estimated to be 2,300,000 yen at the time construction commenced in December 1943. In August 1945, although construction of the plant was well advanced, work was discontinued because of the destruction of the Ebave Company by bombing, at which time the designer was killed, and many of the design details, models, and castings were destroyed.

The plant consisted of two parts. One part comprised the low-temperature and low-pressure rooms and refrigerating means, using Freon 12 and Freon 11 as cooling media. The other part consisted of a single-cylinder aircraft engine testing plant designed for low-temperature, low-pressure-operation. The first section was 80 per cent completed, but the second section reached the design stage only, except for the engine foundations. The plant is described in Enclosure (B)34, which include detailed drawings of the design features, refrigeration and carbon dioxide fire extinguisher systems, and the single-cylinder test installation. These design data are included in Figures 1 to 5, inclusive, and were prepared for the Petroleum Section of the U.S. Naval Technical Mission to Japan. The layout is shown in this much detail in view of the interest in such research in the United States.

B. WARTIME MODIFICATION OF AVIATION GASOLINE SPECIFICATIONS

In 1937, the Japanese Navy's specifications for aviation grade gasoline included 92 minimum octane nemver requirement, a minimum of tetraethyl lead content of 0.1 per cent by volume, and maximum temperature of 105°C. and 150°C. at the 50 percent and 90 per cent distillation points, respectively. These specifications were modified during the war in an attempt to increase the supply of aviation gasoline. The original specification and subsequent modidications are tabulated in TableIV. Significant changes are discussed below.

1. Distillation Range

With the increasing shortage of aviation gasoline, tests were initiated in the middle of 1943 to modify the specifications to permit heavier gasoline. Engine performance tests conducted at the First Naval Fuel Depot and the First Naval Technical Depot showed that the maximum distillation temperatures for the 50 per cent and 90 per cent points could be raised, but that in so doing, the octane number of the product was lowered from 0.2 to 0.8 for each per cent increase in the yield of gasoline from the crude oil due to the lower octane numbers of the higher boiling fractions.

The two alternate specifications investigated are shown as Modification No. 1 and Modification No. 2 in Table IV. Calculations based on the proposed changes indicated an increased yield of aviation gasoline from East Indies crude of 25 per cent by the first modification and 80 per cent by the second modification. This represented an increased production of 300,000 kiloliters and 1,000,000 kiloliters of aviation gasoline per year, respectively, on the basis of expected imports of 8,450,000 kiloliters per year of East Indies crude oil.

Additional service tests carried out at the First Naval Technical Depot showed that starting characteristics, when using Modification No. 1 gasoline, were unsatisfactory at atmospheric temperatures below 10°C., whereas with Modification No. 2, aviation gasoline starting problems were encountered at temperatures below 20°C. To avoid this difficulty, carburetted engines were supplied with five liters of standard aviation gasoline, from a special tank, for starting purposes. Furthermore, lubricating oil analyses after using these two fuels under flight test conditions showed increased dilution, particularly with Modification No. 2 gasoline.

With the above limitations, it was concluded that Modification No. 1 was satisfactory for combat planes even in winter and that No. 2 was satisfactory for use in summer. In view of these findings, the Japanese Navy's specifications for aviation gasoline were changed accordingly and were used successfully during the balance of the war (Enclosures (B)24 (Part I), and (B)25).

2. Octane Number

In 1942 it was found necessary to decrease the specified minimum octane number of aviation gasoline from 92 to 91 because of difficulties in manufacturing a sufficient quantity of the 92 octane fuel. In 1945, coincident with the decrease in volatility, the minimum octane number was lowered to 87 for the summer grade gasoline specified by Modification No. 2.

3. Tetraethyl Lead Content

Engine tests were carried out relative to increasing the tetraethyl lead content to compensate for the loss in anti-knock quality mentioned in the

preceding paragraphs. In 1944 the lead content of aviation gasoline was changed from 0.10 per cent to 0.15 per cent (by volume) to compensate for this. The ethylene dibromide equivalent was maintained at 1.0. Engine tests were also conducted in 1944 using aviation fuels containing 0.3 per cent by volume of tetraethyl lead and with ethylene dibromide equivalents of 1.0, 1.3, and 1.5. Significant findings included the following:

(a) It was found that in endurance tests in full-scale engines using gasolines of low volatility, as discussed under Modifications 1 and 2, the use of 0.3 tetraethyl lead with 1.5 ethylene dibromide equivalent was unsatisfactory, due to the burning of the plugs or fouling with lead deposits, causing the engine to misfire after 10 to 15 hours operating time.

(b) Endurance tests were also made with aviation gasoline of the boiling range specified prior to 1943, but containing 0.3 per cent by volume of tetraethyl lead, and it was found that the most suitable equivalent of ethylene dibromide was 1.3. This finding was of theoretical interest only since it became necessary to obtain increased gasoline production by changing the distillation range (Enclosure (B)24, Part 2, and (B)26).

Table IV
WARTIME SPECIFICATIONS FOR JAPANESE NAVY COMBAT AVIATION GASOLINE

	Date Established	Distillation (°C max)					Sum of 10% 50% and 90% (min)	Reid Vapor Pressure (kg/cm^2 min)	Sulfur (% max)	Unsaturates (% max)	Freezing Point (°C max)	Octane No. C.F.R. Isotor Methods (min)	T.E.L. Volume (% max)
		I.B.P.	10%	50%	90%	97%							
Aviation 92	1937	60	80	105	150	170	260	0.6	0.1	1.0	-50	92	0.10
Aviation 91	1942	60	80	105	150	170	260	0.53	0.1	1.0	-50	91	0.10
Aviation 91 (Mod. 1)	1944	60	90	115	160	170	260	0.6	0.1	1.0	-50	91	0.15
Aviation 87 (Mod. 2)	1945	70	90	125	180	200	260	0.6	0.1	1.0	-50	87	0.15

4. Ethylene Dibromide Substitutes

With the curtailment of imported stocks of ethyl fluid in 1941, coupled with the decrease in production of bromine from brine during the same period, a substitute for ethylene dibromide became an urgent problem, and chlorine compounds were investigated. These studies disclosed that butylene chloride was the most suitable substitute for ethylene dibromide, but when this substance was used, the spark plugs had to be changed after every 25 hours of engine operation (Enclosure (B)27).

C. SPECIAL STOCKS AND BLENDS

1. Aromatics

Engine tests were carried out during the period 1942 to 1944 in connection with the use of aromatic hydrocarbons as aviation fuels. These fuels were produced at the First Naval Fuel Depot and were tested in single cylinder aircraft engines at the First Naval Fuel Depot and multi-cylinder engines at the First Naval Technical Depot. Benzol, toluene, Xylene, solvent naphtha, and "Benzex" (sulphur dioxide extract from East Indian topped gasoline) were investigated. Significant findings included:

(a) Single Cylinder Kinsei Engine

(1) When the concentration of benzol added to gasoline exceeded 20 per cent, detonation occurred in spite of high octane number

as indicated by the C.F.R. engine.

(2) Straight toluene had the best performance of the aromatics tested as aviation fuel and equalled or surpassed iso-octane.

(3) Xylene and higher aromatics gave good anti-knock properties, but these aromatics had poor volatility characteristics.

(b) Multi-Cylinder Engines (Homare 20, Kasai 20 and Atsuta 20)

(1) "Benzex" and solvent naphtha in 85 per cent concentrations both were found unsatisfactory because their volatilities were too low for use even with direct injection engines and the exhaust gases from these fuels contained excessive carbon which coated the spark plugs with heavy deposits after a few hours operation.

(2) The aromatics actually used in aviation gasoline consisted of 20 to 30 per cent of "Benzex" blended with natural gasoline made from EAST BORNEO crude (Enclosure (B)22 and (B)23). This fuel was used principally in the Netherlands East Indies war theater.

2. Oxy-Compounds

In the period 1937 to 1938, research was conducted on oxy-compounds, such as ketones and ethers, as blending stocks in lieu of iso-octane. These compounds were added in 20 per cent concentrations to TALAGIMAR gasoline, which had an octane number of 89.9 when containing 0.1 per cent of tetraethyl lead. While C.F.R. engine tests showed the ketones and ethers promising, aircraft engine tests indicated that these compounds were deficient in anti-knock characteristics (Enclosure (B)31).

3. Ethyl Alcohol

See NavTechJap Report "Japanese Fuel and lubricants, Article 3 - Naval Research on Alcohol Fuel", Index No. X-38(N)-3, Enclosures (B)17 to (B)24, inclusive.

4. Pine Root Oil Gasoline

See NavTechJap Report, "Japanese Fuels and Lubricants, Article 4 - Pine Root Oil Program", Index No. X-38(N)-4, Enclosures (B)10 and (B)11.

D. ANTI DETONANTS AND DOPES

1. Aromatic Amines

The Japanese aviation gasoline octane number (C.F.R. Motor Method) was established in 1942 at a 91 minimum, and gasoline produced from Sumatra crude could not reach this figure with the addition of only 0.15 per cent by volume of tetraethyl lead, the maximum amount permitted as discussed in Section B-2 above. Consequently, tests were carried out in regard to the use of aromatic amines in combination with gasoline produced from Sumatra crude and containing 0.15 per cent by volume of lead. It was found that of the aromatic amines tested, aniline was the most suitable and an octane number of 91 was obtained by the addition of 1 per cent to 3 per cent, although many problems were encountered, such as the formation of supercharger and piston head deposits, solvent action on the paint of the oil tight seams and of the cork in the carburettor float, and corrosive action on copper and iron. Steps were taken to overcome these objections so that this type of fuel could be used in combat planes (Enclosure (B)29), although the application of aromatic amines was not reduced to actual prac-

tice.

2. Selenides

Research was carried out from 1937 to 1939 on the use of selenium compounds as anti-detonants for producing gasolines of more than 100 octane number by the addition of such materials to Stanavo 100 octane fuel. These selenides were tested in a one-cylinder aircraft engine and the results showed that 0.8 per cent by volume of diethyl selenide increased the octane number to 112, as determined by the C.F.R. Motor-Method (by extrapolation), and increased the horse power in single cylinder aircraft engine tests by 15 per cent. It was further determined that diethyl selenide was the most desirable of the selenide compounds tested, that it was not poisonous and did not possess a disagreeable odor, if prepared in a pure state. This research work was not pursued further due to the small amount of selenium available in Japan (Enclosure (B)30).

3. Influence of Moisture on Tetraethyl Lead

Following the findings of J.R. MacGregor, Standard Oil Company of California, tests were conducted from 1942 to 1943 in a C.F.R. engine to determine the effect of the humidity of the air on octane number determinations. These experiments gave the following results:

(a) For unleaded gasoline, the influence of moisture was within one octane number.

(b) With leaded gasolines, the influence of moisture on octane number was appreciable.

A correcting formula was established for leaded gasolines in lieu of using humidifiers attached to the C.F.R. engines in routine knock testing (Enclosure (B)32).

Part III
ENGINE COMBUSTION RESEARCH

This section of the report deals with investigations of flame propagation and detonation in engine cylinders conducted by Engineering Commander K. NAKATA, IJN, over a period extending from 1933 to 1944. These studies are included herein because they relate primarily to aviation fuels.

The research work was done, for the most part, at the First Naval Fuel Depot, YOKOSUKA, and is presented in four papers (Enclosures (B)35 to (B)38, inclusive). In reviewing these papers, it should be borne in mind that the Japanese files had been burned and that the reports were, therefore, prepared by Commander NAKATA from some personal notes and from memory.

It is believed significant that the Japanese Navy was sufficiently research-minded not only to engage in this field of research in peace time, but also to carry on fundamental combustion studies in quartz tubes during the height of the war.

The four reports on combustion research, are briefly discussed below:

A. PHOTOGRAPHIC INVESTIGATIONS OF FLAME PROPAGATION AND DETONATION IN ENGINE CYLINDERS (ENCLOSURE (B)35)

This paper deals with exploratory tests made from 1933 to 1935 on flame travel under detonating and non-detonating conditions. An air-cooled 1½ hp "El" head

single-cylinder test engine with water-cooled head was fitted with a narrow quartz window, through which flame propagation was studied photographically. A film drum was mounted above the engine upon which a standard size film was wound. Sodium bicarbonate was used to color the flame. In view of the low compression ratio of the engine, knocking was induced by the addition of 20 to 30 per cent of ethyl nitrate to the fuel. The findings included:

1. There was no difference in flame velocity for the knocking and non-knocking condition in that portion of the cycle between the spark position and the knocking position.

2. It was impossible to measure flame speed in the knocking region, as here the flame front was always vertical to the time axis.

3. Vertically striped bright flame patterns were observed in the detonation region. The frequency of these patterns was measured and found to decrease as the piston went down in the cylinder, presumably because of the adiabatic compression of burned gas due to detonation waves.

These early flame studies were primarily carried out to acquaint the investigator with some of the fundamentals of engine combustion and to provide a basis for further research in this field.

B. ENGINE DETONATION STUDIES BY PIEZO-ELECTRIC INDICATOR (ENCLOSURE (B)36)

In order to determine whether the bright-striped patterns discussed in the previous section were due to the adiabatic compression or rarefaction in the detonation waves, research was undertaken to measure the pressure inside the cylinder with an indicator of small inertia and high natural frequency. A water-cooled Piezo-electric Indicator had previously been used at Tokyo Imperial University, but its natural frequency was too low. The author developed an air-cooled Piezo-electric quartz pick-up unit having a natural frequency in the order of 50,000 cycles per second, and this design (Enclosure (B)36, Figure 3) gave satisfactory results. A pressure-time diagram was obtained, using an electro-magnetic oscillograph.

With this unit, experiments were carried out on a number of engines, including a C.F.R. engine equipped with a quartz window. On full-scale aircraft engines, vibration attributed to the amplifier tubes occurred in the pressure line when the engine detonated. Significant findings included:

1. When indicator cards were taken simultaneously with photographs of engine flame, the number of vibrations on the pressure line was nearly twice the number of striped patterns observed photographically in the detonating flame. In the case of normal combustion, the pressure curve on the indicator card was smooth, and no striped patterns were observed.

2. Under detonating conditions the frequency of vibrations was greater the smaller the bore of the engine used, and this frequency decreased as the piston progressed downward from the top dead-center position.

No other forms of indicators were built by Comdr. NAKATA, but the French "Detonindex" indicator was tried. This indicator was said to consist of a bouncing pin and induction circuit whereby the EMF produced caused a neon lamp to glow under detonating conditions.

C. FLAME PROPAGATION IN ENGINE CYLINDERS, STUDIES BY THE IONIZATION METHOD (ENCLOSURE (B)37)

During the period 1935 to 1940 flame propagation in aero-engine cylinders was studied by the ionization gap method. This method was utilized in view of the difficulty of installing a quartz window over the head of a full scale aircraft engine cylinder. Tests were made in the DVL variable compression engine equipped

with a water-cooled BMW cylinder. In these tests a number of ionization plugs were installed in the cylinder head and cyligrams were obtained, which were converted to rate of propagation by using the time scale recorded on the same film. The following conclusions are of interest:

1. Flame velocity is higher with high octane fuels than with low octane fuels.

2. Flame velocity is greatly reduced under lean and rich mixture conditions.

3. Velocity of flame propagation is increased with increase in engine speed.

4. There is a slight increase in flame speed with increase in boost pressure.

5. Flame front is markedly distorted by turbulence.

Commander NAKATA concluded that the ionization gap method is well-suited for investigating flame propagation in cylinders of full-scale aircraft engines.

D. STUDIES OF SLOW OXIDATION OF HYDROCARBONS BY ABSORPTION SPECTRA (ENCLOSURE (B)38)

In 1938, after reviewing reports written by Rassweiler and Withrow of the General Motors Research Corporation, Comdr. NAKATA constructed an engine fitted with two quartz windows on opposite sides of the cylinder and a stroboscopic arrangement enabling flame study at any phase of the engine's revolution by observing emission or absorption spectra. However, in view of the difficulties encountered in the engine's operation, this procedure was abandoned and quartz tube slow oxidation research by absorption spectra was undertaken, using the method developed by Ubbelohde and Edgerton.

Tests were carried out with various typical hydrocarbons at different temperatures. Hydrocarbon-air mixtures were used in a mixture strength ratio of 13 to 1, under both flowing and stagnant conditions. The conclusions obtained in these tests include the following:

1. Flow Method

(a) Iso-octane is stable with temperature, but low octane fuel, such as normal heptane, is reactive with oxygen at relatively low temperatures.

(b) The oxygen absorption of cyclo-hexane begins at a temperature between that of heptane and that of iso-octane, and the form of absorption differs from both.

2. Stagnant Method

(a) Octane numbers of hydrocarbons, except aromatics, can be determined by reaction temperatures measured in a quartz tube.

(b) In the case of normal heptane the appearance of absorption bands at 2600 A^{O}, called the "U" band, accompanies a depression of pressure reportedly due to the formation of peroxides.

(c) The presence of tetraethyl lead in normal heptane does not suppress the formation of the substance causing the "U" band, but does have some effect on the spectrum at higher temperatures.

ENCLOSURE (A)

SUMMARY OF AVIATION GASOLINE RESEARCH AT THE FIRST NAVAL FUEL DEPOT, OFUNA

by

CHEM. ENG. LT. COMDR. H. HOSHIMIYA

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

December 1945

ENCLOSURE (A), continued

LIST OF TABLES
AND ILLUSTRATIONS

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ENCLOSURE (A)

INTRODUCTION

During the war, the urgent demand for large quantities of aviation fuel of superior quality compelled investigation of the possibilities of producing it from all sources, both foreign and domestic. Since the resources of natural high octane crudes in Japan were very poor, synthesis of aviation gasoline was planned.

In 1942, high quality crude oil became available from the East Indies, but unfortunately imports did not last as long as desired.

Research on synthesis of fuels was, therefore, again emphasized and the use of pine root oil and alcohols was investigated. Progress in the investigations of aviation gasoline by the Japanese Navy is summarized as follows:

SUMMARY OF RESEARCH

During the period up to 1940 efforts were made primarily to improve the quality of aviation gasoline. Since 1935, aviation gasoline had been obtained by distillation of crude oil and thermal cracking of naphtha or light oils.

However, it became necessary to improve the octane value of these fuels.

The techniques acquired in the studies on coal liquefaction were applied, and soon the commercial production of aviation gasoline by hydrocracking of natural oils was achieved. (In 1938, 92 octane fuel was made by hydrocracking at TOKUYAMA.) Later, however, it was found that 92 octane rating gasoline could not be obtained by hydrocracking crude oil from North Sumatra over Mo-Ni-catalyst. Therefore, studies for improving hydrogenation catalyst were made, but it was not possible to produce 92 octane rating gasoline from this crude, although a number of experiments were made. (Encl. (B)16, Parts 1-6, Encl. (B)9).

In 1939, research on catalytic cracking of naphtha and light oil was started, studying several types of catalysts. It was found that active acid clay served to give 91 octane rating gasoline, and a commercial plant was constructed at YOKKAICHI in 1942. This type plant required less construction materials than a hydrogenation plant, as is indicated below:

Table I(A)
STEEL REQUIRED FOR PLANT CONSTRUCTION

Plant	Steel Required (Tons/Kl AvGas/yr)	
	Ordinary	Special
Hydrogenation Process	0.3	60
Catalytic Cracking Process	1.17	6

In 1936, 100 octane gasoline was required. In this connection, studies were made on synthesis of high octane components from waste gas in the cracking process of petroleum, and the next year, a study of polymerization of butylenes using H_3PO_4 catalyst was started. Shortly afterwards a commercial plant was constructed at TOKUYAMA. Due to a deficiency of butylenes in Japan, an investigation was made on the synthesis of isobutylene from acetylene. Although the acetylene process was started on a commercial scale at KONAN, North Korea, difficulties due to corrosive action and short duration of catalyst activity were encountered with the phosphoric acid catalyst used for conversion of n-butylene to iso-butylene. (Encl. (B)2, (B)10, (B)11, (B)13, (B)14, (B)15).

ENCLOSURE (A), continued

After discovering that aluminum silicate was usable instead of H_3PO_4, this catalyst was used in the iso-octane plant in Formosa.

Another source of butylene was butanes in refinery gas (Encl. (B)1).

In addition to isooctane, preparation of other high octane blending compounds such as isohexane and isododecane was studied, but these compounds were not used in practice. (Encl. (B)4, Parts I, II, (B)12).

Preparation of high octane isoparaffines by H_2SO_4 alkylation of isobutane was investigated in 1939, and a commercial plant was constructed at YOKKAICHI in 1942. (Encl. (B)8). To supply isobutane for this process, the isomerization of n-butane and Fischer condensate oil or wax was studied. (Encl. (B)6, (B)3). The production of isobutane by these methods was accomplished only on a pilot plant scale.

Antidetonants for aviation gasoline were also investigated with regard to the problems of high octane fuels. Some selenium, oxygen compounds and the substitutes of ethylene-dibromide also were studied, but these compounds were not used on commercial scale. (Encl. (B)27, (B)30, (B)31).

During the war, 91 octane aviation gasoline was required. This demand was partly met in 1941, by adding 0.15% tetra ethyl lead to the gasoline from California crude oil. The stability of tetra ethyl lead was studied in 1940. (Encl. (B)28).

In trying to solve this problem studies were made on adding isooctane or small amounts of aniline to Sumatra naphtha and on the influence of moisture on octane value. (Encl. (B)29, (B)32). The scheme of adding aniline was not used in practise.

The isomerization of gasoline in the presence of $AlCl_3$ was also tried, but in vain. (Encl. (B)5, (B)7).

The synthesis of gasoline by the catalytic cracking or hydrogenation of the dry-distilled product from natural rubber was studied on semi-commercial plant scale and also the dry-distillation or high pressure hydrocracking of Soya-bean oil. (Encl. (B)17, (B)18, (B)19).

From 1943 onwards efforts were made primarily to increase the supply of aviation fuel and standard fuel. (Encl. (B)20). One device used for this purpose was to modify the quality of gasoline as indicated by the following table: (Encl. (B)23, (B)24, Part I(B)25, (B)26).

Table II(A)
SPECIFICATIONS FOR 91 OCTANE FUEL

		1939	1940	1944	1945
Octane Rating	(C.F.R.)	92 min.	91 min.	91 min.	91 min.
Distillation	10 %	80° max.	80° max.	80° max.	90° max.
	50 %	105° max.	105° max.	115° max.	125° max.
	90 %	150° max.	150° max.	160° max.	180° max.
	97 %	170° max.	170° max.	170° max.	200° max.

ENCLOSURE (A), continued

Another plan was the manufacture and use of alcohols, first in blends and finally in the pure state.

After September 1944 intense efforts were made to solve the aviation fuel supply problem by using pine root oil as a source. The catalytic cracking of the light oil and hydrocracking of the middle oil were investigated, and production of 91 to 95 octane rating fuel was starting at the end of the war.

A description of engine test methods employed for testing aviation fuel at OFUNA is given in Encl. (B)33. A low temperature-low pressure laboratory to study fuel and lubricant behaviour under high altitude conditions was also under construction at the close of the war. (Encl. (B)34).

Some research was also done at OFUNA on gasoline resistant paints. (Encl. (B)21).

ENCLOSURE (B) 1

STUDIES ON THE DEHYDROGENATION OF n-BUTANE

by

CHEM. ENG. LT. COMDR., M. KUMAMOTO

Research Period: 1938-1942

Prepared for and reviewed with author by the
U.S. Naval Technical Mission to Japan

Dec. 1945

ENCLOSURE (B)1

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ENCLOSURE (B)1

SUMMARY

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

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

I - INTRODUCTION

A. HISTORY OF PROJECT

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

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

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

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

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

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

II - DETAILED DESCRIPTION

A. DESCRIPTION OF TEST APPARATUS

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

B. TEST PROCEDURES

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

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

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

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

ENCLOSURE (BJ1

Preparation of Catalyst - Freshly precipitated aluminium hydroxide was prepared, carefully washed, and ignited at 550°C. The alumina was mixed with CrO_3 (12% as Cr_2O_3) and dried at 120°C.

C. EXPERIMENTAL RESULTS

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

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

Ex. No.		1	2	3
Conditions	Temp. (°C)	550	560	570
	Space* velocity	1080	1080	1080
Composition of Gas Produced	Total olefines (%)	15.0	18.7	12.8
	C_4H_8 (%)	12.0	10.2	5.0
	H_2 (%)	10.3	10.5	8.0
	C_nH_{2n+2} (%)	74.3	70.8	79.2

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

The effects of temperature and space velocity in presence of Al_2O_3-Cr_2O_3 were investigated and are tabulated in Tables II(B)1 and III (B)1.

Table II(B)1
YIELD OF BUTYLENES FROM BUTANE AT VARYING TEMPERATURES IN PRESENCE OF Al_2O_3-Cr_2O_3 CATALYST

Ex. No.		5	6	7	8	9	10
Analysis of Gas produced	Temp. (°C)	350	400	450	500	550	600
	Space velocity	1100	1100	1100	1100	1100	1100
	Total olefines (%)	4.2	7.1	10.8	14.6	25.0	28.0
	C_4H_6 (%)	4.1	6.8	10.0	14.0	23.5	22.0
	H_2 (%)	3.5	7.5	13.2	14.1	20.2	21.2
	C_nH_{2n+2} (%)	92.3	85.3	76.0	71.3	54.8	50.8

ENCLOSURE (B)1

Table III(B)1
YIELD OF BUTYLENES FROM BUTANE AT VARYING SPACE VELOCITY IN PRESENCE OF Al_2O_3-Cr_2O_3 CATALYST

Ex. No.		11	12	9	13	14	15
Conditions	Space* velocity	500	1000	1100	1500	1800	2000
	Temp. (°C)	550	550	550	550	550	550
Composition of Gas Produced	Total olefines (%)	28.2	25.7	25.0	21.7	19.0	12.5
	C_4H_8 (%)	20.0	22.5	23.0	19.2	17.6	11.0
	H_2 (%)	23.0	23.1	20.2	17.8	17.0	10.5
	C_nH_{2n+2} (%)	48.8	51.2	54.8	60.3	64.0	77.0

* cc/hr/cc of catalyst.

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

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

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

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

Ex. No.		17	18
Conditions	Temp. (°C)	520	540
	Space velocity	1100	1120
Composition of Gas Produced	H_2 (%)	16.8	17.0
	CH_4 (%)	1.6	2.3
	C_2H_4 (%)	0.5	0.7
	C_2H_6 (%)	1.0	0.4
	C_3H_6 (%)	2.5	2.0
	C_3H_8 (%)	7.5	6.2
	C_4H_8 (%)	20.1	21.2
	C_4H_{10} (%)	50.0	50.2

ENCLOSURE (B)1

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

Table V(B)1
THE YIELD OF CARBON DEPOSIT

Conditions	Temp. = 550°C.		space velocity = 1100	
Time (hr)	0.5	1.0	1.5	3.0
Yield of Carbon (%)	0.2	0.8	3.5	17.0
Total Olefines (%)	25.0	26.2	26.0	25.8
H_2 (%)	20.2	19.4	16.2	17.8
C_nH_{2n+2} (%)	54.8	54.4	57.8	56.4

III - CONCLUSIONS

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

The activity of Al_2O_3-Cr_2O_3 catalyst decreased after one hour of reaction. This reduction in activity may be attributed to excessive carbon deposits.

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

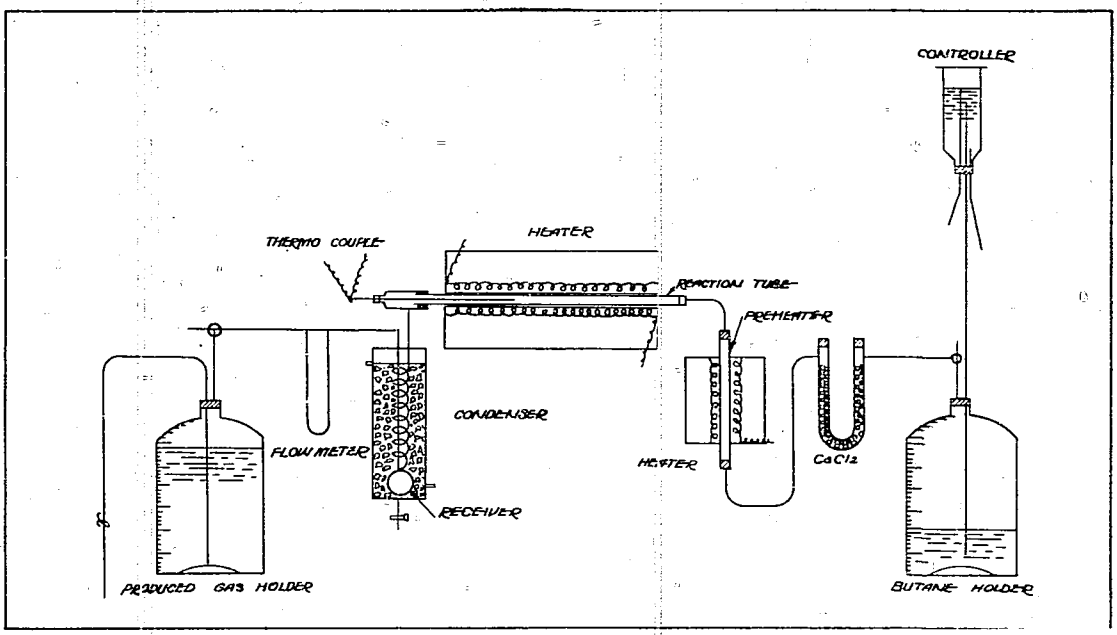

Figure 1(B)1
TEST APPARATUS FOR DEHYDROGENATION

ENCLOSURE (B) 2

POLYMERIZATION OF BUTENES IN THE PRESENCE OF PHOSPHORIC ACID

by

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Research Period: 1941-1943

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

December 1945

ENCLOSURE (B)2

LIST OF TABLES AND ILLUSTRATIONS

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Table	III(B)2	Relative rates of polymerization of 1-butene and 2-butene	Page 39
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ENCLOSURE (B)2

SUMMARY

To prepare an aviation gasoline from iso-butene, it was found that the best catalyst for polymerization was a mixture of phosphoric acid and barium sulphate. Iso-octane prepared from n-butene by use of this catalyst was hydrogenated to iso-octane consisting of 2, 3, 4-trimethyl pentane, 2, 2, 3-trimethyl pentane and 2, 2, 4-trimethyl pentane.

I - INTRODUCTION

The polymerizing action of sulphuric acid and phosphoric acid has been known for some time, and when the lower polymerides of iso-butene are required, polymerization is most conveniently effected by acid catalyst, e.g. sulphuric or phosphoric acid. Phosphoric acid is one of the most successful polymerization catalysts, in supported form, so-called "solid phosphoric acid" catalyst, in commercial use on a large scale in the production of high octane number polymer gasolines from cracked gases.

The author (H. FUJIMOTO) supposed that the polymerization activity of solid phosphoric acid catalyst depends on the catalyst support and studied, from 1937 to 1939 at TOKUYAMA, various materials such as $BaSO_4$, $CaSO_4$, $PbSO_4$, MgO, HgO, SiO_2, $Mn_3(PO_4)_2$, $Ni_3(PO_4)_2$, H_3PO_4, and $Hg_4P_2O_7$ as supports and found that sulphates of Ba, Ca and Sr were the most successful materials for polymerization of iso-butylene. A catalyst composed of 95% of $BaSO_4$ and 5% of H_3PO_4 was used in a commercial unit at TOKUYAMA, (employing C_3 and C_4 hydrocarbon gas mixture as feed stock) and it was indicated that the catalyst gave better results with regard to activity and especially in its selectivity, compared with U. O. P. catalyst.

Next Y. MOMOTARI and Y. KAKIUCHI tried to prepare high octane gasoline by polymerizing n-butene in the presence of the above mentioned catalyst and to analyze it by means of Raman effect.

II - DETAILED DESCRIPTION

A diagram of the test apparatus used in the following experiments is given in Figure 1(B)2.

A. POLYMERIZATION OF ISO-BUTENE

Experimental results on polymerization of iso-butene at atmospheric pressure in the presence of the various catalysts are shown in Table I(B)2. The iso-butenes were prepared from iso-butanol by decomposition over alumina at 450°C. Catalyst size was about 5 mesh.

TABLE I(B)2

	H_3PO_4(wt %)	Temp. (°C)	Gas S.V. (V/v/hr.)	Yield of Polymer (wt %)
$BaSO_4$	5-10	125-150	270	90
$CaSO_4$	10-20	125-150	500	90
$PbSO_4$	5-15	125	500	80
MgO	71	125	275	80
HgO	25 and 40	120	100	80
SiO_2	30	170	40	72
$Mn_3(PO_4)_2$	55-60	125	500	68
$Ni_3(PO_4)_2$	40	150	36	65
Hg_3PO_4	0	200	280	16
$Hg_4P_2O_7$	0	180	200	30

ENCLOSURE (B)2

On the basis of the above data $BaSO_4$ and H_3PO_4 appeared to be the most effective catalyst. The following data were obtained to determine the optimum composition and operating conditions for this catalyst.

TABLE II(B)2

	Reaction Temp. (°C)	Gas rate (cc/hr/cc)	Polymer (%)	d^{20}_4 of Polymer
$BaSO_4:H_3PO_4$ = 95:5	75	300	52.2	0.7136
	100	300	81.3	0.7220
	125	300	88.6	0.7236
	150	300	92.6	0.7246
	175	300	86.8	0.7205
	200	300	78.8	0.7124
$BaSO_4:H_3PO_4$ = 90:10	75	300	69.8	0.7245
	100	300	77.8	0.7172
	125	300	88.2	0.7234
	150	300	86.4	0.7242
	175	300	86.1	0.7207
	200	300	73.2	0.7182
	225	300	71.8	0.7082
$BaSO_4:H_3PO_4$ = 85:15	125	300	58.0	0.7186
	150	300	63.0	0.7175
	175	300	80.3	0.7206
	200	300	81.1	0.7171
	225	300	72.1	0.7163
$BaSO_4:H_3PO_4$ = 80:20	100	300	26.3	0.7221
	125	300	60.1	0.7171
	150	300	75.2	0.7144
	175	300	84.1	0.7148
	200	300	78.0	0.7147
	225	300	67.2	0.7136
$BaSO_4:H_3PO_4$ = 75:25	125	300	24.3	0.7238
	150	300	57.5	0.7215
	175	300	68.6	0.7182
	200	300	70.8	0.7136
	225	300	75.8	0.7140

ENCLOSURE (B)2

B. POLYMERIZATION OF n-BUTENES

Experiments showed that n-butenes react with H_3PO_4-$BaSo_4$ (10:90) catalyst at relatively low temperatures and under atmospheric pressure to form high octane number polymer. These results were as follows:

1. Relative rates of polymerization of 1-butene and 2-butene

1-Butene was obtained from normal butanol by dehydration in the presence of alumina at 400°C with purity of 94.7%, as determined by the low temperature fractional distillation method of Podbielniak; 2-butene was prepared from 2-butanol with purity 98.8%.

TABLE III(B)2

	1-butene	2-butene
Temp. (°C)	150	150
Pressure	atmospheric	atmospheric
Gas rate cc/hr/cc cat	150	150
Yield of polymer -wt%	41.0	33.2
Dimer fraction -wt%	68.7	71.0
Octane No. of hydrogenated polymer	89.5	88.0

2. Effects of operating conditions

Varying temperature with H_3PO_4-$BaSO_4$(10:90) catalyst at constant gas rate and atmospheric pressure, influenced the octane rating of the iso-octane fraction: (see Table IV(B)2).

TABLE IV(B)2

MIXTURE OF 1-BUTENE AND 2-BUTENE (94.7% 1-BUTENE)

Temp.(°C)	Gas Rate cc/hr/cc cat.	wt % Polym.	% Dimer Fraction	Hydro. Dimer Octane No.
150	300	9.9	78.9	90.8
170	300	16.7	81.2	88.6
200	300	25.1	80.2	86.3

Variation of the gas-rate at constant temp. of 150°C, and 200°C and atmospheric pressure did not appreciably influence the octane No. of the iso-octane fractions.

ENCLOSURE (B)2

TABLE V(B)2

Gas Rate	Temp.(°C)	(%) Polym.	(%) Dimer	Hydro. Dimer Octane No.
150	150	20.7	78.7	90.5
300	150	9.9	78.9	90.8
150	200	49.1	78.3	86.0
300	200	25.1	80.2	86.3

Variation of the pressure at constant temperature 150°C, influenced the yield of iso-octanes.

TABLE VI(B)2

Press(kg/cm^2)	Gas Rate cc/hr/cc	(%) Polym.	(%) Dimer	Hydro. Dimer Octane No.
0	150	20.7	78.7	90.5
5	150	28.1	56.4	90.2

Change of temperature under 5 kg/cm^2 pressure influenced the octane No. and the yield (Table VII(B)2).

TABLE VII(B)2

Temp.(°C)	Press(kg/cm^2)	Gas Rate	(%) Polym.	(%) Dimer	Hydro. Dimer Octane No.
150	5	150	28.1	56.4	90.2
175	5	150	44.8	62.2	88.9
200	5	150	75.8	50.8	83.8

3. Catalyst

Effect of content of phosphoric acid (Table VIII(B)2) at atm. pressure:

TABLE VIII(B)2

% of H_3PO_4	Temp.(°C)	Gas Rate	(%) Polym.
10	150	150	6.0
13	150	150	13.7
15	150	150	24.9
17	150	150	20.1
20	150	150	8.1

ENCLOSURE (B)2

Effect of state of Phosphoric acid:

TABLE IX(B)2

	Temp.(°C)	Gas Rate	(%) Polym.
Ortho phosphoric acid	150	150	40.7
Pyro phosphoric acid	150	150	24.7

It is seen that ortho phosphoric acid-barium sulphate is much more active for the polymerization of butene-1.

Effect of 5% by weight of phosphate promoter added to (90:10 catalyst):

TABLE X(B)2

Promoter	(%) Polym.	Promoter	(%) Polym.
None	35.5	B PO_4	0
Na_3PO_4	0	Al PO_4	0
K_3PO_4	0	$Pb_3(PO_4)_2$	2.3
$Cu_3(PO_4)_2$	32.5	Cr PO_4	4.8
Ag_3PO_4	40.0	$Fe_3(PO_4)_2$	0
$CO_3(PO_4)_2$	0	Fe_3PO_4	6.4
$Zn_3(PO_4)_2$	1.8	$CO_3(PO_4)_2$	0
$Cd_3(PO_4)_2$	29.8	$Ni_3(PO_4)_2$	12.4
$Hg_3(PO_4)_2$	34.6		

Note: Temp(°C) 150, Gas rate 150.

From these results, it was deduced that Ag and Hg-phosphates were the most active promoters, but yield improvement was insufficient to justify use of promoter.

C. ANALYSIS OF THE SAMPLE BY MEANS OF RAMAN EFFECT

The sample taken was the so-called iso-octane fraction produced by the polymerization of 1-butene under conditions of atm. pressure, temperature of 150°C, space velocity of 300 and % of polymerization 9.9. The octane rating of the sample was 90.8.

The Raman spectrum of the sample was photographed and the spectrum density was measured with the eye. The result was compared with the known data of pure samples and a rough estimate of the percent of principal components of the sample was made as follows:

2, 3, 4 - Trimethylpentane ..... 35-40 %
2, 2, 3 - Trimethylpentane ..... 35-40 %
2, 2, 4 - Trimethylpentane ..... 20-25 %

ENCLOSURE (B)2

The physical constants of the sample are given in table XI(B)2.

TABLE XI(B)2

	Obs.	Calc.
Density (d_4^{20})	0.7116	0.712
Refractive Index (n_D^{20})	1.4013	1.401
Mean M. W.	115	114.1

III. CONCLUSIONS

On the basis of the data obtained, the following conclusions can be drawn:

1. $BaSO_4$-H_3PO_4 catalyst is an active catalyst for the polymerization of isobutenes.
2. The preferred composition of catalyst is $BaSO_4/H_3PO_4$=95/5-90/10.
3. The best temperature for the polymerization of iso-butenes is between 125° and 150°C, and the yield of polymer is 90%.
4. The best conditions for the polymerization of n-butene to obtain the 91 octane polymer are as follows:

   Temperature ..... 150°C
   Pressure ..... Atmospheric
   S. V. 150

5. A hydrogenated 91 octane polymer consists mainly of 2, 3, 4-trimethylpentane, 2, 2, 3-trimethylpentane and 2, 2, 4-trimethylpentane.

ENCLOSURE (B)2

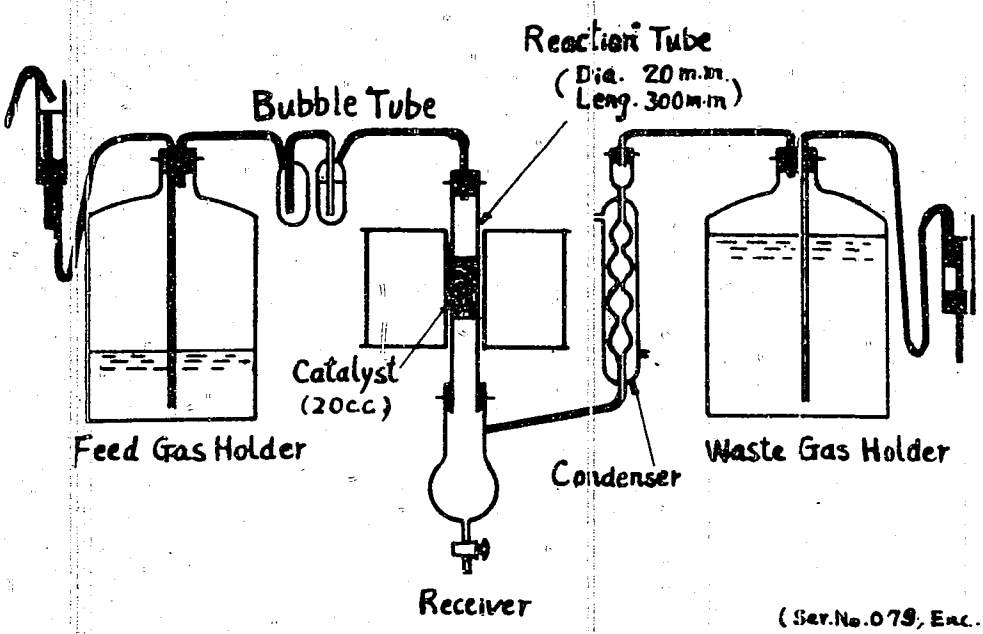
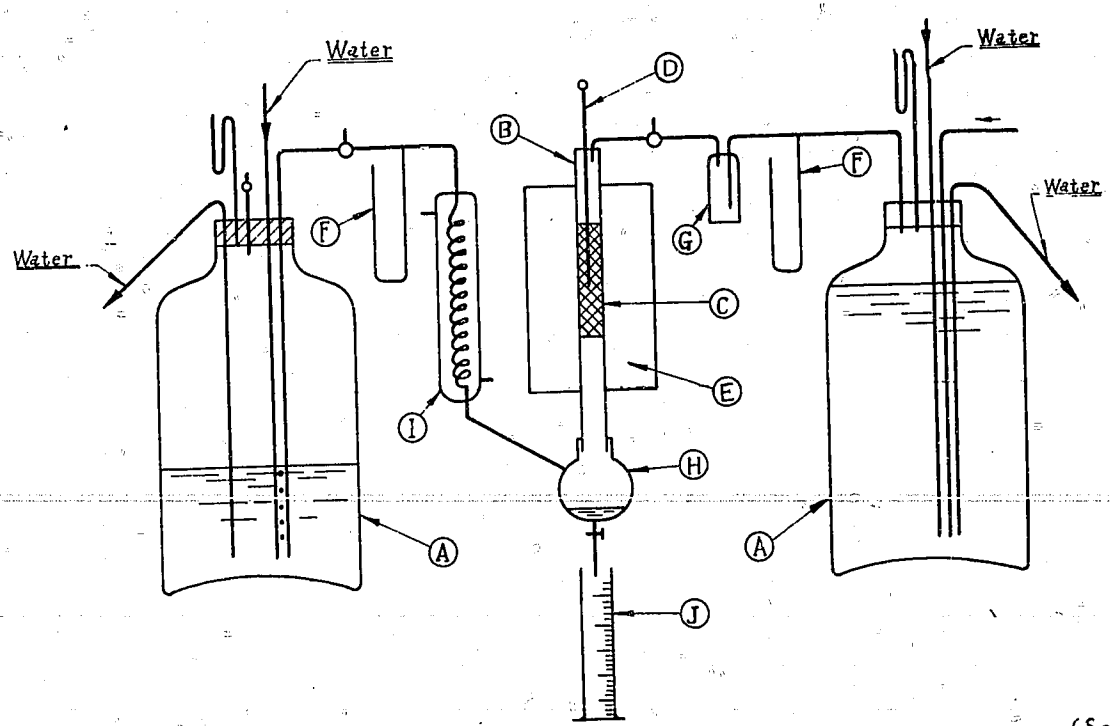


Figure 1(B)2

APPARATUS FOR POLYMERIZATION OF BUTENE



Ⓐ GAS-BOTTLE (20L)
Ⓑ QUARTZ TUBE (DIA.20mm)
Ⓒ CATALYST
Ⓓ THERMOMETER
Ⓔ ELECTRIC FURNACE
Ⓕ FLOW METER
Ⓖ TRAP
Ⓗ RECEIVER
Ⓘ COOLER
Ⓙ MEASURING CYLINDER

(Ser. No. 079 Enc. B-2)

ENCLOSURE (B)2

Figure 2(B)2
APPARATUS FOR POLYMERIZATION OF BUTENE

RESTRICTED

ENCLOSURE (B) 3

RESEARCH ON THE PRODUCTION OF ISOBUTANE

by

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Chem. Eng. T. SHINODA
Chem. Eng. O. MIYATA

Research Period: 1937-1944

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

Dec. 1945

ENCLOSURE (B)3

SUMMARY

Fischer condensate oil was cracked in a pilot plant at 220°C, under atmospheric pressure, using 30 wt.% of anhydrous $AlCl_3$ as the catalyst. Yields of 28.6 wt.% of isobutane and 30-40 wt.% of gasoline of 95 octane (with 0.15% lead) were obtained.

This process is considered a promising source of aviation gasoline.

I. INTRODUCTION

A. HISTORY OF PROJECT

The production of isobutane from wax had been studied of OFUNA from April 1937 to September 1944.

The first work was done on laboratory glass scale and included an investigation of i-butane production by isomerization of various types of charge stocks with $AlCl_3$. It was found that addition of HCl increased yield. The yield also increased proportionately to the amount of $AlCl_3$ used, up to a certain maximum.

Typical data are given below for optimum conditions.

TABLE I(B)3

	$AlCl_3$ used % by wt.	HCl used % by wt.	Yield of isobutane % by wt.	Yield of gasoline % by wt.
Crude shale wax	20	5	27.5-33	32-33
Pure Shale wax	15	5	34-42	27-36
Wax from East Indies oil	10	5	43-44	30-32

On the basis of these early studies the following conclusions were drawn.

1. The wax from the East Indies oil was the best raw material for production of isobutane.

2. The reaction temperature range was 200-300°C and when the amount of catalyst was increased, the reaction temperature was lowered.

3. About 8-10 hours were required for the completion of the reaction.

4. The largest part of the products from wax was isobutane, and the formation of higher hydrocarbons was small.

5. Hydrocarbons containing less than 3 carbon atoms were not produced, and all hydrocarbons were isomeric paraffines with one, or sometimes two, methyl branches.

In April, 1943, a pilot plant was installed to at OFUNA to investigate production of isobutane. A run was made on crude shale wax but was unsatisfactory due to plugging difficulties caused by the high melting point.

ENCLOSURE (B)3

Subsequent pilot plant work, was then concentrated on Fischer-Tropsch condensate oil, which contained straight chain paraffines of lower melting point.

Work on this project was stopped in September 1944 due to limitations in the supply of waxy oils.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

Chem. Lt. Comdr. H. HOSHIMIYA and Chem. Lieut. T. OTSUKA.

II. DETAILED DESCRIPTION

A flow sheet of the pilot plant for isobutane production is given by Fig. 1(B)3. Properties of the Fischer condensate oil are given below.

The feed oil and the catalyst ($AlCl_3$) were stirred to a homogenous state in the mixer and pumped to the reaction chamber.

The necessary amount of HCl gas was then added to the reaction chamber. Pressure of the reaction chamber was atmospheric. The reaction mixture was circulated by the hot oil pump through the pipe still, continuously.

Isobutane and light hydrocarbons were removed overhead, condensed and caustic washed.

Periodically the sludge was drawn off from the bottom of the reaction chamber, and batches of fresh oil and $AlCl_3$ were added from the mix-tank.

TABLE II(B)3

		Run No.		
		1	2	3
Isobutane Pilot Plant Results	$AlCl_3$, wt. % of oil charge	30	20	20
	HCl, wt. % of catalyst	0	0	6.5
	Temperature of mixer, °C	120-135	150-170	150-170
	Temperature of reaction chamber °C	180-210	170-220	170-220
	Duration of reaction, hrs.	4-12	8-12	8-12
Average Yield, wt.% Oil Charge	Isobutane	(28.6)22%	16%	3.5%
	Isopentane	(14.2)12%		
	Gasoline	(30.0)32%	21%	46%
	Propane	4%		

Note: Figures in parentheses indicate maximum yield observed.

ENCLOSURE (B)3

TABLE III(B)3

Properties of Gasoline

		Run No. 1	Average of 2 and 3
d_4^{15}		0.696	0.677
ASTM Distillation	I.B.I.	22.5°C	21.0°C
	10%	44.0°C	30.0°C
	50%	151.0°C	71.0°C
	90%	213.0°C	205.0°C
	97%	233.5°C	220.0°C
	D.P.	237.0°C	223.0°C
Octane No.	clear	71.3	75.5
	0.1% lead	90.3	94.3
	0.15% lead	95.1	97.3
Yield of av. gush below	130°C,(vol%)	40	40

Because of a shortage of HCl, the experiments using HCl were not completed, but its beneficial effect in increasing yield of i-C_4 is apparent.

III. CONCLUSIONS

A. This process was considered promising as a source of aviation gasoline since 30% of isobutane and 30-40% of high octane gasoline could be produced from the Fischer-Tropsch condensate oil. By modification of plants to handle higher melting point stocks, it is considered that the comparatively abundant waxy stocks from shale wax and East Indies oil could be used as food stocks.

B. The amount of catalyst ($AlCl_3$) was decreased by the use of hydrogen chloride.

C. A reactor of the semi-continuous type is preferable for long time operation to allow for periodic removal of sludge.

D. It would be essential to recover the aluminum chloride from the cracked residue in a large scale plant. No investigations were made of the problems of such recovery.

ENCLOSURE (B)3

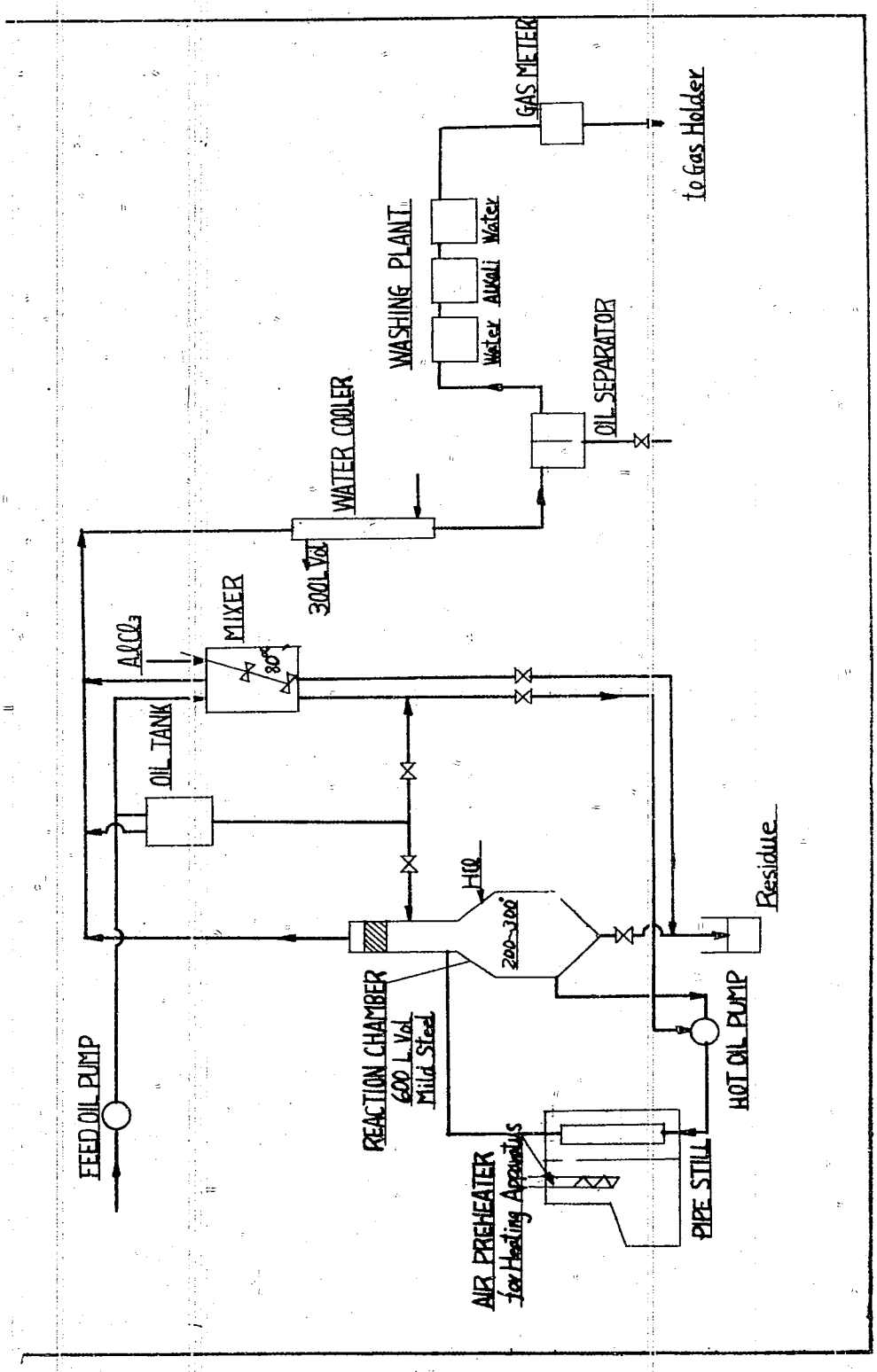
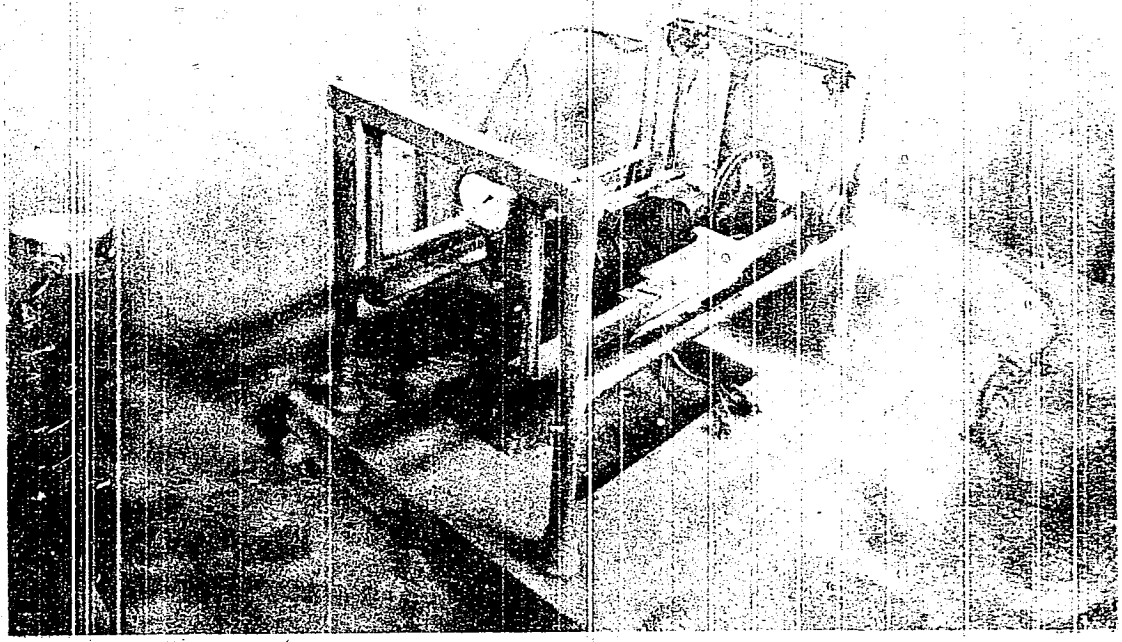


Figure 1(B)3
ISOBUTANE PILOT PLANT



ENCLOSURE (B)3

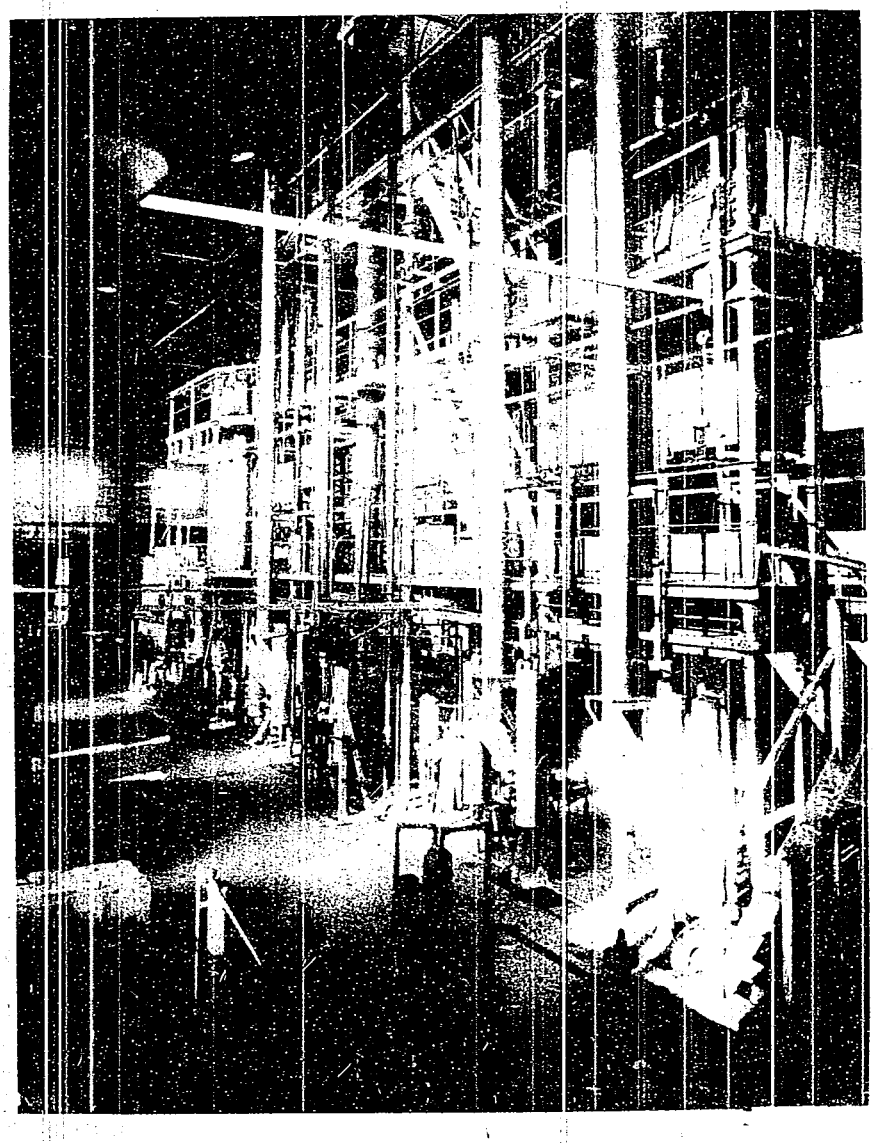


Figure 3(B)3
ISOMERIZATION PLANT OF n-BUTANE

ENCLOSURE (B) 4

S Y N T H E S I S O F I S O P A R A F F I N S

(In Two Parts)

by

Chem. Eng. Lieut.
(Lt. Comdr.) S. NISHINO

Prepared For and Reviewed With Author by the
U.S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)4

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ENCLOSURE (B)4

PART I

STUDIES ON THE SYNTHESIS OF ISOMERIC HEXANES

by

Chem. Eng.

Lieut. S. NISHINO

Research Period: 1940-1941

SUMMARY

Studies were made of the synthesis of isomeric hexanes, useful as a high octane rating aviation blending fuel, from pinacone, $(CH_3)_2$-C-(OH)-(OH)-C-$(CH_3)_2$, and pinacoline, $(CH_3)_3$-C-CO-CH_3, obtained by the electrolytic reduction of acetone.

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

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

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

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

Reaction temperature	330°C
Reaction time	½ hr
Amount of catalyst	8%
Yield	above 90%

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

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

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

3. When nickel oxide is used with diatomaceous earth or acid clay as catalyst carrier, the yield of hexanes is raised. Using the acid clay catalyst, 2.2-dimethylbutane is also formed as in the case of the molybdenum oxide catalyst. Though the mixed catalyst of molybdenum oxide and nickel oxide shows better yields than either alone, it is less effective than the copper-chromium oxide catalyst.

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

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

I. INTRODUCTION

A. HISTORY OF PROJECT

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

B. Maldvskii and T. Nizovkina obtained 65% yield of tetramethylethane from pinacoline with molybdenum sulphide catalyst at 340-350°C.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

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

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

II. DETAILED DESCRIPTION

A. DESCRIPTION OF TEST APPARATUS

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

B. TEST PROCEDURE

Conventional hydrogenation procedure was used.

C. EXPERIMENTAL RESULTS.

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

Food (B.P. 170-173°C. Mp. 35-38°C) ..... 120gm used
Catalyst (Cu-Cr-O) 10gm
Reaction temperature ..... 350°C
Reaction time ..... 1 hr
Initial hydrogen pressure ..... 100 atm
Upper layer of products 75gm
Properties of product:

d_4^{18} 0.6620

n_D^{15} 1.3765

Distillation data ..... Boiling range 47-59.5°C
Yield ..... 73gm from 75gm

d_4^{18} 0.6631

n_D^{15} 1.3770

Theoretical yield of isohexane 86%
Actual yield of isohexane 62%

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

Food 100gm
Catalyst (Cu-Cr-O) 10gm
Reaction temperature ..... 330°C
Reaction time ..... ½ hr
Initial pressure ..... 115 atm
Products
Upper layer 81gm
Lower layer 13gm
Physical properties of upper layer

d_4^{18} 0.6625

n_D^{15} 1.3755

Distillation data ..... 47-49°C; 79gm
Theoretical yield 93%
Actual yield 79%

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

III. CONCLUSIONS

Since pinacone is easily produced by electrolytic reduction of acetone which is readily obtainable as a by-product of the fermentation industry, 2.3. dimethylbutane will be easily produced by high pressure catalytic reduction of pinaccline which has been dehydrated by waste sulphuric acid from the electrolytic preparation of pinacone.

TABLE I(B)4

HYDROGENATION OF PINACELINE

		Catalyst components		
		Cu-Cr-O	NiO 1 Cu-Cr-O 2 diatomaceous earth 5	MoO 1 NiO 2 acid clay 2
Reaction temperature, (°C)		330-340	330-340	330-340
Space Velocity		1	1	1
Initial-hydrogen pressure atm.		100	100	100
Duration, (hr.)		48	112	80
Reaction rate. (%)		85	90	80
Hydrogen charge, (l/hr)		260	260	170
Waste gas, (l/hr)		150	150	90
Oil charged, (cc/hr)		197	195	196
Oil produced, (cc/hr)		202 (H_2O 1/5)	200 (H_2O 1/5)	198 (H_2O 1/5)
Distillation of upper layer		38-62°C 75% d_4^{18} 0.662 (55-60°C 82%) 62-73°C 10% 0.670 73-115°C 10% loss 5%	34-73°C 90% d_4^{18} 0.660 (unsaturated 5% 55-60°C 83%) 73-110°C 7% loss 3%	30-62°C 50% d_4^{18} 0.660 (47-57°C 27%) (57-60°C 45%) 62-75°C 10% 0.675 75-110°C 20%
Yield of tetramethylethane, %		82	83	45
Octane rating	mixture unleaded		94	
	0.05% Pb added		103	
	0.1% Pb added		110	

ENCLOSURE (B)4

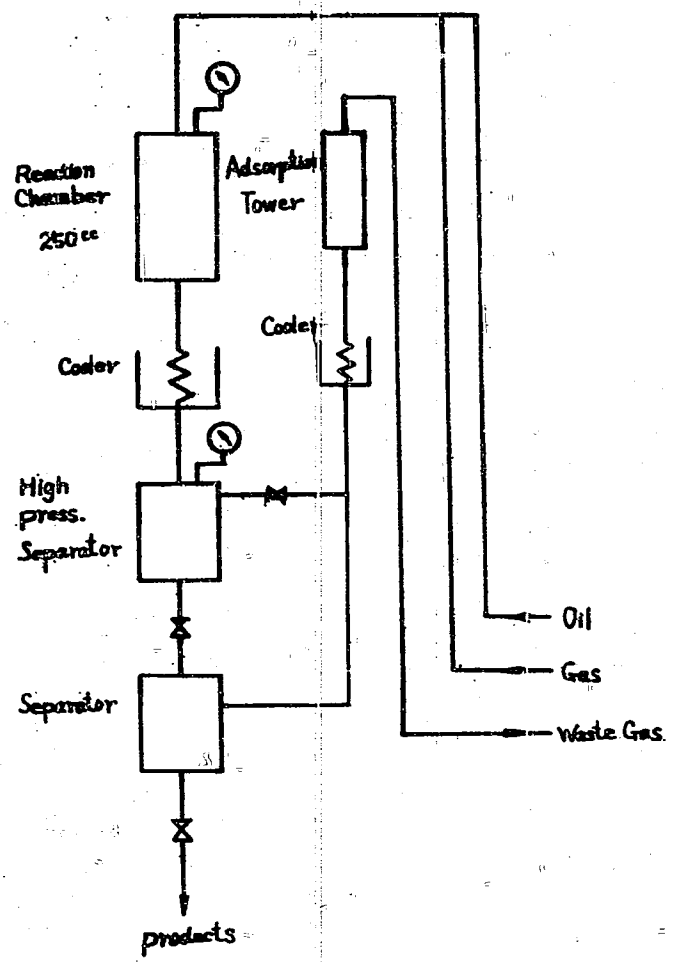

Figure 1(B)4

FLOW SHEET OF LABORATORY HIGH PRESSURE HYDROGENATING UNIT

ENCLOSURE (B)4

PART II

STUDIES ON THE SYNTHESIS OF ISODODECANE

by

Chem. Eng. Lt.
Comdr. S. NISHINO

Research Period: 1941-1942

SUMMARY

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

$$(CH_3)_3-C-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}H-C(CH_3)_3$$

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

Polymerization of 2.3-dimethylbutene (2) by sulphuric acid yielded 85% of another isodoecane, having a boiling range of 170-190°C, under the following conditions:

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

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

INTRODUCTION

A. HISTORY OF PROJECT

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

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT

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

ENCLOSURE (B)4

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

II. DETAILED DESCRIPTION

A. ISODODECANE BY THE CONDENSATION OF PINACOLINE

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

$$(CH_3)_3C-CO\cdot CH_3 \xrightarrow{Na} Na-\text{pinacoline}-\text{pinacolate} \longrightarrow \text{pinacoline}-$$

$$\text{pinacolone} \longrightarrow (CH_3)_3C\cdot CH_2\cdot CH_2\cdot \underset{CH_3}{CH}-C(CH_3)_3$$

Details of procedures were as follows:

a. 1 mol. of pinacoline and 1 mol. of sodium are heated in an autoclave with hydrogen at atmospheric pressure and at 100-110°C for 12 hrs.

b. The produced yellow solid, sodium-pinacoline-pinacolate, is dissolved in 2 volumes of ether and water is added slowly.

c. Pinacoline-pinacolate is separated from the upper layer, dried by Glauber's salt and dehydrated by anhydrous oxalic acid to remove hydroxyl radicals.

d. The product is hydrogenated using mixed copper-chromium oxide catalyst in an autoclave and is purified by distillation in a Podbielniak distillation apparatus.

2. Experimental results:

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

TABLE II(B)4

PHYSICAL AND CHEMICAL PROPERTIES OF INTERMEDIATES

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

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

Boiling range		178-182°C
Specific gravity d_4^{20}		0.7469
Refractive index n_D^{20}		1.4259
Freezing point		-110°C
Vapour pressure		0.009kg/cm²
Octane rating		98%
Elemental analysis	determined	calculated
C%	84.75	84.70
H%	15.18	1530

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

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

150gm. of 2.3.dimethylbutene-(2) (d_4^{20} = 0.7011 : n_D^{20} = 1.4113) are added slowly. The temperature is kept at 15°C and the mixture is stirred at the rate of 300 revolutions per minute.

2. Experimental results:

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

TABLE III(B)4

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

Conc. of H_2SO_4 (%)	Duration of stirring (min.)	Upper layer produced (gm)	Yield of dimer (%)
82	30	135	no reaction
85	15	140	90%
87	30	140	50%
92	15	141	70%
94	--	143	10%

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

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

ENCLOSURE (B)4

Specific gravity of product (d_{4}^{20})	0.7682
Refractive index of product (n_{D}^{20})	1.4325

Elemental analysis	determined	calculated
C%	84.69	84.70
H%	15.30	15.30

Distillation data of product

Boiling range	percent
170-175°C	5%
175-180°C	30%
180-185°C	35%
185-190°C	30%

Octane rating	
unleaded	93.1
lead added 0.1%	105.4
Vapour pressure	0.01kg/cm²
Flash point	54°C
Freezing point	below 80°C

C. RESULTS OF PERFORMANCE TEST OF ISODODECANE

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

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

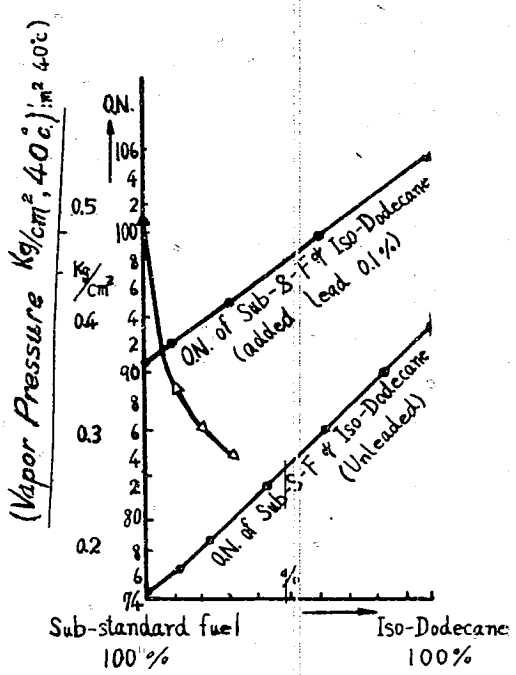

Figure 2(B)4

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

ENCLOSURE (B)4

III. CONCLUSIONS

A. Isododecane was synthesized and its physical properties were determined.

B. The prepared isodocane was considered to have good blending properties and to be of value as a safety fuel.

C. The mechanism of the polymerization of isohexene and the condensation of pinacoline were also studied.

ENCLOSURE (B) 5

I S O M E R I Z A T I O N O F n-H E X A N E

by

Eng. Lt. Comdr. H. HOSHIMIYA
and
Eng. Lt. Comdr. M. KATO

Research Period: 1942-1943

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

December 1945

ENCLOSURE (B)5

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Table II(B)5 Effect of Mo-Compounds in Isomerization of n-Hexane ..... Page 68

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Table V(B)5 Representative Results of Isomerization of n-Hexane ..... Page 70

ENCLOSURE (B)5

SUMMARY

As a fundamental work pertaining to the isomerization of gasoline, the isomerization of n-hexane was tried.

To obtain isomerizates containing 20% of isomeric paraffin hydrocarbons from n-hexane using Mo-compounds as the catalyst, high temperatures and pressures, such as 400°C and 200kg/cm2, are required.

Isomeric hexanes were obtained from n-hexane at 110°C in 16-18% yield and 62.5-64.5% selectivity using anyhydrous aluminium chloride catalyst which was regenerated by hydrogen chloride.

Some decomposition of product occurred and the yield of liquid per initial content of n-hexane was about 50%.

Hydrogen pressure was effective in suppressing the decomposition, and the results of some experiments under pressure are as shown in Table I(B)5.

TABLE I(B)5

Initial hydrogen pressure (atm.)	Reaction temperature (°C)	Yield of isomer (%)	Selectivity (%)
40	120	67.5	97.4
40	160	72.3	93.4

At temperatures above 200°C, decompositions occurred in spite of the application of hydrogen pressure.

I. INTRODUCTION

A. There are many reports on the isomerization of C5-C8 normal paraffin hydrocarbons. Aluminium chloride was reported to be the most effective isomerizing agent when compared with molybdenum trisulphide, zinc chloride, etc.

B. KEY RESEARCH PERSONNEL WORKING ON PROJECT:

Eng. Lt. Comdr. H. HOSHIMIYA and Eng. Lieut. M. KATO.

II. DETAILED DESCRIPTION

A. DESCRIPTION OF TEST APPARATUS

1. The Reaction Under Pressure

A shaking autoclave having a capacity of one litre was used.

2. Flow Method Under Atmospheric Pressure

A silica tube, 1,500mm in length, 20mm in diameter and slightly inclined, was placed in an electric furnace and from its upper side the raw materials were charged.

ENCLOSURE (B)5

TABLE II(B)5

EFFECT OF MO-COMPOUNDS IN ISOMERIZATION OF n-HEXANE

No.	Catalyst	Catalyst used (wt. raw material)	Reaction temp. (°C)	Pressure (kg/cm2)	Liq-yield (%)	Isomerizate (% raw material)	Octane rating C6-frct.
24	MCl	25	400	00	76.5	14.5	31.5
27	MS	7.5	300	15	80.0	3.2	30.8
33	MCl	25	400	30	76.7	9.2	31.1

Note: Raw Material - Octane rating C6-frct. of 33.2.
MCl - ammonium thiomolybdate on active charcoal.
MS - molybdenum trisulfide.

TABLE III(B)5

ISOMERIZATION WITH $AlCl_3$ AT ATMOSPHERIC PRESSURE

No.	$AlCl_3$ used, (wt. % of raw mat.)	HCl used, (wt. % of raw mat.)	Reaction temp., (°C)	Gas produced. (wt.%)	Yield of liquid, (wt. %)	Isomeric hexane, (%)	Selectivity of isomerization (%)	Octane rating
Raw material								33.2
71	25	63	85	20.5	66.0	7.8	38.0	40.4
72	25	88	85	25.0	69.0	8.2	31.0	
73	25	86	90	34.0	60.0	10.4	46.0	
74	25	105	90	30.0	61.5	10.8	48.5	
75	25	93	95	24.0	56.0			49.5
76	25	75	95	23.0	62.5	10.4	33.3	
77	25	73	95	28.0	56.0	7.0	42.9	
78	25	75	100	28.5	56.0	8.9	33.3	
79	25	75	100	30.0	57.5	8.8	40.5	
80	25	73	105	32.0	54.0	11.2	54.8	42.3
81	25	95	105	33.5	50.5	10.9	60.0	
82	25	72	110	29.5	57.5	18.6	64.5	
83	25	72	110	38.0	48.0	15.7	62.5	
84	25	63	115	40.0	46.0	17.7	69.2	
85	25	73	115	37.0	48.0	13.1	44.1	
86	25	55	120	38.0	48.0	12.7	54.3	
87	25	65	120	37.5	48.0	12.2	63.2	

TABLE IV(B)5

ISOMERIZATION WITH $AlCl_3$ UNDER PRESSURE

No.	$AlCl_3$ used, (wt. % of raw mat.)	Reaction temp. (°C)	Duration (hr)	H_2 initial pressure (atm.)	Yield of liquid, (wt. %)	Yield of iso-C_6 (%)	n-C_6 reacted (%)	Selectivity of isom. (%)	Composition of products				
									C_4 and below	C_5	i-C_6	n-C_6	C_7 and higher
91	10	120	6	00	80	12.8	50	32.0	12	14	16	48	8
92	10	120	6	20	61	18.3	80	37.5	11	27	30	18	12
93	10	120	6	40	72	33.8	91	51.6	8	30	47	7	6
94	10	120	6	60	88	59.8	69	98.5	1	0	68	29	0
95	10	80	6	40	93	44.6	56	85.7	1	6	48	32	1
96	10	160	6	40	83	59.0	77	92.3	1	4	71	14	1
97	10	200	6	40	60	24.6	88	46.5	13	23	41	10	11
98	10	120	3	40	87	52.2	80	75.0	8	9	60	17	3
99	10	120	9	40	90	67.5	77	87.4	0	2	75	18	0
100	10	200	3	40	49								
101	0	200	9	40	60	30.6	91	56.1	13	25	51	6	2
102		160	6	40	85	72.3	91	93.4	4	2	85	4	0

$$\text{Selectivity} = \frac{\text{i-C6 Produced}}{\text{n-C6 Reacted}} \times 100$$

ENCLOSURE (B)5

ENCLOSURE (B)5

TABLE V(B)5

REPRESENTATIVE RESULTS OF ISOMERIZATION OF n-HEXANE

	Number		
	78	95	99
Pressure (atms.)	1	40	40
Reaction temperature (°C)	100	80	120
Yield of liquid (%)	56	93	90
C_4 and lower (%)	12	1	0
C_5 (%)	15	6	2
2.2-Dimethylbutane (%)	0	7	0
2.3-Dimethylbutane (%)	5	18	12
2-Methylpentane (%)	2	6	15
3-Methylpentane (%)	8	27	48
Total i-Hexane (%)	15	58	75
n-Hexane (%)	52	32	18
C_7 and higher (%)	3	1	0

B. TEST PROCEDURES

1. Method Under Pressure

n-Hexane and catalysts were charged and air was replaced by hydrogen chloride or hydrogen. They were then heated under the given conditions.

2. Flow Method

Catalysts were placed in the reaction tube and heated by means of an electric furnace. As soon as the reaction tube reached the desired temperature, n-hexane was introduced at the rate of 1 cc/min. The products were withdrawn from the lower side of the tube.

3. Analysis of the Products

To determine the amount of isomeric paraffin hydrocarbons, the precise fractional distillation was adopted using the standard Podbielniak apparatus.

C. EXPERIMENTAL RESULTS

1. Isomerization in the Presence of Mo-compounds

The results shown in Table II(B)5 indicate that Mo-compounds were of little effect since the octane ratings of the products were not increased in spite of the fact that fractional distillation data show that some branched isomers were produced. The lowering of the octane rating of product could be caused by the formation of higher hydrocarbons.

2. Isomerization With $AlCl_3$ at Atmospheric Pressure

As shown in Table III(B)5, n-hexane was isomerized to isomeric hexanes with yields of 7-18%, and the octane rating increased from 7-16 numbers. However, the liquid yield was low, since decomposition accompanied the reaction.

3. Isomerization With $AlCl_3$ Under Pressure

As shown in Table IV(B)5, hydrogen pressure was necessary not only to suppress the decomposition but to promote isomerization.

Some representative results are tabulated in Table V(B)5.

III. CONCLUSIONS

A. The best conditions for the isomerization of n-hexane were as follows:

Catalyst	$AlCl_3$ and HCl
Hydrogen pressure	about 50 atms
Reaction temperature	120-140°C
Amount of catalyst	10% by weight based on raw material
Duration of reaction	3-5 hrs

B. Under the above conditions the results are as follows:

Yield of isomeric hexanes	60-70%
Selectivity of isomerization	93-97%

ENCLOSURE (B)5

C. Because of the mild conditions and plentiful supply of catalyst, the use of aluminum chloride in the isomerization of low grade paraffine gasoline offers promise for commercial application. However, additional experimentation is required.

ENCLOSURE (B) 6

STUDIES ON THE ISOMERIZATION OF n-BUTANE

by

CHEM. ENG. LT. CCMDR. H. HOSHIMIYA

Research Period: 1940-1944

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

December 1945

ENCLOSURE (B)6

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Table II(B)6 Effect of Reaction Temperature ..... Page 76

Table III(B)6 Catalyst Life without HCL ..... Page 77

Table IV(B)6 Catalyst Life with Addition of HCL ..... Page 77

Figure 1(B)6 Isomerization Plant of Gasoline ..... Page 79

Plate I(B)6 Flow Sheet of Reaction Section n-Butane Isomerization Pilot Plant

ENCLOSURE (B)6

SUMMARY

Normal butane was isomerized in liquid phase, using $AlCl_3$ catalyst and HCl as a promoter, and a maximum yield of 66% isobutane was obtained. Best conditions for the reaction were as follows:

Contact time	2 hrs
Amount of $AlCl_3$	118 wt%
Amount of HCl	25 wt%
Temperature	110°C
Pressure	15-20 kg/cm^2
Support	Japan acid clay

I. INTRODUCTION

Isomerization of n-butane to isobutane with aluminum chloride catalyst has been well known since 1937. In 1940 it was desired to investigate the production of isobutane from the normal butane contained in refinery waste gases.

Laboratory work on this subject was carried on from Sept., 1940 to April, 1941, and pilot plant work from Dec., 1942 to March, 1944. The laboratory test results checked those reported in the literature and are reported herewith. (Ind. Eng. Chem., vol. 26, 461 (1936); Rec. d. Trav. Chem., vol. 59, 793 (1940) etc.)

Although a pilot plant was considered in 1941, it was not constructed until after the author had inspected the Nederlandsche Kolonial Petroleum Maastchappii unit at PALEMBANG in the autumn of 1942. Reports of pilot plant tests were all destroyed, but it is recalled that the results were practically identical with the laboratory tests, except for HCl corrosion, especially in the hydrogen chloride gas compressor.

A. Laboratory tests

The laboratory tests were carried out in a horizontal shaking steel autoclave of 600cc total volume. This apparatus was equipped with external electric heaters and a thermocouple in the center of the hollow shaft extending through the autoclave.

Anhydrous $AlCl_3$ was first charged to the autoclave, then normal butane, cooled by dry ice-alcohol solution, and finally crystals of HCl produced by cooling with liquid air. The autoclave was closed, and brought up to the desired temperature. After the desired reaction time, gas was released to a gas meter. The gas was analyzed by Podbielniak and Hempel methods. Experimental data secured are summarized in the following tables.

Table I(B)6 shows effect of reaction time on yield. In this table the rate of isomerization is defined as the yield of i-butane as wt% of n-butane charged. Selectivity is defined as the wt% of the normal butane which is converted. (i.e. n-butane charged less n-butane unconverted). It is concluded from these data that the required reaction time is 90 minutes or over.

Table II(B)6 shows the effect of reaction temperature. It is concluded that the optimum temperature range is 110-115°C.

Tables III(B)6 and IV(B)6 show the effect of HCl addition on life of the $AlCl_3$ catalyst. In Table III(B)6 catalyst life in absence of HCl is

ENCLOSURE (B)6

Table I(B)6

EFFECT OF REACTION TIME

Test No.	Time (min)	Temp. °C (max)	Press. (kg/cm²) max	Produced gas (l)	Gas Analysis (% by Volume)					Degree of Isomerization (%)	Selectivity (%)
					H_2-C_2H_6	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
101	30'	110(110)	14.7	33.2	5.3	20.6	22.3	5.7	46.1	23.8	45.7
102	60'	110(110)	16.5	32.8	5.8	17.9	34.0	1.6	35.7	33.5	64.0
15	90'	110(112)	17.3	36.6		17.6	60.6		21.8	62.7	81.0
16-1	120'	110(111)	16.2	39.0		23.8	59.3		17.4	65.7	81.5
14	180'	110(110)	16.5	35.7		16.0	60.5		23.5	61.0	80.2
9	240'	110(110)	16.0	35.0		10.9	65.6		23.4	65.2	87.2

Conditions

n-C_4H_{10} ..... 150cc (89.4% purity)
$AlCl_3$ ..... 100 gm
HCl ..... 2.5 gm (crystal state)

Table II(B)6

EFFECT OF REACTION TEMPERATURE

Test No.	Reaction Temp. °C	Press. kg/cm²(max)	Produced gas (l)	Gas Analysis (% by Volume)					Degree of Isomerization (%)	Selectivity (%)
				H_2-C_2H_6	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
120	105(103)	10.2	34.6		15.4	30.2	4.0	50.6	34.3	37.0
16-1	110(111)	16.2	39.0		23.8	59.3	0	17.4	65.7	81.5
121	115(117)	17.2	35.2		19.6	51.1	2	26.8	59.5	86.4
124	130(13[illegible])	15.5	35.5		57.5	10.5		32.5	10.1	15.5

Conditions

n-C_4H_{10} ..... 150cc (84.4% purity)
$AlCl_3$ ..... 100 gm
HCl ..... 2.5 gm (crystal state)
Reaction time ..... 120 min

ENCLOSURE (B)6

Table III(B)6

CATALYST LIFE WITHOUT HCl

Test No.	Time of Using same catalyst (hrs)	Pressure (kg/cm^2) max	Produced gas (l)	Gas Analysis (% by Volume)					Degree of Isomerization	Selectivity
				$C_2H_6-H_2$	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
18-1	0	12.9	35.5	1.9	14.3	43.5		40.3	45.6	88.8
18-2	4	11.6	33.0	2.4	13.9	42.7	3.6	37.4	44.7	73.5
18-4	6	12.3	36.0	0	29.5	23.5		47.0	34.2	93.3
18-6	10	12.5	35.5	3.0	26.7	19.5	2.3	48.5	44.5	98.8
18-16	30	7.8	36.5	3.0	8.1	4.8	3.2	81.0	5.0	87.4
18-20	38	7.5	35.0	2.0	3.0	8.8	5.8	80.4	10.8	100

Conditions

$n-C_4H_{10}$ ..... 150cc (89.4% purity)
$AlCl_3$ ..... 100 gm
HCl ..... not used
Reaction time ..... 120 min
Reaction temp. ..... 110°C

Table IV(B)6

CATALYST LIFE WITH ADDITION OF HCl

Test No.	Time of Using same Catalyst (hrs)	Pressure (kg/cm^2) max	Produced gas (l)	Gas Analysis (% by Volume)					Rate of Isomerization	Selectivity
				$H_2-C_2H_6$	C_3H_8	i-C_4H_{10}	C_4H_8	n-C_4H_{10}		
17-1	0	15.8	31.3		11.4	66.1		22.3	58.4	71.5
17-2	2	14.5	34.3		13.5	63.5		23.2	61.4	79.2
17-3	4	14.3	31.8		16.9	59.0		24.1	51.8	66.3
17-4	6	14.3	37.2		11.2	53.3		35.5	56.4	89.1
17-6	8	15.1	34.8		16.5	55.0		28.5	54.5	75.7
17-8	10	15.0	33.8		19.2	47.0		33.7	45.0	66.2
17-12	14	12.5	34.1		13.1	44.2		42.7	45.0	79.2
17-16	18	14.5	32.2		16.9	44.8	4.7	53.5	43.3	68.0
17-22	22	14.2	31.3		9.3	44.7		46.0	39.9	58.3
17-25	28	12.3	34.5		13.3	43.5		43.3	42.8	73.2
17-29	42	12.1	33.5		25.6	39.3	3.3	31.8	43.5	72.6
17-36	48	13.5	34.3		18.7	39.1	3.2	39.0	44.2	71.8
17-40	56	14.5	34.6		23.4	34.2	3.2	39.2	38.7	69.2

Conditions

Same as Table III(B)6 with 2.5 gm HCl added

seen to decline rapidly after 10 hours. In Table IV(B)6, with all conditions the same except for addition of 2.5 g m of HCl every two hours, the catalyst life exceeds 56 hours.

B. Pilot plant tests. See Figure 1(B)6.

A flow sheet of the reaction section of the pilot plant constructed to investigate isomerization of n-butane and also the processing of spent butanes from the alkylation pilot plant at CFUNA, is given by Plate I(B)6 Spent hydrocarbon gases from the alkylation pilot unit were compressed, liquefied and pumped into the gas separation unit, where pentane and heavier propanes and isobutane fractions were removed.

The normal butane was washed with 98% sulphuric acid to remove water and sent together with HCl gas into the reaction chambers, filled with anhydrous aluminum chloride supported on acid clay or bauxite and heated to about 110°C.

Since 1942 only three complete tests were made on this unit and all data were destroyed. The important problems in operating this plant were as follows:

1. Dehydration of HCl was necessary to prevent corrosion. Drying of the HCl gas was very difficult. Washing with 98% H_2SO_4 and passing through layers of $AlCl_3$ crystals or Zn-metal was not satisfactory and corrosion of cast iron and other metals in the compressor piston, piston rings, etc. was severe. Also there was difficulty with stuck valves due to sludge deposition. It was also necessary completely to remove Cl_2 from HCl to prevent an explosion with excess H_2 in the compressor. The purification of hydrochloric acid was finally accomplished by washing the HCl gas with a saturated solution of stannous chloride.

2. The life of the catalyst was five days. In order to reduce the consumption of $AlCl_3$, the recovery of the catalyst would be necessary in a large scale plant. This was not done on a pilot plant scale.

II. CONCLUSIONS

It was concluded from these experiments that the liquid phase isomerization of n-butane was practical for a larger scale application. Pilot plant difficulties were mainly centered on corrosion in the HCl compression and handling system. To the writer's knowledge, no commercial application has been made of this process in Japan.

ENCLOSURE (B)6

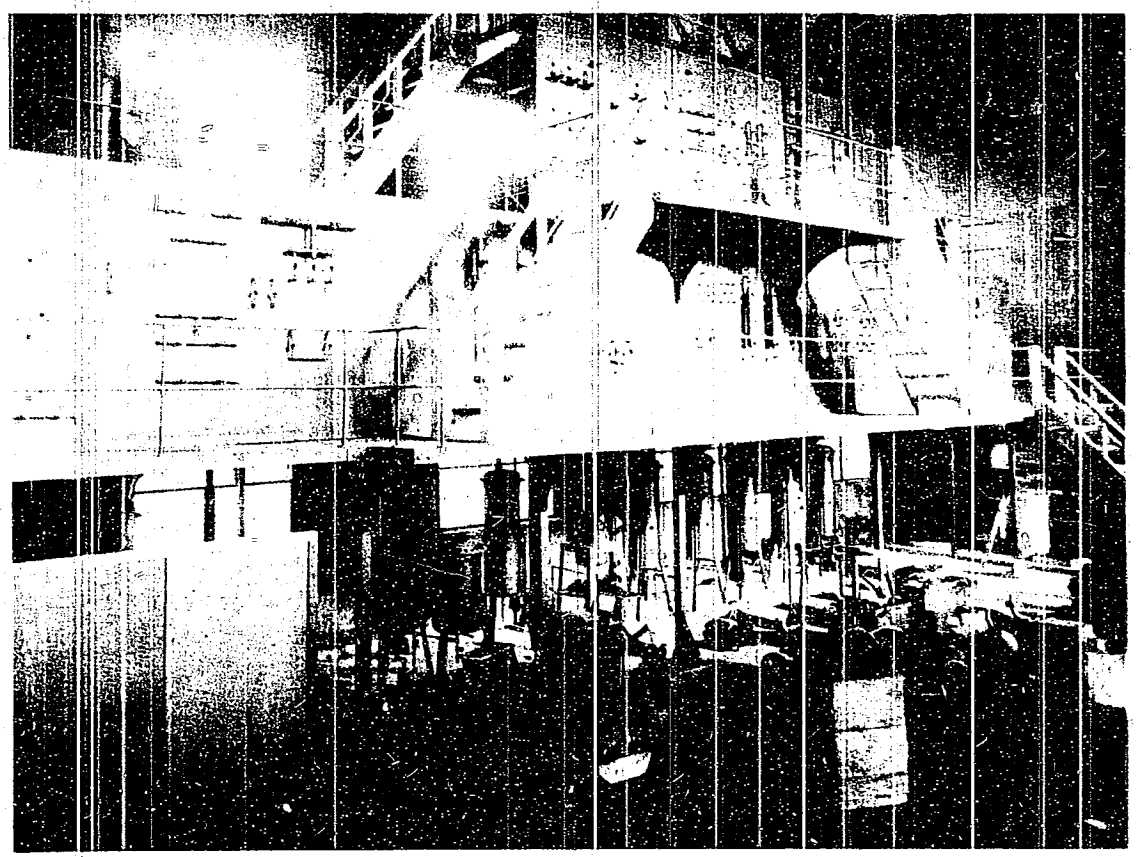
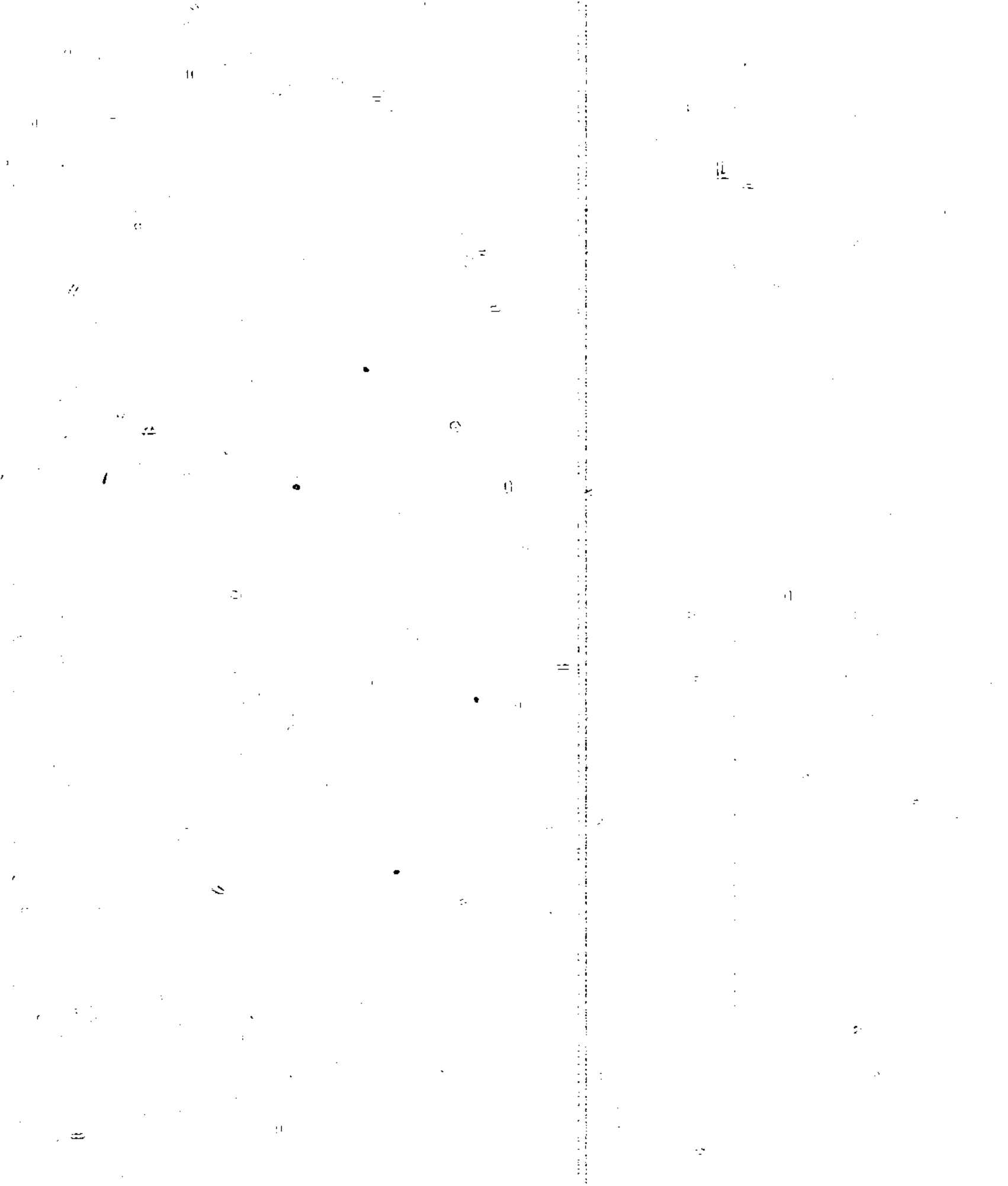
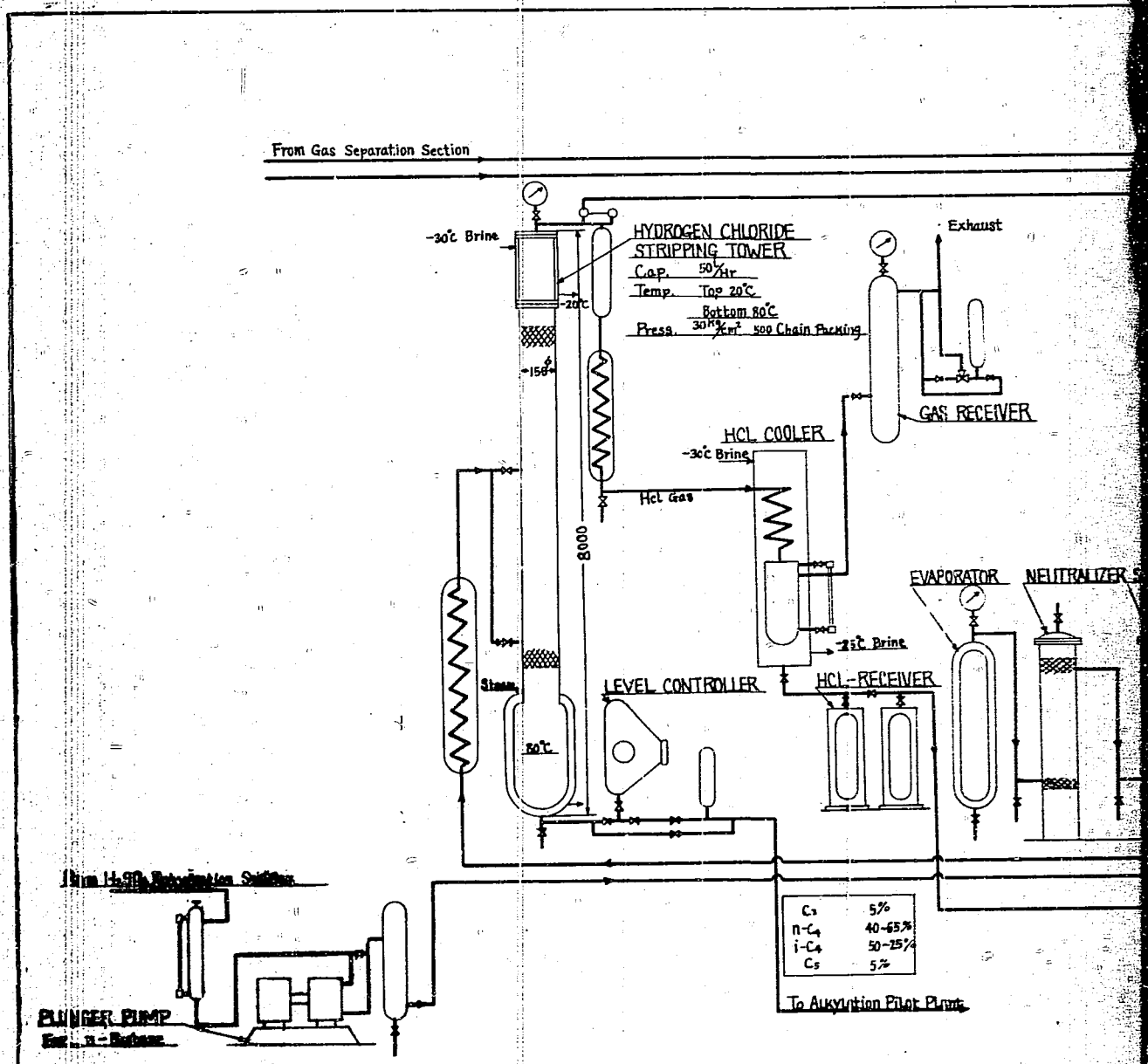
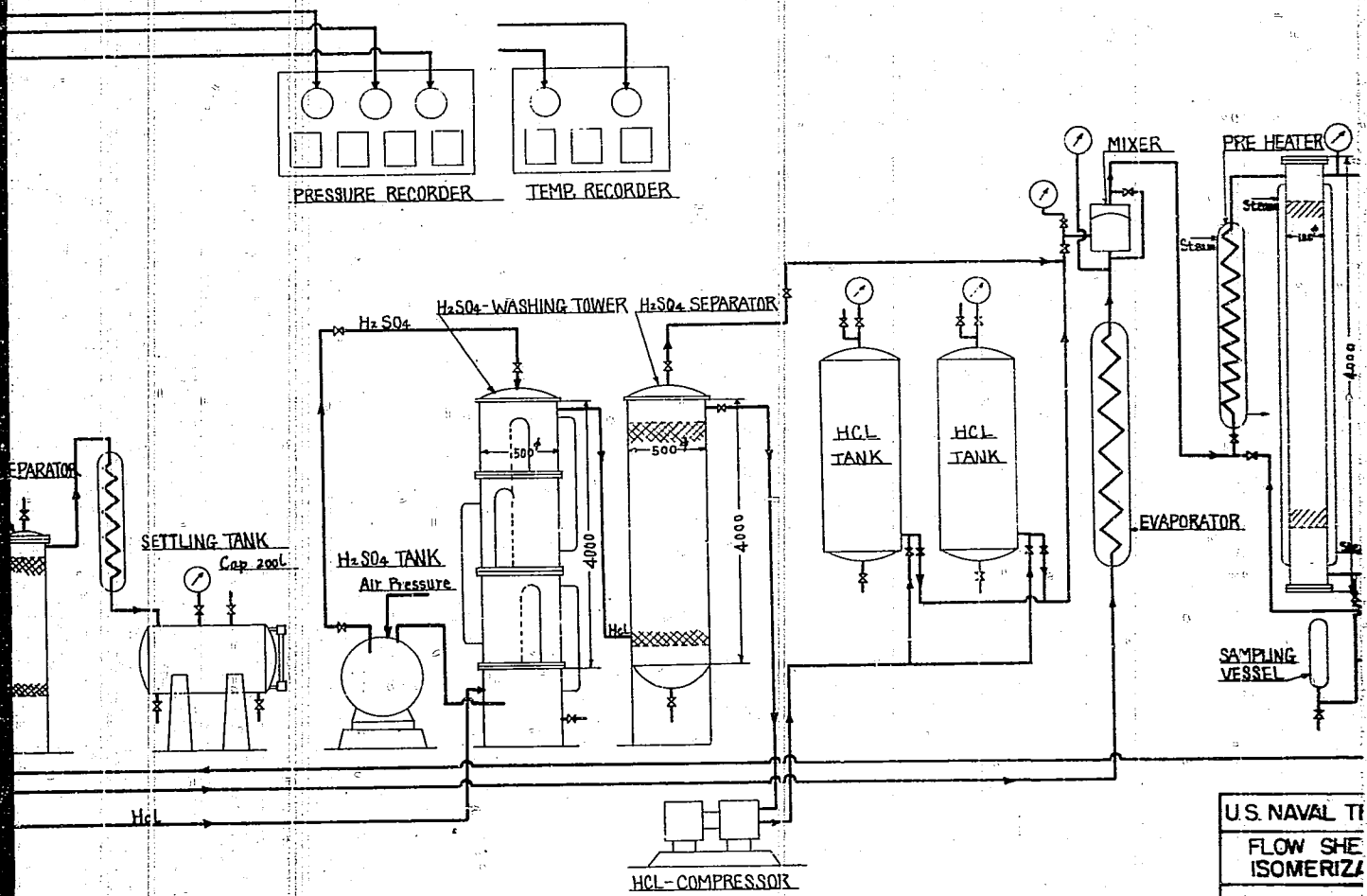


Figure 1(B)6
ISOMERIZATION PLANT OF GASOLINE




From Gas Separation Section
-30°C Brine
HYDROGEN CHLORIDE STRIPPING TOWER
Cap. 50%/Hr
Temp. Top 20°C
Bottom 80°C
Press. 30kg/cm² 500 Chain Packing
-20°C
Exhaust
GAS RECEIVER
HCL COOLER
-30°C Brine
Hcl Gas
8000
EVAPORATOR
NEUTRALIZER
-25°C Brine
Steam
80°C
LEVEL CONTROLLER
HCL-RECEIVER
C₃ 5%
n-C₄ 40-65%
i-C₄ 50-25%
C₅ 5%
To Alkylation Pilot Plant
PLUNGER PUMP



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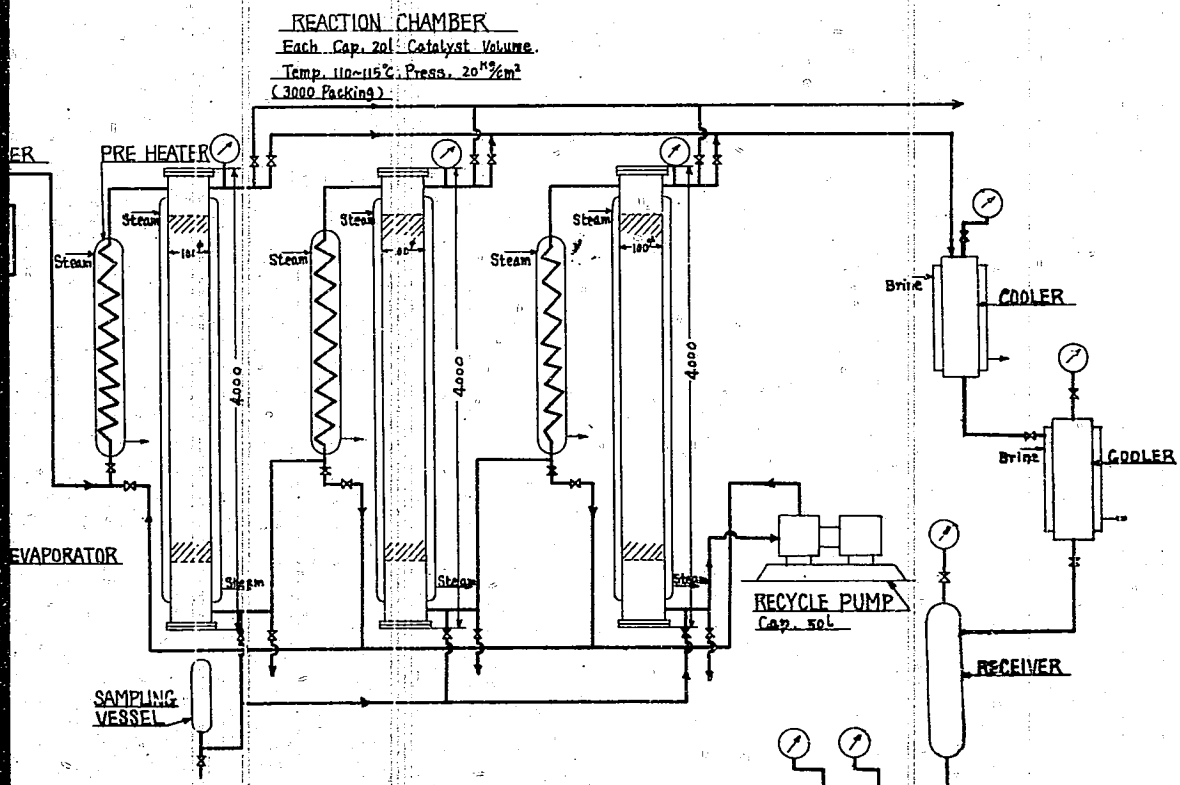

U.S. NAVAL TECHNICAL MISSION TO JAPAN	RESTRICTED
FLOW SHEET OF REACTION SECTION N-BUTANE ISOMERIZATION PILOT PLANT	
22 DEC. 45	PLATE I(B) 6 X-38(N)-2

ENCLOSURE (B) 7

STUDIES ON MATERIALS RESISTANT TO CHLORINE COMPOUNDS

by

Chem. Eng. Lieut. H. KAMOGAWA

Research Period: 1944-1945

Prepared for and Reviewed With Author by the
U.S. Naval Technical Mission to Japan.

December, 1945

ENCLOSURE (B)7

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ENCLOSURE (B)7

SUMMARY

Studies were made with object described below:

1. To make clear the influence of water vapor on the corrosion of cast iron by HCl gas, and to find the necessary drying limit to prevent corrosion.

2. To find suitable materials for an HCl gas compressor and a liquid HCl vessel by testing the corrosion losses of some kinds of metals under those conditions.

3. To find a suitable material for the reaction vessel in the dichlor-ethane formation.

Results obtained were as follows:

1. Influence of water vapor content on corrosive properties of HCl gas.

   a. It is quite difficult to dry the HCl gas sufficiently to prevent the corrosion of a gas compressor made with cast iron.

   b. The gas dried through sulphuric acid towers is not sufficiently dry to prevent the corrosion of cast iron.

   c. Connecting an aluminum chloride tower has a considerable drying effect but is not completely satisfactory.

   d. Connecting metal towers such as iron or zinc in the drying train shows a large effect but is still not sufficient to keep the compressor in operation.

   e. It is not satisfactory to use cast iron as the compressor material.

2. Materials for HCl gas compressor and liquid HCl vessel.

   a. A steel bomb is suitable for the liquid HCl vessel.

   b. Silver based alloys, such as Ag-Sn, Ag-Sb, are suitable for the valve materials of the liquid HCl bomb.

   c. No entirely satisfactory material was found for the HCl gas compressor, but silver, nickel, copper and 18-8-2 chrome-nickel-molybdenum steel showed better results than cast iron.

3. Material for dichlor-ethane reaction vessel.

   a. Lead is the most suitable material for the reaction vessel.

   b. The purer the lead the better the results obtained.

   c. Silver-lined iron is the best for the lid of reaction vessel which has no contact with catalytic solution but which does contact the reaction gases.

ENCLOSURE (B)7

I. INTRODUCTION

It would be very convenient for both inorganic and organic industries, if liquid HCl manufacture reaches an industrial scale. It would decrease the neccessity of synthetic HCl installations even when HCl gas is needed in the reaction.

On this account, we tried formerly in this institute to operate an HCl gas compressor but because of the sticking of valves it was inevitably stopped within a few hours. The materials of the compressor used in the former experiment were:

Cylinder liners	semi-steel cast iron
Piston rings	cast iron
Lubricant	liquid paraffin

The HCl gas was made by the synthetic process and dried through two sulphuric acid towers filled with Raschig rings, and a tower filled with zinc granules. The zinc tower was afterwards replaced by an annydrous aluminum chloride tower by the author.

For this report, the influence of the water vapor in HCl gas on the corrosion of cast iron was tested to see whether cast iron is useful as the compressor material. Corrosion tests of metals in HCl gas were made to find a suitable material for the HCl gas compressor. Studies were also made on the liquid HCl vessel.

In the dichlor-ethane formation, using such corrosive reagents as ferric chloride and water as the catalyst, hydrogen chloride, alcohol and dichlor-ethane as the reacting agents, and chlorine as the reactivator of the catalyst, the reaction proceeds at 130°C. It is difficult to find materials for the reaction vessel resistant to corrosion under such severe conditions. Even using such metals as Ta, Pt, W and other special alloys considered to be resistive to Cl-compounds it is questionable whether they are sufficiently resistant under these severe conditions. These metals also have disadvantages which condemn their practical use; i.e., some are too expensive, others cannot be worked easily. Non-metals such as stoneware are too fragile. Rubber lined iron vessels have no resistance under these conditions.

For these reasons, homogeneous lead linings have been in use up to this time for the vessels, but their resistance is not satisfactory.

For this report, some kinds of metals and alloys which are considered to have comparatively good resistance to hydrogen chloride were tested as to whether they are suitable as materials for the reaction vessel in the dichlor-ethane formation. The influence of minor constituents in lead were also tested.

These studies were started in May, 1944 and were in progress when the war ended.

II. DETAILED DESCRIPTION

A. Corrosion of Metals by Wet HCl Gas - Statically.

1. Description of apparatus.

The corrosion vessel shown in Fig. 1(B)7 contains in the bottom 35 or 40% hydrochloric acid, and above it test pieces were placed in contact with the acid vapor. The humidities of the hydrochloric acid vapors are shown in Table I(B)7.

ENCLOSURE (B)7

Table I(B)7

HUMIDITIES OF HYDROCHLORIC ACID VAPORS

Acid (%)	Temp. (°C)	Partial V.P. (mm Hg)		Humidity (%)
		H_2O	HCl	
40	20	2.00	399	0.50
	35	2.88	515	0.56
	30	4.09	627	0.65
35	20	3.42	75.0	4.4
	25	4.88	100	4.7
	30	6.70	130	4.9

2. Test procedure.

a. The influence of surface condition on the corrosion of cast iron was tested.

b. The influence of time on the corrosion of cast iron was tested.

c. The corrosion resistance of some kinds of metals and alloys were compared. Constituents of metals and alloys used in the tests are as shown below.

Table II(B)7

COMPOSITION OF IRON AND STEEL USED IN CORROSION TEST

	T.C.	Si	Mn	S	P
Cast iron	3.90	2.12	1.68	0.09	0.35
Steel	0.20	0.05	0.56	0.04	0.04

Table III(B)7

COMPOSITION OF METALS AND ALLOYS USED IN CORROSION TEST

Silver ..... chemical pure silver
Copper ..... electrolytic copper
Nickel ..... electrolytic nickel
Ag-Cu(1) ..... Ag 95; Cu 5
Ag-Cu(2) ..... Ag 72; Cu 28
Ag-Sb ..... Ag 96.8; Sb 3.2
Ag-Sn ..... Ag 89; Sn 10.3
Brass ..... Cu 64.0; Zn 36.4
Bronze ..... Cu 85.7; Sn 10.3; Zn 4.0
Cu-Ni ..... Cu 75; Ni 25
Constantan ..... Cu 58.5; Ni 40; Fe 1; Mn 0.5
18-8 steel ..... Cr 16.33; Ni 7.52
18-8-2Mo steel ..... Cr 18; Ni 8; Mo 2.3
13 Cr steel ..... Cr 11.95; C 0.05

The dimensions of the test pieces are as follows:

Metals other than silver and silver based alloys: 20x50mm
Silver and its alloys: 1x20x50mm

ENCLOSURE (B)7

3. Experimental results.

The experimental results are recorded in Tables IV(B)7, V(B)7, and VI(B)7.

4. Discussion.

It is clear from Table IV(B)7 that corrosion is largely dependent on the surface condition. Corrosion is great when the surface is uneven and decreases with the surface smoothness.

Observing the corrosion of cast iron, it was observed that iron chloride is formed on the surface as the corrosion proceeds, and by its hygroscopic nature it absorbs the humidity in HCl gas so that the surface of the test piece is covered with a saturated iron chloride solution. This markedly decreases the corrosion of the test piece as with time. Discussion of the corrosion of metals and alloys in wet static HCl gas are included in Enclosure (B)4.

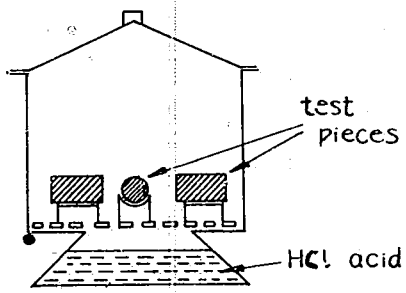

Figure 1(B)7

CORROSION VESSEL, STATIC TYPE

Table IV(B)7

DIFFERENCES DUE TO THE SURFACE CONDITION OF TEST PIECE
(test piece cast iron, liquid phase 35%HCl, room temp, 25°C)

Surface conditions	Time (min)	Corrosion loss		
		mg/dm^2	mg/dm^2day	Average (mg/dm^2day)
Polished	210	102 99	699 679	689
Wiped off the corrosion product of test piece	210	67 59	459 405	432
Wiped off the corrosion product of test piece once more	210	65 57	446 390	418

ENCLOSURE (B)7

Table V(B)7

DIFFERENCE DUE TO THE TIME OF EXPOSURE
(test piece cast iron, liquid phase 35%HCl, room temp. 25°C)

Surface condition	Time (min.)	Corrosion loss		
		mg/dm^2	mg/dm^{2}day	Average (mg/dm^{2}day)
Polished	60	38 33	919 799	859
Wiped off the corrosion product of test piece	60	29 25	696 596	646
Wiped off the corrosion product of test piece once more	900	148 135	237 216	227

Table VI(B)7

CORROSION OF METALS AND ALLOYS IN HYDROCHLORIC ACID VAPOR

Test piece	Conc. of HCl in liquid phase (%)	Temp. (°C)	Time (hr)	Surface Condition	Corrosion loss	
					mg/dm^2	mg/dm^{2}day
Silver	45	5	15x24	polished	334	22
Ag-Cu(1)	40 35	25-29	24	Wiped off the corrosion produced on the test piece after testing in presence of dry and wet HCl gas (Table 10)	- 28 - 31	-- 28 -- 31
Ag-Cu(2)	40 35				- 23 70	-- 23 70
Ag-Sb	40 35				- 4.5 - 34	-- 4.5 -- 34
Ag-Sn	40 35				26 - 7.8	26 -- 7.8
Copper	40 35				- 51 847	-- 51 847
Steel	40 35		48		194 194	97 97
Cast Iron	40 35				780 367	390 184
18-8 Steel	40 35		48 24		548 433	274 433
18-8-2Mo Steel	40 35		48 24		259 356	130 356
Bronze	35	20-25	48		3080	1540
Nickel	35				148	74
Cu-Ni	35				4630	2315
Constantan	35		24		2340	2340
13 Cr Steel	35				583	583

(- means increase in weight after corrosion)

ENCLOSURE (B)7

B. Corrosion of Metals by Dry and Wet HCl Gas - Dynamically.

1. Description of apparatus.

The apparatus is shown in Fig. 2(B)7.

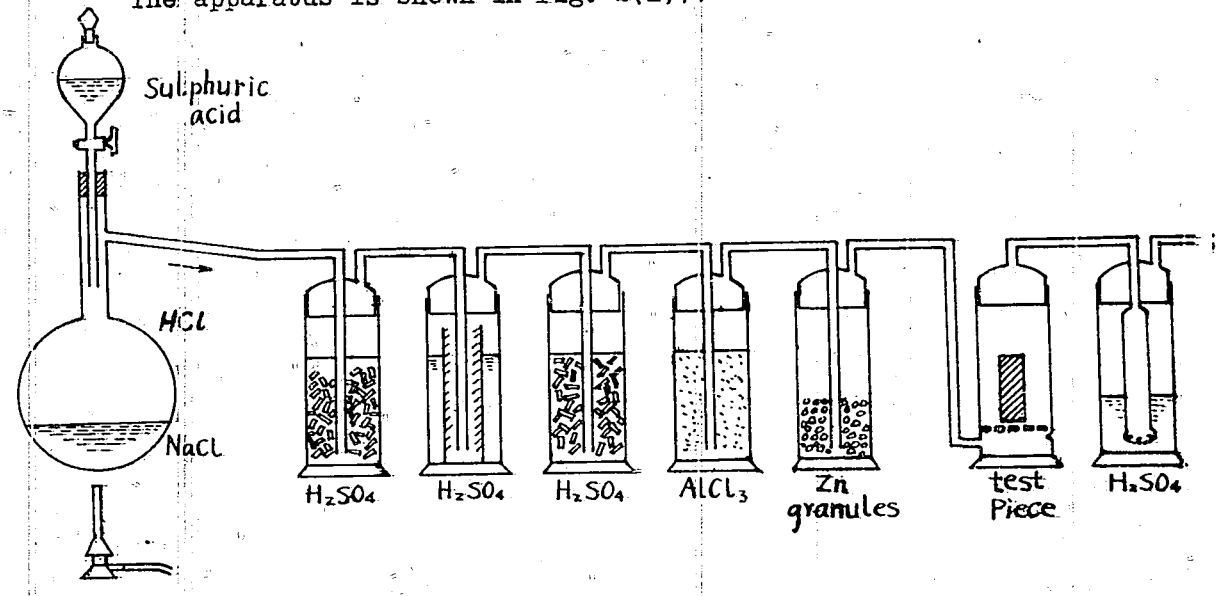

Figure 2(B)7

CORROSION TEST, DYNAMIC

HCl gas was generated by Le Blanc's method and the concentration of sulphuric acid used was 85%.

Three sulphuric acid towers were used to dry the gas. The first and the third tower contained 200cc and the second tower contained 300cc of acid. The 1st and the 3rd towers were filled with Rashig's rings, and the 2nd tower was an Ichinose washing bottle by which the velocity of the gas was controlled. The depth of liquid in each tower was about 10cm.

The aluminum chloride tower was filled with anhydrous aluminum chloride, and the layer of drying agent was about 10cm. The zinc tower contained about 35g of zinc granules and its thickness was about 5cm. The tests were made at room temperature and the velocity of HCl flow was about 200 cc/min.

2. Test procedure.

Tests are made under 3 conditions.

a. Varying the drying method for HCl gas, the corrosion of cast iron was tested. (See Table XII(B)7)

b. Drying the gas with three sulphuric acid towers, the corrosion of metals and alloys were tested.

c. After drying with sulphuric acid, the gas was introduced into the corrosion vessel which contained saturated (nearly 45%) HCl acid in the bottom (Fig. 3(B)7), and the corrosion of metals and alloys was tested. For this case the humidity in the gas is about 0.04%.

ENCLOSURE (B)7

The constituents of metals and alloys used in these tests are shown in Tables II(B)7, and III(B)7.

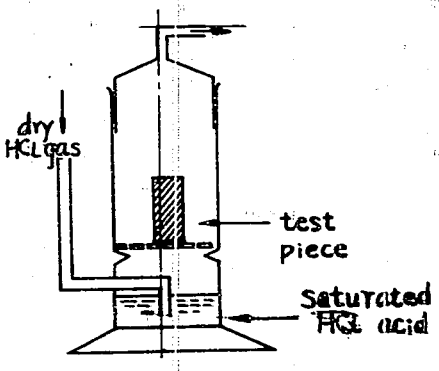

Figure 3(B)7
CORROSION VESSEL

3. Experimental results.

The experimental results are recorded in Tables 8, 9, and 10.

Table VII(B)7

METHODS OF DRYING HCL GAS

No.	Drying Method			
1	is not dried			
2	is dried through	three	85%	sulphuric acid towers
3			98%	
4			85%	sulphuric acid towers and one aluminum chloride tower
5			98%	
6	contacts 35 cm^2 iron piece	before H_2SO_4	dried like No.	4
7				5
8		after H_2SO_4		4
9				5
10	is dried through one $CaCl_2$ tower	before H_2SO_4	dried like No.	5
11	contact 35 cm^2 iron piece			10
12	is dried through one zinc tower after			5

(Calcium chloride tower contains about a 10 cm thickness of anhydrous $CaCl_2$)

ENCLOSURE (B)7

Table VIII(B)7

CORROSION OF CAST IRON BY HCL GAS DRIED BY DIFFERENT METHODS
(Room temp. 20-25°C)

Surface Condition	Drying Method	Time (min)	Corrosion Loss		
			mg/dm^2	mg/dm^2day	Average (mg/dm^2day)
Polished	1	180 210 360	80 93 154	640 640 620	633
	2	140 210	172 281	1770 1927	1849
	3	200 210	82 88	590 603	597
	4	210	98 80	672 548	610
	5		55 54	377 370	374
	6		66	453	453
	7		48	329	329
	8		46 73	315 501	408
	9		32 34	219 233	226
	10	250 240	54 66	311 396	354
	11	180 360	24 31	192 124	158
	12	210	41 41	281 281	281
Polished (HCl is generated by 98/H_2SO_4)	5		17	117	117

ENCLOSURE (B)7

Table IX(B)7

CORROSION OF METALS AND ALLOYS IN DRY HCL GAS
(Room temp. 20-22°C)

Test Piece	Surface Condition	Time (hr)	Corrosion Loss	
			mg/dm^2	mg/dm^2day
Silver	Polished	6	7.6	34
	Wiped off the corr. prod. of test piece	25	10.1	9.7
Ag-Cu(1)	Polished	6	43.5	174
	Wiped off the corr. prod. of test piece	25	−14.1	−14
Ag-Cu(2)	Polished	6	12.5	50
	Wiped off the corr. prod. of test piece	25	34.4	33
Ag-Sb	Polished	6	25.9	104
	Wiped off the corr. prod. of test piece	25	7.8	7.5
Ag-Sn	Polished	6	30.0	120
	Wiped off the corr. prod. of test piece	25	3.9	3.7
Copper	Polished	6	6.7	27
	Wiped off the corr. prod. of test piece	25	29.3	28
Brass	Polished	6	191	762
	Wiped off the corr. prod. of test piece	25	89.5	86
Nickel	Polished	6	0.0	0
	Wiped off the corr. prod. of test piece	25	29.8	29
Steel	Polished	6	27.8	111
	Wiped off the corr. prod. of test piece	25	94.0	90
Cast Iron	Polished	6	25.9	104
	Wiped off the corr. prod. of test piece	25	69.0	66
18-8 Steel	Polished	6	7.5	30
	Wiped off the corr. prod. of test piece	25	66.8	64
18-8-2Mo Steel	Polished	6	11.1	44
	Wiped off the corr. prod. of test piece	25	43.4	42

ENCLOSURE (B)7

Table X(B)7

CORROSION OF METALS AND ALLOYS IN WET HCL GAS
(Contact with vapor of 45% HCl, Room Temp. 20-22°C)

Test Piece	Surface Condition	Time (hr)	Corrosion Loss	
			mg/dm^2	mg/dm^2day
Silver	Wiped off the corrosion product on the test piece after the dry gas corrosion tests.	25	5.0	4.8
Ag-Cu(1)			-29.5	-28
Ag-Cu(2)			39.6	38
Ag-Sb			-7.9	-7.6
Ag-Sn			-30.1	-29
Copper			39.6	38
Brass			294	282
Nickel			21.3	20
Steel			134	129
Cast Iron			190	181
18-8 Steel			83.9	81
18-8-2Mo Steel			59.7	57

4. Discussion.

The HCl dried through 85% sulphuric acid towers corrodes the cast iron to a far greater extent than when the gas is not dried. The corrosion with gas dried by 98% sulphuric acid is appreciable, even though it shows a little decrease compared to the case when the gas is not dried. Connection of an aluminium chloride tower gives good results and the corrosion loss greatly decreases.

A very effective method to decrease the humidity in HCl gas is to contrast the gas with metals whose chlorides are very hygroscopic, such as iron. Contact with iron after drying the gas with sulphuric acid shows better results than when the gas contacts it before drying with sulphuric acid. A zinc tower shows the same effect as iron to HCl gas, and this is a result of the hygroscopic nature of the corrosion product, zinc chloride.

Connection of a calcium chloride tower shows little effect in decreasing the humidity of the gas, but is effective in preventing the dilution of sulphuric acid. However, when accompanied by contact with iron the corrosion of the test piece shows a considerable decrease.

The corrosion by the gas generated with 98% sulphuric acid is far less than that by the gas generated with 85% acid. This shows the poor efficiency of sulphuric acid towers.

Corrosion resistance of silver is great both to dry and wet HCl gas.

Corrosion in Ag-Cu alloys is greater than in silver, but its fine corrosion product acts as a protective coating. These alloys have a tendency to increase their weight by corrosion. Silver-copper alloy rich in copper shows a poor result in wet HCl gas.

Ag-Sb alloy shows better results than Ag-Cu alloys. It also forms a protective coating.

Ag-Sn alloy condenses moisture on its surface even in dry HCl due to the hygroscopic nature of its corrosion product, stannous chloride, but the corrosion loss is small.

Copper shows good results in dry HCl gas. Its corrosion product is fine and sticks to the surface, but its corrosion loss greatly increases following the increase in water vapor content in HCl gas, and the corrosion product strips off easily.

Next to silver, nickel has good resistance to HCl gas. The corrosion loss of nickel increases slightly with the increase in humidity of the gas.

Alloys such as brass, bronze, constantan, etc., show poor results in the corrosion tests. Selective corrosion was recognized in such alloys.

Humidity in HCl gas has little effect on the corrosion of steel as long as electrolytic corrosion on steel does not occur.

Cast iron shows better results in dry HCl gas than steel, but with increasing humidity the corrosion loss becomes greater than that of steel.

18-8 chrome nickel steel shows good resistivity to dry HCl gas, but is badly corroded in wet HCl gas.

18-8-2 chrome-nickel-molybdenum steel shows better results than 18-8 chrome-nickel steel, but corrosion is high in wet HCl gas.

13 Cr steel shows poor results in either wet or dry HCl.

C. Material for Liquid HCl Vessel.

1. Description of apparatus.

The test piece was placed in a autoclave made of 18-8 chrome nickel steel. The HCl gas dried by sulphuric acid was introduced into the autoclave, which was dipped in liquid air for 30 minutes. The valve was closed, and the autoclave was placed at room temperature.

2. Test procedure.

Tests in liquid HCl were made with steel only. The analytical data of the steel are shown in Table II(B)7. Dimensions of the test piece were 3 x 5 x 50 mm.

3. Experimental results.

The experimental results are recorded in Table XI(B)7.

ENCLOSURE (B)7

CORROSION OF STEEL IN LIQUID HYDROGEN CHLORIDE

Table XI(B)7
(room temp. 15-20°C)
(test piece: steel)

Surface Condition	Time (hr)	Corrosion Loss	
		mg/dm^2	mg/dm^2day
Polished	120	190	38
Wiped off the corr. prod. of test piece	200	70	8

4. Discussion.

The surface of steel dipped in liquid HCl is more matted when compared with the surface of steel exposed to the vapor.

D. Material for Dichlor-Ethane Vessel.

1. Description of apparatus.

The apparatus is shown in Fig. 4(B)7. The first corrosion vessel made of stoneware contains 500g of $FeCl_3 \cdot 6H_2O$ as a catalyst for the reaction, and the second is empty. Both vessels are placed in oil thermostat, the temperature of which is kept at 130°C. HCl gas generated by Le Blanc's method and alcohol vapour are led into the first vessel and the reacted gas goes out from the second vessel. This process continues 5 hours and then the flow of HCl gas and alcohol are stopped and chlorine gas is introduced into the first vessel for 5 hours.
These processes are alternated for 40 hours. Constituents of metals and alloys tested in this experiment are as follows:

ALLOYS AND METALS TESTED AS DICHLOR-ETHANE VESSELS
Table XII(B)7

Test Piece	Constituents	Dimension (mm)
Silver	Chemical pure silver	1 x 20 x 50
Pb-Sb(1)	Sb 0.2%	20 ø x 50
Pb-Sb(2)	Sb 5.0%	
Tungsten	Pure tungsten wire	1 ø x 50

ENCLOSURE (B)7

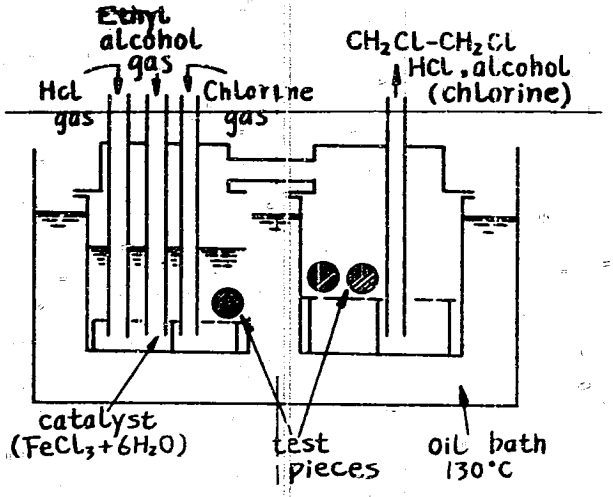

Figure 4(B)7

DICHOR-ETHANE CORROSION TEST

Table XIII(B)7

COMPOSITION OF LEAD SPECIMENS TESTED IN DICHLOR-ETHANE APPARATUS
(Dimension of test pieces 20mm x 50mm)

Test Piece	Silica	Cu	Fe	Bi	Zn	As	Sb	Sn	Cd	Ni	Pb
Lead(1)	0.002	0.001	0.007	0.004	0.005	-	-	-	-	-	99.981%
Lead(2)	0.001	0.001	0.003	0.006	0.001	-	0.001	0.019	-	0.005	99.963
Lead(3)	Ag 0.33 %				Lead(10) Zn 0.15% was added to lead(1)						
Lead(4)	Cu 0.20										
Lead(5)	Bi 0.17										
Lead(6)	Sn 0.31				Was added to lead (1)						
Lead(7)	Sb 0.20										
Lead(8)	As 0.15										
Lead(9)	Cd 0.13										

ENCLOSURE (B)7

2. Test procedure.

The corrosion was tested both in the liquid and gaseous phases.

a. A comparison between different metals and alloys was made.

b. The influence of minor constituents in lead was tested.

3. Experimental results.

The experimental results are recorded in Table XIV(B)7.

Table XIV(B)7

CORROSION OF METALS AND ALLOYS

Test Piece	Time (hr)	Corrosion Loss			
		Liquid Phase		Gaseous Phase	
		mg/dm^2	mg/dm^2day	mg/dm^2	mg/dm^2day
Lead (1)	40	2368	1420	1218	732
Pb-Sb(1)		4077	2443	3164	1900
Pb-Sb(2)		4591	2755	3032	1820
Silver		2831	1698	21	13
Tungsten		57	34	0	0

4. Discussion.

Tungsten has a good resistivity for corrosion in the dichlor-ethane forming reaction. This is especially true in the gaseous phase where no corrosion loss was found.
Silver shows poor results in the liquid, but in the gaseous phase it shows very good results.

Corrosion resistance of antimonial lead is very poor under these conditions.

The presence of minor constituents in lead shows a bad influence on lead corrosion. Especially, the existence of As and Sb in lead causes excessive corrosion both in liquid and gaseous phase. The presence of Bi has comparatively small effect on lead corrosion.

Lead (2) used in the 3rd Naval Fuel Depot as the material for reaction vessel in dichlor-ethane formation, shows a worse result than Lead (1).

ENCLOSURE (B)7

Table XV(B)7

THE INFLUENCE OF MINOR CONSTITUENTS IN LEAD

Test Piece	Time (hr)	Corrosion Loss			
		Liquid Phase		Gaseous Phase	
		mg/dm^2	mg/dm^2day	mg/dm^2	mg/dm^2day
Lead (1)	40	2076	1237	657	392
Lead (2)		3072	1833	1843	1102
Lead (3)		2570	1536	2067	1234
Lead (4)		2641	1577	1850	1103
Lead (5)		2446	1461	877	523
Lead (6)		3036	1812	978	585
Lead (7)		3999	2383	2592	1547
Lead (8)		3740	2232	2826	1687
Lead (9)		3143	1879	2178	1300
Lead(10)		2595	1550	2750	1641

III. CONCLUSIONS:

A. In the actual operation of an HCl gas compressor, the corrosion product will be wiped off continuously, and the surface condition will be exactly similar to one which is continuously polished with emery paper. For this reason, the corrosion loss in such a case will be far greater than the one shown in this report. The corrosion loss of cast iron by dried HCl gas is about 200 mg/dm^2day disregarding entirely the influence of defacement. Actually, the removal of ferrous chloride film due to the rubbing of iron surface results in the formation of a new active surface, and the formation of scrap will increase the formation of ferrous chloride and the defacement of iron as much as ten or more times. These corrosion products mixed with lubricant cause the sticking of valves, and make it impossible to keep the compressor in motion. Therefore, the use of cast iron as the compressor material is not suitable.

B. HCl gas is very hygroscopic. This makes it difficult to dry the gas to the extent necessary to keep the compressor in motion using ordinary drying agents which are in industrial use. Metal towers such as iron or zinc have a great efficacy in decreasing the humidity of HCl gas, but these metals will lose their efficacy when a saturated metal chloride solution is formed on the surface of the metals. Furthermore, it is questionable whether a metal drying tower will keep its great efficacy after a prolonged continuous flow of the gas as with an HCl gas compressor.

C. No completely satisfactory material was found for the HCl gas compressor. Even silver and its alloys which show good resistance for HCl gas were corroded considerably when the surfaces were polished. Silver, copper, nickel and 18-8-2 chrome nickel molybdenum steel show relatively good resistance to HCl gas. The practical tests of these metals as the compressor materials will be worthwhile and interesting.

D. The use of a lubricant which has a low viscosity such as liquid paraffin greatly accelerates the defacement of cylinder liners and piston rings. Thus its use as the lubricant in the compressor should be avoided. Lubricating oils suitable to the HCl gas compressor must have high viscosity, stability to the gas, and low solubility of the gas.

E. From the appearance of test pieces the use of steel bombs for liquid HCl vessels may be satisfactory, though the determination of suitability should be done after measuring its mechanical strength after corrosion.

F. Silver and its alloys have good corrosion resistance even in wet HCl gas, and they are suitable for the valve material of the liquid HCl bomb. Silver is too soft for the valve material, so Ag-Sb and Ag-Sn alloys are better than silver.

G. Homogeneous lead linings are best for the reaction vessel in dichlorethane formation. The purer lead gives better results.

Tungsten has a very good resistivity for this condition, but its practical use is out of the question. Silver has a very good resistivity if there is not contact with the catalytic solution but only contact with the reaction gases. Therefore, silver-lined cast iron is suitable for the lid of the reaction vessel.

ENCLOSURE (B) 8

STUDIES ON THE ALKYLATION OF ISO-BUTANE

by

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Research Period: 1939-1942

Prepared for and reviewed with author by the
U.S. Naval Technical Mission to Japan

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ENCLOSURE (B)8

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Plate I(B)8 Reaction Section Alkylation Pilot Plant

ENCLOSURE (B)8

SUMMARY

Iso-butane and propylene were alkylated using the concentrated sulphuric acid process and 16.5 wt % yield of crude alkylate to charged propylene was obtained. The octane value of the alkylate was 85 to 90, and 100 octane aviation gasoline could be made by blending 60% of alkylate with 40% of 92 octane base gasoline and adding 0.1% of tetra ethyl lead.

The optimum conditions of the alkylation process were determined to be as follows:

H_2SO_4 concentration	97 to 99%
Ratio of charging stock and H_2SO_4	1 : 1 (vol)
Reaction temperature	25 to 30°C
Reaction pressure	5 kg/cm^2
Contact time	60 min
Stirring rate	300 RPM
Catalyst	0.2% chromic acid

I. INTRODUCTION

Since Elkington (Bataafsche Petroleum Maatschappii Engineer) discovered, in 1937, the process of condensation of paraffinic and olefinic hydrocarbons in presence of concentrated sulphuric acid, the production of high octane gasoline by the method of "alkylation" has been studied by many (for example, Birch, Dunstan, Fidler, Dim, Tait, Gard, Blaunt, Karpi, Caeser, Francis, McAllister, Anderson, Ball, and Ross).

In this investigation the author has studied the alkylation reaction, especially the following aspects of the reaction of iso-butane with propylene: determination of best conditions of alkylation; reaction promoters; and properties of the alkylate.

The author established that alkylation was not direct condensation only, but was also accompanied by the eight reactions (Hydrogenation, Polymerization, Depolymerization, Rearrangement, Isomerization, Carbon to carbon cleavage, Dehydrogenation and addition of radicals).

The vital point of the alkylation reaction, the emulsification of catalyst and hydrocarbons, was studied mainly with regard to the formation of emulsion by two mechanical methods: stirring and injection.

In laboratory tests these two methods were almost equal, but in pilot plant tests stirring gave better results.

A pilot plant with total hydrocarbons plus sulphuric acid charging capacity of 10 to 20 lit/hr was constructed and operated during 1941-1942. All reaction conditions compared well with the results of laboratory tests.

Although the author observed the alkylation plants of Nederlandsche Kolonial Petroleum Maatschappii and Bataafsche Petroleum Maatschappii at Palembang in 1942 and admired both the alkylation feed gas fractionation equipment and the simple stirring type reactor, yet the design could not be directly utilized in Japan owing to the very limited supply of alkylation feed gases, especially iso-butane. In this latter connection the author has also made studies of methods for producing alkylation feed gases.

ENCLOSURE (B)8

II. DETAILED DESCRIPTION

A. Laboratory Test

Details of the laboratory apparatus used in alkylation studies are given by Figures 1(B)8 and 2(B)8.

Iso-butane and propylene were mixed in the gas holder at given ratio, compressed in a one hp - compressor and liquefied by cooling with solid CO_2 - alcohol solution in the measuring cylinder I. Autoclaves I and II were filled with concentrated H_2SO_4 from measuring cylinder II and the motor driver stirrers started. Liquefied hydrocarbons were introduced into the autoclaves in the required amounts. The temperature of the reaction was regulated by circulation of cooling water. When the reaction was over, unreacted gases were released through the gas meter to the gas holder. The volume and concentration of spent sulphuric acid were measured. The volume and specific gravity of the alkylate were also determined and it was then distilled into three fractions, the first up to 30°C, second 30 to 170°C, and the third over 170°C.

1. Effect of reaction time

A reaction time of at least 60 minutes is required. (See Table I(B)8 and Figure 3(B)8.

Conditions for these tests were:

H_2SO_4 Volume	150cc
Conc.	98%
Reaction temp.	25°C
RPM	300
Liquid charge C_3H_6 and i-C_4H_{10}	400cc

2. Effect of reaction temperature and concentration of sulphuric acid.

Alkylation cannot proceed with an acid concentration below 85% ($H_2SO_4.H_2O$), and a concentration of 96 to 100% is best. The relation between concentration of H_2SO_4 and reaction temperature is very interesting; refer to Table II(B)8. See also Figures 4(B)8 to 6(B)8.

Conditions for these tests were:

Volume of H_2SO_4	150cc
Feed	400cc
RPM	300

In conclusion, the best conditions are given below: (other conditions same as Table I(B)8.)

Reaction temperature °C under best condition	Conc. of H_2SO_4	Max. yield
10°	99%	150%
25°	99%	165%
30°	98%	163%
40°	97%	164%

3. Effect of amount of H_2SO_4

The volume ratio of liquid raw material of H_2SO_4 must be less than 3/1, as Table III(B)8 and Figure 7(B)8.

Conditions for these tests were:

Conc. of H_2SO_4	98%
Feed	400cc
RPM	300
Temp.	30°C

4. Effect of pressure

A reaction pressure higher than 5 kg/cm^2 had no effect; refer to Table IV(B)8 and Figure 8(B)8.

Conditions for these tests were:

H_2SO_4 Volume	150cc
Conc.	98%
Reaction temp.	30°C
Ratio	i.c_4/c_3 = 3/1
RPM	300
Reaction time	60 min
H_2 pressure used	

5. Effect of stirring

The effect of stirring is very important. In the autoclave 60 to 120 RPM was too little (in such a case polymerization or esterification of propylene only occurs), and 300 RPM was found to be the optimum rate. See Table V(B)8 and Figure 9(B)8.

Conditions for these tests were:

Ratio	i.c_4/c_3'' = 3/1
Volume of H_2SO_4	150cc
HC feed	400°C (liquid)
Reaction time	60 min

6. Effect of feed gas ratio

The iso-butane to propylene ratio should be over three. If the ratio is less than three, polymerization of propylene occurs. (See Table VI(B)8 and Figure 10(B)8.

Conditions for these tests were:

H_2SO_4 Volume	150cc
Conc.	98%
HC feed	400cc
RPM	300
Reaction time	60 min

7. Effect of emulsifiers

ıe results of adding emulsifiers were not good, refer to Table II(B)8.

ENCLOSURE (B)8

Conditions for these tests were:

H_2SO_4 Volume	150cc
Conc.	98%
Ratio $i.c_4/c_3^=$	3/1
Reaction Time	60 min
Temp.	30°C
RPM	135
HC feed	400cc

8. Effect of electrolytes

Nitric acid and ferric sulphate were more effective, but not as attractive as the use of oxydizing agents; refer to Table VIII(B)8.

Conditions for these tests were:

H_2SO_4 Volume	150cc
Conc.	98%
HC feed	400cc
Temp.	30°C
RPM	300
Gas ratio	3 : 1

9. Effect of oxydizing agents

Oxydizing agents were very good promoters.

The concentration of spent sulphuric acid was higher and the yield of aviation gasoline also was higher; refer to Table IX(B)8.

Conditions for these tests were:

Volume of H_2SO_4	150cc
Feed	400cc
Reaction time	60 min
Gas ratio	3 : 1
Reagents	0.2% (wt)

10. Properties of alkylate

The 30° to 170°C fraction of alkylates was good aviation fuel, having the following properties.

Sp. gr. 20°/40	0.6821
Oct. No.	100 (0.1% lead)
Vap. press	0.56 kg/cm^2
Freezing pt.	-50° max
Fract. distillation	
Initial pt.	48°C
10%	63.5°C
50%	92°C
90%	124°C
97%	170°C

11. Corrosion test of materials of construction

The results are given below:

13% Cr-steel ..... slightly corroded
18-8 stainless ..... no change
Ni-Cr-W steel ..... no change
85 kg Ni-Cr-steel ..... poor
35 kg Ni-Cr-steel ..... very bad
Mild steel ..... very bad
Abesta 832S stainless steel ..... no change

13% Cr-steel was selected out of the above seven steels as material for alkylation plants construction.

B. Pilot Plant

A flow sheet of the reaction section of the continuous pilot plant is given in Plate I(B)8.

Pure iso-butane and propylene, or catalyst cracking plus hydrocracking gas, were used as raw materials.

The feed stock was compressed, liquefied by brine cooling, and stored in a cooled tank. The liquefied gas and concentrated sulphuric acid were sent to the reaction chamber by plunger type pumps. After the reaction the emulsion was settled and separated into product and spent sulphuric acid. The product was washed by caustic soda and water.

Since 1941 five runs were made, but all data were burnt this year, and only the following points can be recalled:

1. The plunger pump for concentrated sulphuric acid was not satisfactory, because the asbestos packing and plungers (even stellite welding) were corroded by the acid.

2. The injection type reactor was also not satisfactory, because it was soon plugged by dirt and impurities in the feed.

3. The stirrer type reactor was very good and all pilot plant results using this type agreed with laboratory data (165 to 170% yield and 85 to 90 octane rating), but total olefine content of the feed stock should be less than 20% to maintain sufficiently high acid concentration.

4. The separation of hydrocarbons and sulphuric acid from the emulsion was very difficult, requiring two hours settling time minimum.

TABLE I(B)8

EFFECT OF REACTION TIME

Test No.	Conditions of Reaction			Properties of Products							
	Reaction Time (min.)	Press. (Kg/cm^2)	C_3'' content (vol. %)	Spent gas (lit)	Spent H_2SO_4 Vol.(cc)	Spent H_2SO_4 Conc. (%)	Total oil Product	30~170° (cc)	Yield % to C_3''	Blending O.N.	170°~ (cc)
285	20	5.7	24.7	55.5	153	90.06	122	50	73.4		16
156	60	4.9	27.1	40.9	143	94.18	165	101.1	143.9	88.8	11.5
162	120	4.2	25.1	34.6	155	94.91	165	98.3	149.9	86.5	9.7
163	180	4.9	25.5	36.8	150	94.62	170	102	155.0		9.8

TABLE II(B)&

EFFECT OF REACTION TEMPERATURE AND CONCENTRATION OF SULPHURIC ACID

Conditions							Properties of Products												
Test No.	Conc. of H_2SO_4 (%)	Reaction Temp. (°C)	Max. Temp. (°C)	Reaction pressure (Kg/cm^2) Initial	Reaction pressure (Kg/cm^2) Final	Content of $C_3^=$ (mol.%)	Spent gas	$C_3^=$ mol. % in spent gas	Spent H_2SO_4 (cc)	Conc. of spent H_2SO_4 (%)	Total oil product (cc)	~30°C fraction (cc)	Light alkylate Amount	Light alkylate Sp. Gr. (15°/4°)	Light alkylate Yield to $C_3^=$ (%)	Br No.	Heavy alkylate Amount (cc)	Heavy alkylate Br No.	Blending O.N.
25	102	-30	-26.0	0	0	25.0	103.6	24.75	155	81.4	0								
21	102	-10	-8.6	2.0	1.5	25.0	54.1	2.0	200	82.6	56	12.5	100		15.3		33.0		
17	102	± 0	1.7	4.5	3.8	25.0	76.7	4.05	220	92.2	46	18.0	100		15.3		28.0		
9	102	10	14.3	6.2	5.8	25.0	78.0	4.62	182	78.2	78	22	48.0	0.6893	73.5		8.0		
8	101	10	13.3	10.5	9.0	25.0	78.0	3.46	225		45	9.5	19.0	0.6872	29.0		17.5		
133	101	30	32.6	4.5	4.0	24.25	50.0	1.34	180		90	35.6	45.4	0.6960	71.4	0.1	9.0	1.7	82.8
7	100	10	12.8	10.0	8.7	26.0	70.7	3.10	200		47	3.5	25	0.6946	37.5		15.5		
118	100	20	23.0	3.1	2.5	25.2	13.3	0.1	168	93.14	135	46.4	78.6	0.6948	120.8	0.4	10.0	0.9	82.3
152	100	25	26.0	3.2	3.0	26.7			172	93.82	141	41.0	92.0		131.2	0.4	8.0	0.3	
153	100	30	32.0	5.0	3.7	26.7	50.0		163	93.41	127	48.0	63.0	0.6906	90.6		6.0		
119	100	40	42.6	5.0	3.8	25.2	37.0	1.28	150	95.69	97	38.5	45.5	0.6869	68.1	1.0	13.0	1.3	
148	99	10	12.3	3.2	2.7	4.25		1.2	170	94.56	158	52.5	96.0	0.6978	151.3	0.6	9.5	1.4	89.8
300	99	20	20.5	5.3	4.4	24.4	53.8	10.9	157	94.09	143	49	80	0.6979	125.3		14		
154	99	25	26.0	4.0	3.3	27.1	58.6		140	94.76	205	69.5	118.5	0.6913	168.2	0.6	17.0	1.4	88.8
155	99	30	30.5	3.5	3.3	27.1		0.66	150	94.06	200	98.5	92.5	0.7006	133.0	0.3	9.0	1.9	
167	99	35	35.8	5.2	4.7	24.71	47.0	0.63	150	92.8	180	46.0	91.0	0.7049	143.5	0.1	13.0	1.3	
151	99	40	40.2	5.0	4.9	26.7	46.8	0.83	164		120	39.3	68.7	0.9026	100.5	0.2	12.0	0.5	76.3
3	98	10	12.8	31.8	31.2	25.0	101.3	0.55	163	89.9	92	22.0	50.5	0.6968	68.1		19.5		
156	98	25	25.2	4.9	3.5	27.1	40.9	0.85	145	94.18	165	42.4	101.1	0.6936	143.9	0.2	11.5	2.0	88.8
194	98	30	31.5	4.8	3.7	24.7	41.7	0.6	163	93.99	178	67.5	105	0.7017	165.4		5.7		86.6
169	98	35	36.5	5.0	4.2	24.7	45.9	0.3	115	93.23	140	45.5	85.5	0.7056	135.8		9.0		82.3
170	98	40	41.0	5.8	5.2	24.7	46.6	1.28	145	92.50	140	56.0	70.0	0.7011	110.5		14.0		82.3
122	97	20	21.0	2.8	2.1	25.8	51.2	0.77	145	93.50	137	57.0	74.0	0.6971	109.8	0.3	6.0	3.1	86.3
123	97	25	26.6	3.8	2.9	25.8	46.2	1.3	170		160	55.5	95.0	0.6896	141.3	0.4	9.5	2.0	87.3
159	97	30	30.0	4.9	3.6	27.1		0.66	158	90.97	175	67.0	95.0	0.6932	125.3	0.4	13.0	2.3	88.8
292	97	35	36.0	5.5	5.0	24.7	43.5	2.7	169	91.83	162	54	84.0	0.7024	131.5		24.0		84.0
172	97	40	40.0	4.9	3.9	24.7	37.0	1.08	158	91.66	168	48.5	107.5	0.7029	167.9		12.0		84.8
4	96	10	11.0	9.0	9.0	25.0	76.4	0.74	237	55.1	690	9.0	32.0	0.6949	49.4		28.0		
160	96	25	25.3	4.8	3.9	27.1	42.6	0.84	170	91.93	140	39.3	88.2	0.6350	115.0	0.1	12.5	2.0	89.8
161	96	30	30.6	5.8	3.5	25.5	35.0	0.77	150	90.63	150	48.0	90.0	0.6987	138.1	0.5	12.0	3.0	88.8
173	96	35	35.2	4.8	4.2	24.99	34.6	1.04	172	89.56	168	63.0	95.0	0.7015	148.0		10.0		88.3
174	96	40	43.4	6.0	5.0	24.99	40.8	1.02	152	87.97	158	50.0	100.5	0.7052	157.4		7.5		87.3
190	95	35	35.0	5.5	5.1	24.7	50.0	0.75	170	89.89	110	43.0	59.7	0.7099	95.4		7.3		
191	95	40	40.3	6.0	5.0	24.7	44.0	1.33	170	90.92	130	36.5	84.5	0.7018	123.6		9.0		88.8
192	94	35	34.5	5.5	4.0	24.7	48.7	1.11	159	88.34	118	50.5	57.5	0.7036	91.1		10.0		
193	94	40	42.2	5.1	4.2	24.7	42.2	0.4	165	89.74	135	54.7	71.3	0.7016	112.6		9.0		89.8

ENCLOSURE (1)8

RESTRICTED

ENCLOSURE (B)8

Test No.	Conditions							Properties of Products												
	Amount of H_2SO_4 (cc)	Amount of Raw Material (cc)	Reacting Temp. (°C)	Reaction Pressure (Kg/cm²)			Content of $C_3^{=}$ (mol.%)	Spent gas (lit)	$C_3^{=}$ mol. % in spent gas	Amount of Spent H_2SO_4 (cc)	Conc. of Spent H_2SO_4 (%)	Total oil products (cc)	~30°C fraction (cc)	Light alkylate			Heavy alkylate		Blending O.N.
				Initial	Max.	Final								Amount (cc)	Sp. Gr. (15/4°)	Yield to $C_3^{=}$ (%)	Br No.	Amount (cc)	Br No.	
102	400	400	31.0	3.3	3.7	2.1	25.1	50.3	2.8	388	97.69	203	92.7	100.1	0.6892	122.5	1.1	10.2	10.9	83.8
166	200	400	30.8	4.5	5.0	3.8	25.1	43.2	0.99	200	94.8	160	47.0	97.0	0.6877	147.5	0.0	14	1.5	91.8
194	150	400	31.5	4.8	8.2	3.7	24.7	41.7	0.60	163	93.99	178	67.5	105	0.7017	16.9		5.7		84.4
46	100	400	31.0	5.8	5.8	4.7	25.4	38.6	0.80	118	94.67	134	51	65	0.7035	101.7		11	3.3	77.8
45	75	400	31.8	6.2	6.2	5.0	25.0	72.6	1.6	160		10	"	5		9.7				
44	50	400	32.6	7.5	7.5	6.1	25.0	63.5	5.4	151		1	0	1		1.9		0		
103	100	100	30.2	3.5	4.1	3.0	25.2	21.3	7.36	110	96.54	30	10	15.0	0.7176	23.7	20.7	5.0		
104	100	200	32.0	3.7	4.1	2.4	25.2	29.2	1.4	113	97.28	62	24.8	24.2	0.7061	37.8	1.2	11.0	39.1	
105	100	300	30.3	3.0	4.5	3.0	25.2	37.9	0.88	100	94.11	108	52.4	45.2	0.7040	70.4	6.2	11.3	36.9	
106	100	600	30.0	3.8	4.4	3.6	25.4	104.6	1.8	175	69.56	30	10	15.0	0.7141	23.7	66.8			

Test No.	Pressure (Kg/cm²)			Properties of Products							
	Inital	Max	Final	Spent gas		Spent H_2SO_4		Total oil (cc)	Light Alkylate (30°~170°)			Heavy Alkylate (cc)
				Amount (lit)	$C_3^{=}$ vol. %	Amount (cc)	Conc. (%)		Amount (cc)	Yield to $C_3^{=}$ (%)	Blending O.N.	
521	4.5	10.1	10.1	46.4	0.3	155	92.85	160	81	123.9	84.3	11.0
522	4.7	15.1	15.1	57.0	0.59	150	96.81	173	93	141.3	82.8	13.0
523	6.0	20.0	20.0	76.6	0.55	150	93.92	160	83	126.8	85.3	19.0
524	6.0	30.0	30.0	89.0	0.85	153	92.81	170	87	132.9	87.3	11.2
194	4.8	3.7	3.7	41.7	0.60	163	93.99	178	105	165.9	86.6	5.7

Test No.	Conditions of Reaction				Properties of Products							
	Conc. of H_2SO_4 (%)	Temp. (°C)	Press. (Kg/cm²)	Stirrer (RPM)	Spent gas (lit)	Spent H_2SO_4 (cc)	Conc. of H_2SO_4 (%)	Total oil product (cc)	30°~170° (cc)	Yield % to C_3H_6	Octane value	170°~ heavy oil (cc)
107	93	30	4.5	60	70.8	188		40	10	15.1		17
295	93	30	5.7	120	58.7	180		72	22	34.5		25
157	93	30	4.6	300	36.8	164	94.31	180	111	158.8	88.3	11.4
294	99	25	5.8	60	72.7	180	92.92	30	7	10.9		17
293	99	25	5.1	120	57.0	170	90.44	75	24	37.7		26
154	99	25	4.0	300	58.6	140	94.76	205	118.5	168.2	88.8	17

ENCLOSURE (B)8

Table VI(B)8
EFFECT OF FEED GAS RATIO

Test No.	Conditions of Reaction				Properties of Products							
	Feed gas ratio, i C_4/C_3	Max. temp. (°C)	Max. Press. (Kg/cm^2)	C_3'' content (mol. %)	Spent gas (lit)	Spent H_2SO_4 (cc)	Conc. of spent H_2SO_4 (%)	Total oil products (cc)	30°~170° (cc)	Yield % to C_3''	Blending O.N.	170°~ (cc)
26	1/1	34.5	7.3	50.0	50.0	215	60.6	60	24.5	18.4		10.0
28	2/1	32.0	5.0	33.3	43.6	160		230	160.	185.2	79.8	17.5
194	3/1	31.5	4.8	24.7	41.7	160	93.99	178	105	165.9	86.6	9.0
120	5/1	31.4	3.9	16.9	45.6	153	97.22	157	89	202.8	88.3	13.0
32	8/1	33.4	6.0	11.1	39.5	150		155	76.5	271.5		9.2

Table VII(B)8
EFFECT OF EMULSIFIER

Test No.	Conditions of Reaction				Properties of Products			
	Reagents added	Amount of Reagent (gm)	Temp. max. (°C)	Press. range (Kg/cm^2)	C_3'' in spent gas (cc)	Sp. gr. ($15°/4°$)	Total oil product (cc)	Yield % to C_3H_6
241	Benzenesulphonic Acid	1	34.5	17~15	0.76	0.6811	37.0	75.4
235	Toluenesulphonic Acid	1	36.3	14~12	1.87	0.7001	46.0	96.4
239	Naphtholsulphonic Acid	1	39.5	13~12	1.80	0.7035	33.4	70.4
237	Naphthylaminesulphonic Acid	1	34.9	16	3.20	0.6839	52.2	106.9
250	Stearic Acid	0.2		17~14	0.76	0.6918	41.4	87.5
250'		0.1	32.0	17~14	1.13	0.7001	60.3	126.0
205	None	0	31.5	17~16	0.37	0.6898	61.2	126.2

ENCLOSURE (B)8

Table VIII(B)8
EFFECT OF ELECTROLYTES

Test No.	Conditions			Properties of Products							
	Reagents added	Amount (gm.)	Press. max.	Spent H_2SO_4 Amount (cc)	Spent H_2SO_4 Conc. (%)	Spent gas (lit.)	Oil product (cc)	30°~170° (cc)	Yield (%)	O.N. Blend	170°~ (cc)
146	None	0	4.1	150	94.77		125	83	126.9	84.8	17.0
125	SeO_2	0.59	4.5	149	89.93	69.5	141	72	111.1	85.3	8.7
126	HNO_3	2	4.5	160	93.11	53.4	137	86	136.2	84.8	11.0
127	HCl	2	4.1	145	94.88	55.2	132	83.5	131.3	84.8	9.0
129	$ZnSO_4$	0.4	4.0	153	89.40	51.6	118	86	124.5	85.3	7.0
130	$Al_2(SO_4)_3$	0.4	4.5	155	94.92	58.8	121	75.6	118.1		7.5
131	$Fe_2(SO_4)_3$	0.4	5.0	150	94.17	49.8	142	87	138.1	87.8	8.5
128	H_3PO_4	5.0	5.9	209		72.2	10		15		

Table IX(B)8
EFFECT OF OXIDIZING AGENTS

Test No.	Conditions				Properties of Products						
	Reagents	Conc. of H_2SO_4 (%)	Temp. (°C)	Press. (Kg/cm^2)	Spent H_2SO_4 (cc)	Conc. of H_2SO_4 (%)	Spent gas (lit)	Oil product (cc)	30°~170° (cc)	Yield	Octane Value
567	none	97	35	5.5	150	93.51	38	157	89	135.9	84.0
568	$K_2Cr_2O_7$	97	35	5.1	160	94.34	39	182	99	151.1	87.0
573	$(NH_4)_2S_2O_8$	97	35	5.0	160	94.14	38	165	88	135.2	87.8
554	none	98	30	5.4	158	93.49	46	140	98	159.0	87.8
555	$K_2Cr_2O_7$	98	30	5.0	154	93.04	44	160	91	140.7	
572	$(NH_4)_2S_2O_8$	98	30	4.9	150	95.13	38	180	108	164.9	89.0

ENCLOSURE (B)8

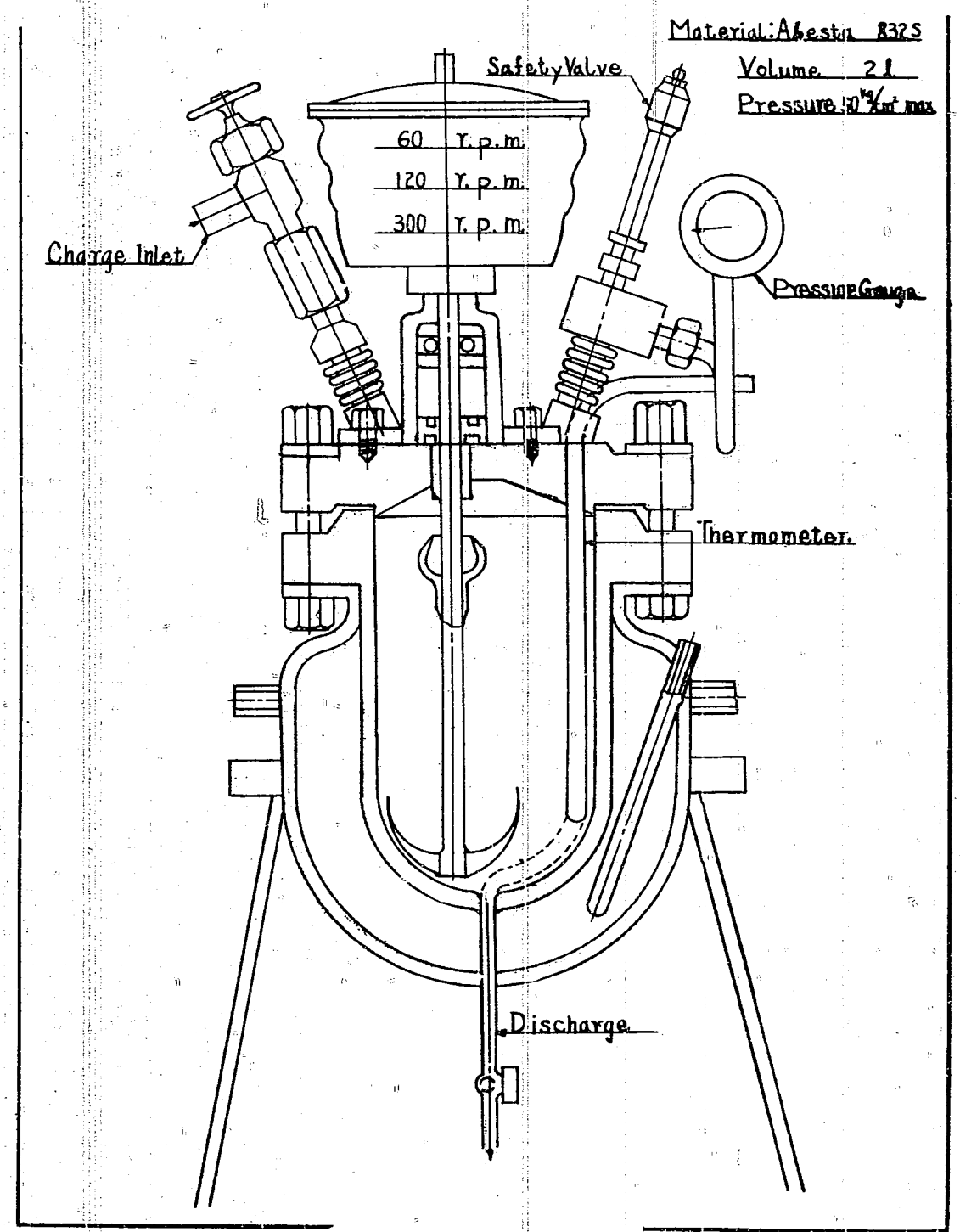


Figure 1(B)8
AUTOCLAVE FOR ALKYLATION

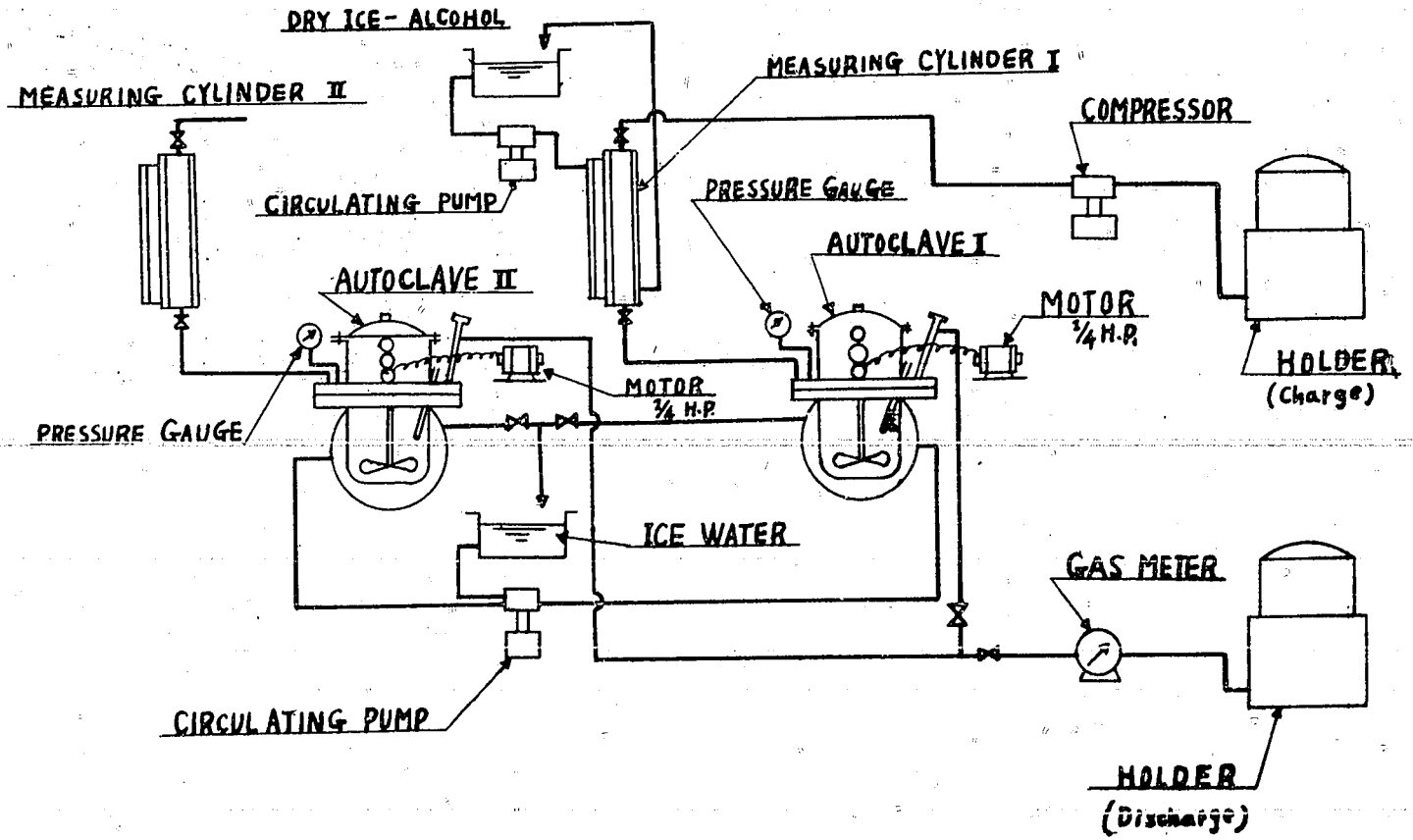


Figure 2(B)8

LABORATORY APPARATUS FOR ALKYLATION

ENCLOSURE (B)8

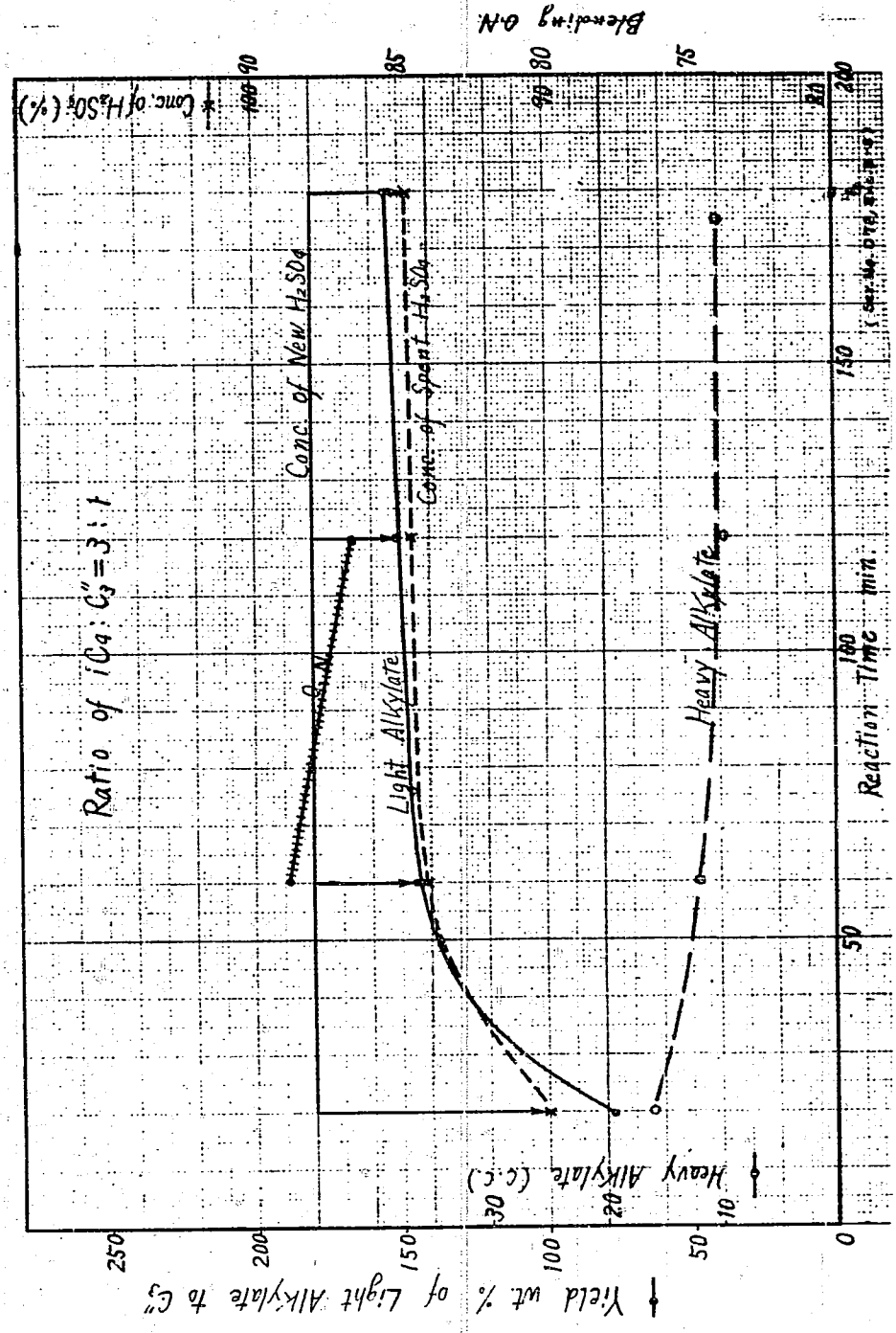


Figure 3(B)8
EFFECT OF REACTION TIME

ENCLOSURE (B)8

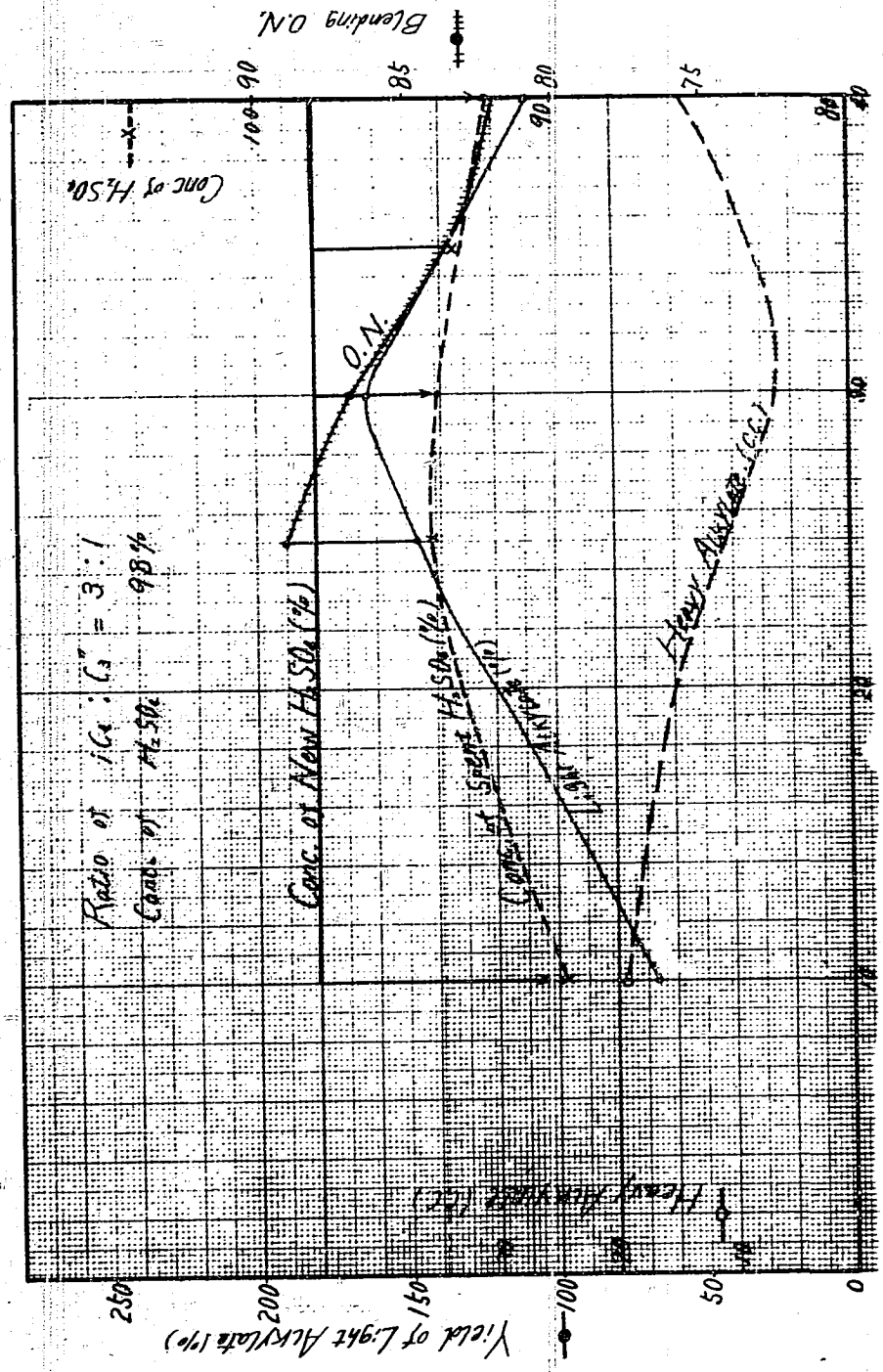


FIGURE 4(B)8
EFFECT OF REACTION TEMPERATURE (D)

ENCLOSURE (B)8

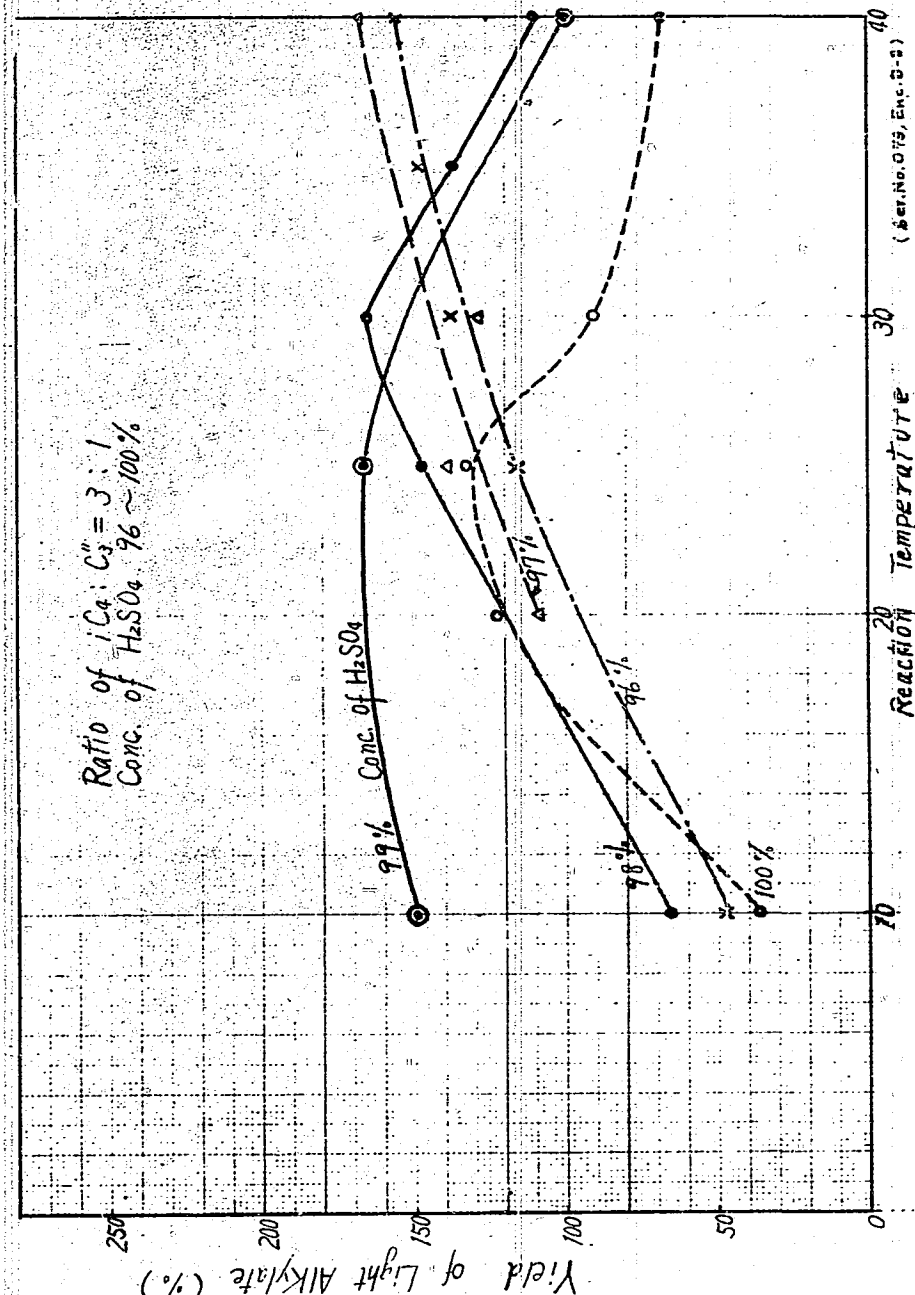


FIGURE 51B18

EFFECT OF REACTION TEMPERATURE (5)

ENCLOSURE (B)8

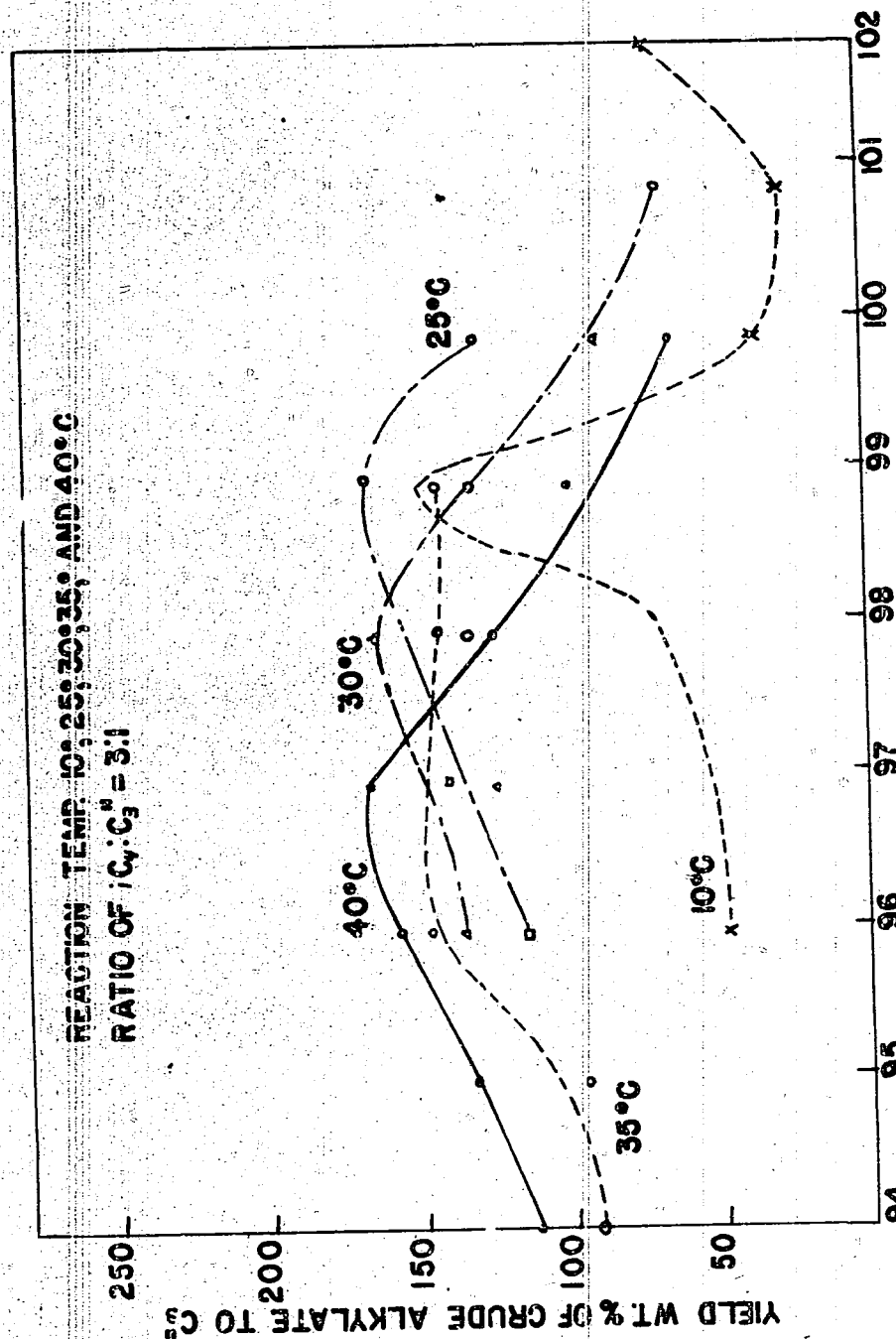
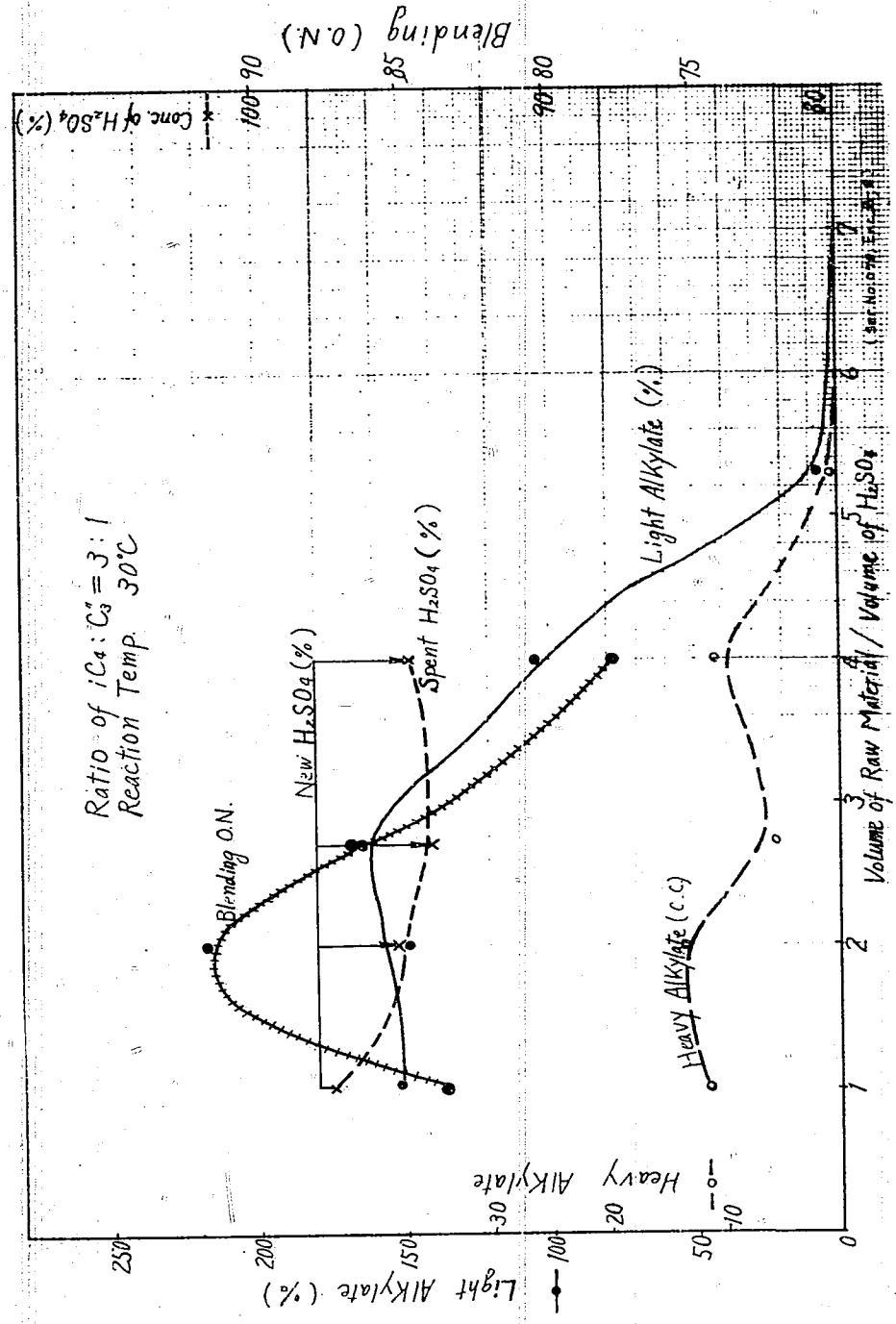


Figure 6(B)8

CONCENTRATION OF H_2SO_4 AND YIELD

ENCLOSURE (B)8



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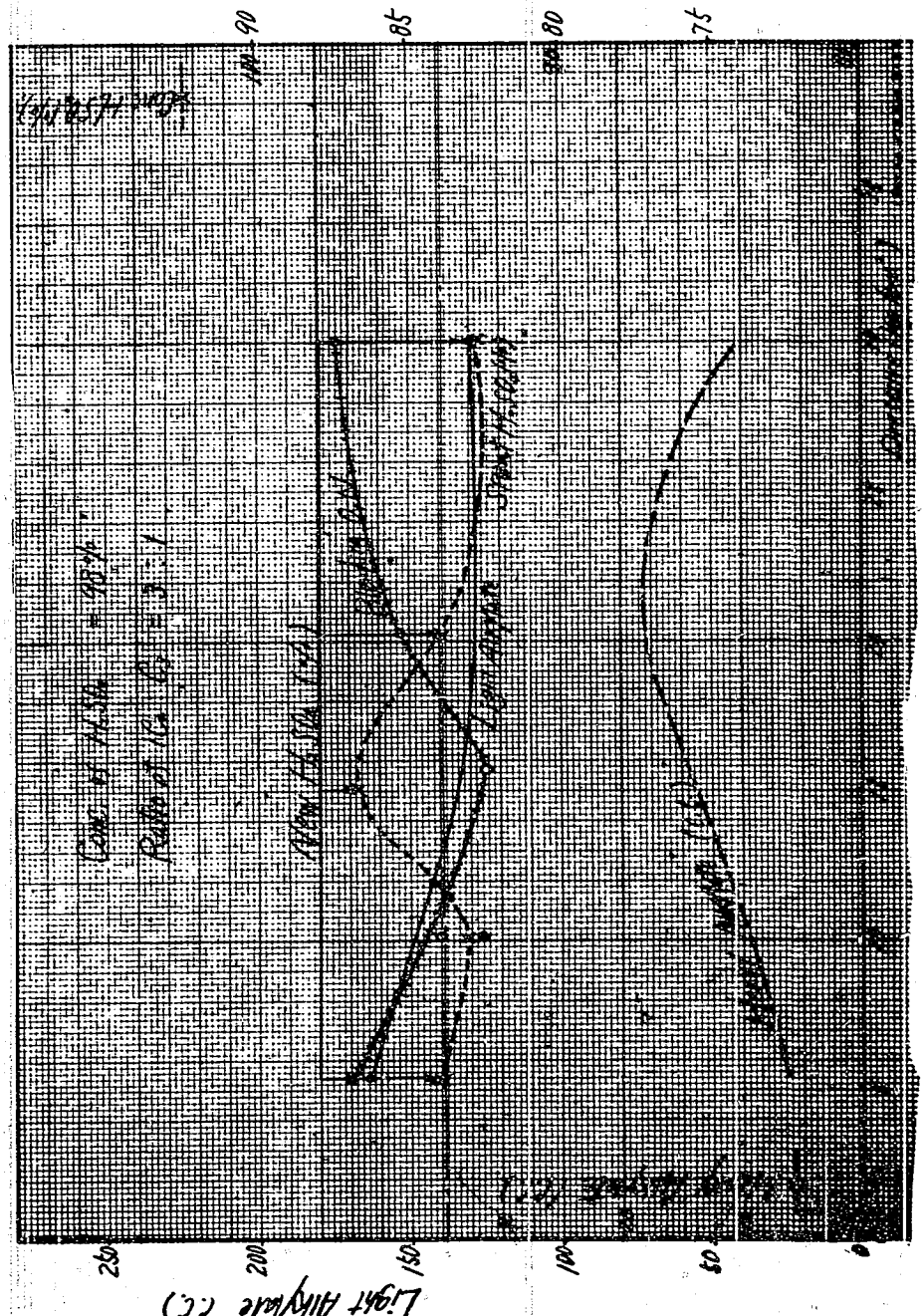


FIGURE 8(N)8
EFFECT OF PRESSURE

ENCLOSURE (B)8

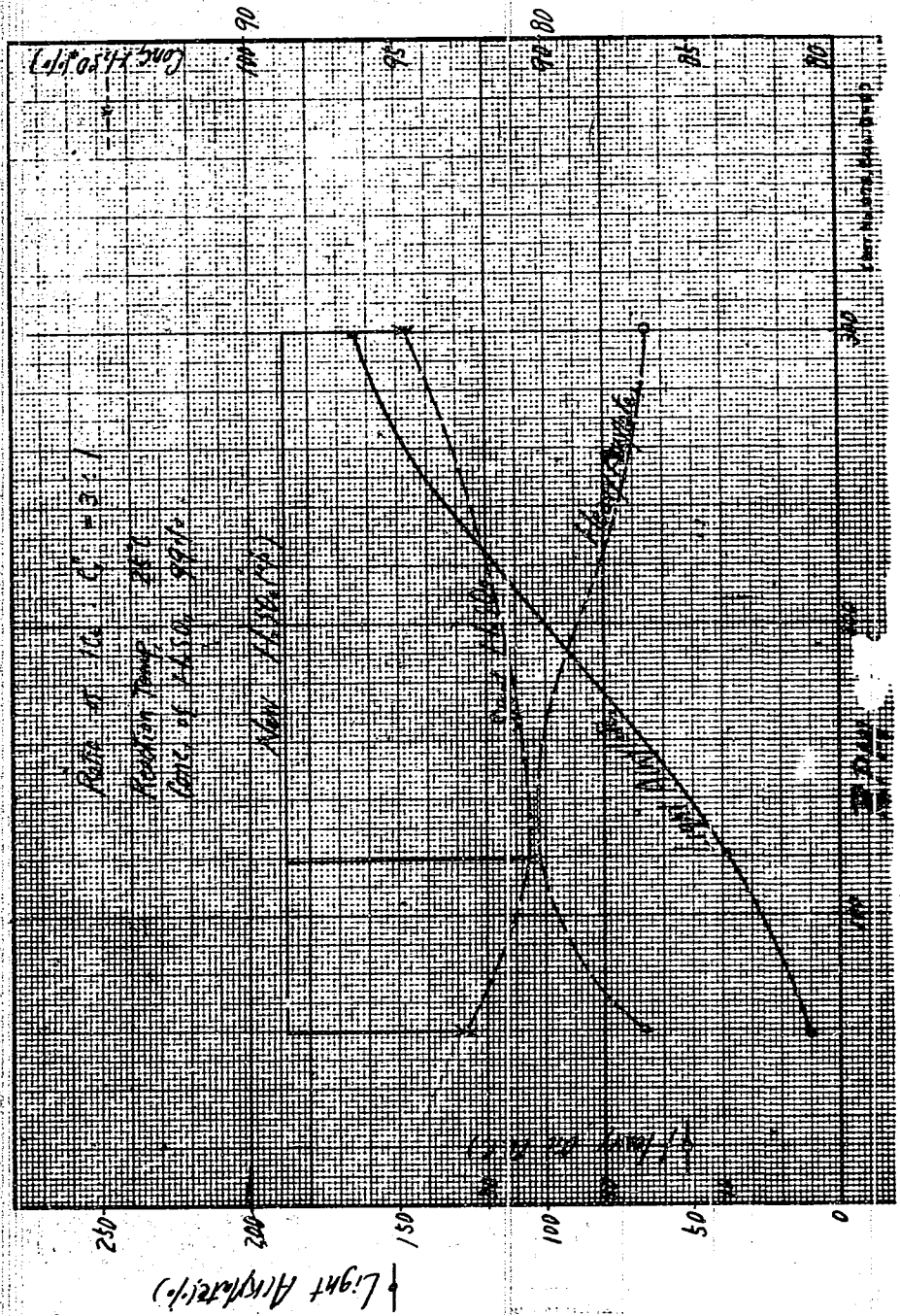
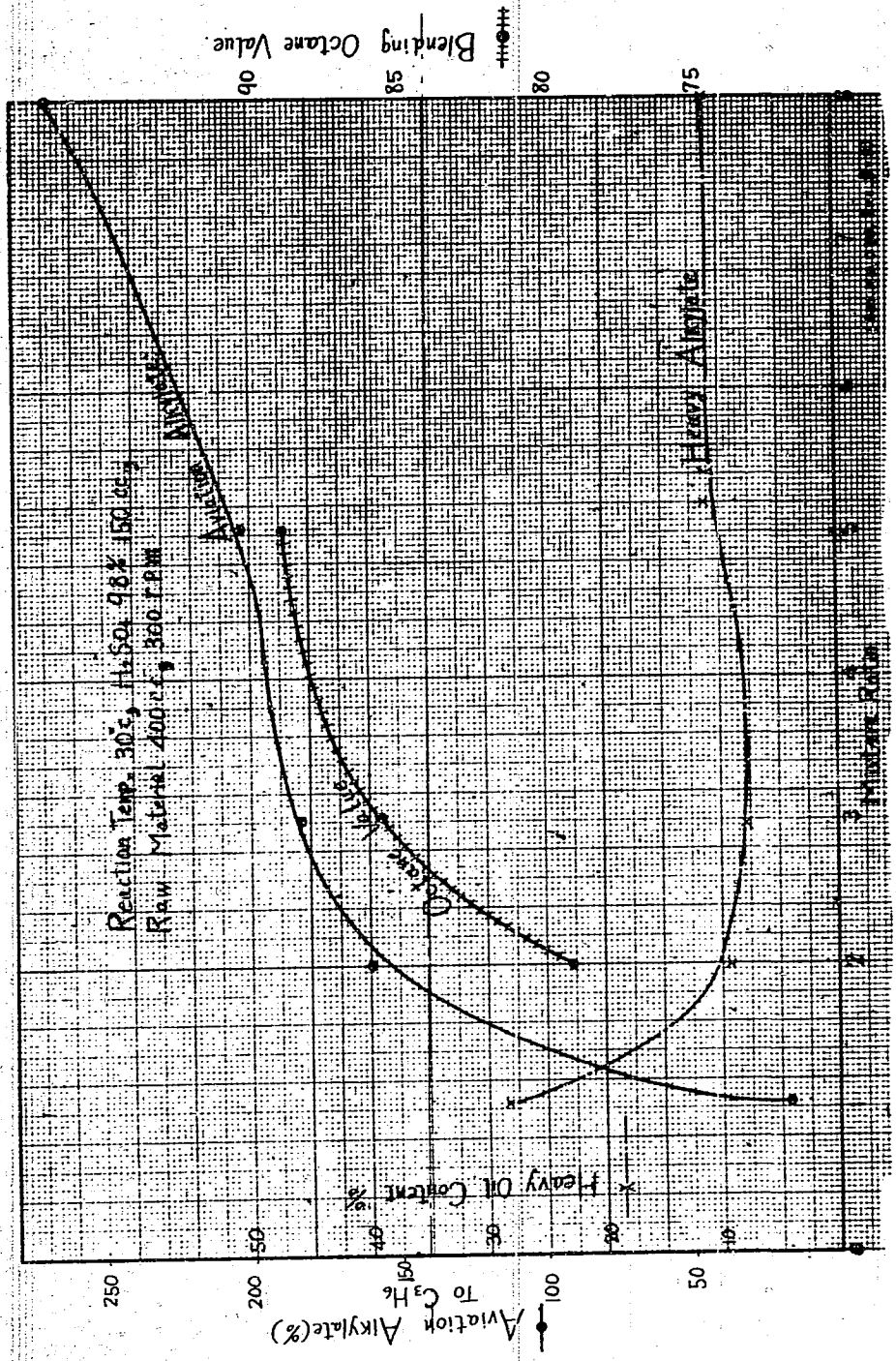


Figure 8(B)8
DIAGRAM OF SWIMMING

ENCLOSURE (B)8



ENCLOSURE (B)8

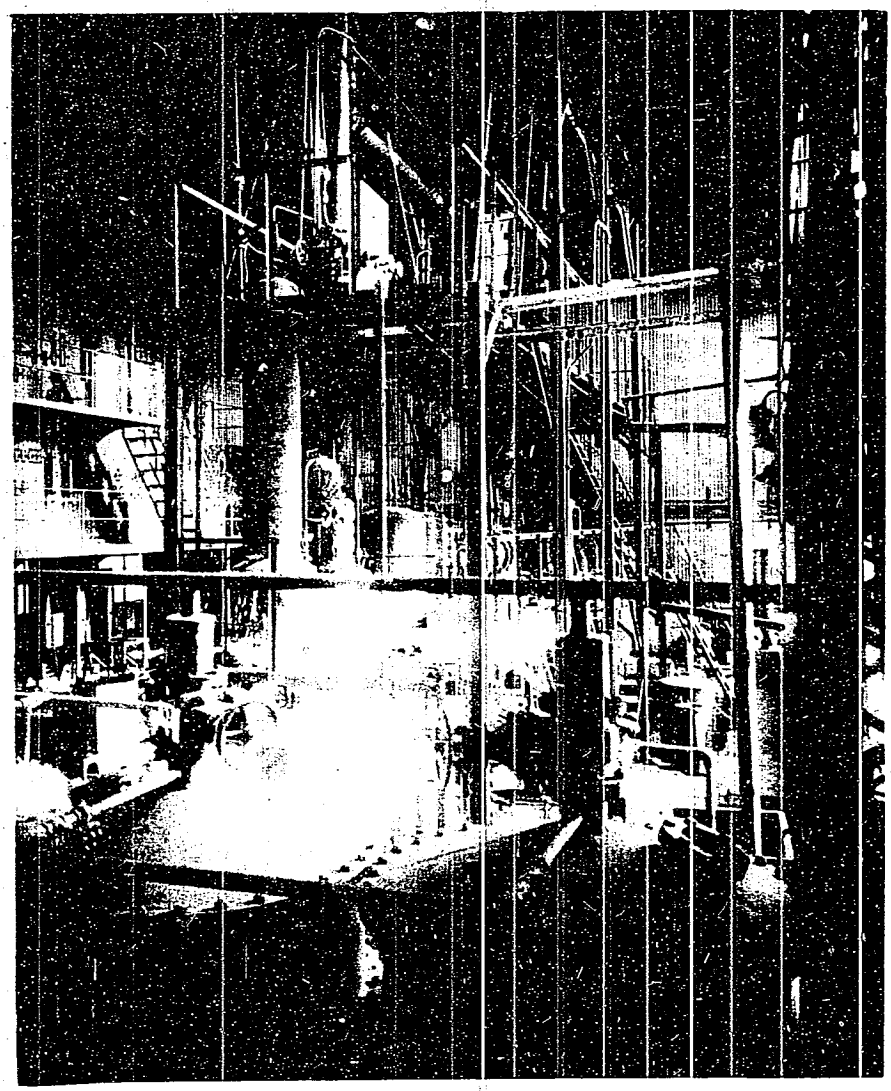


Figure 11(B)8

ENCLOSURE (B)8

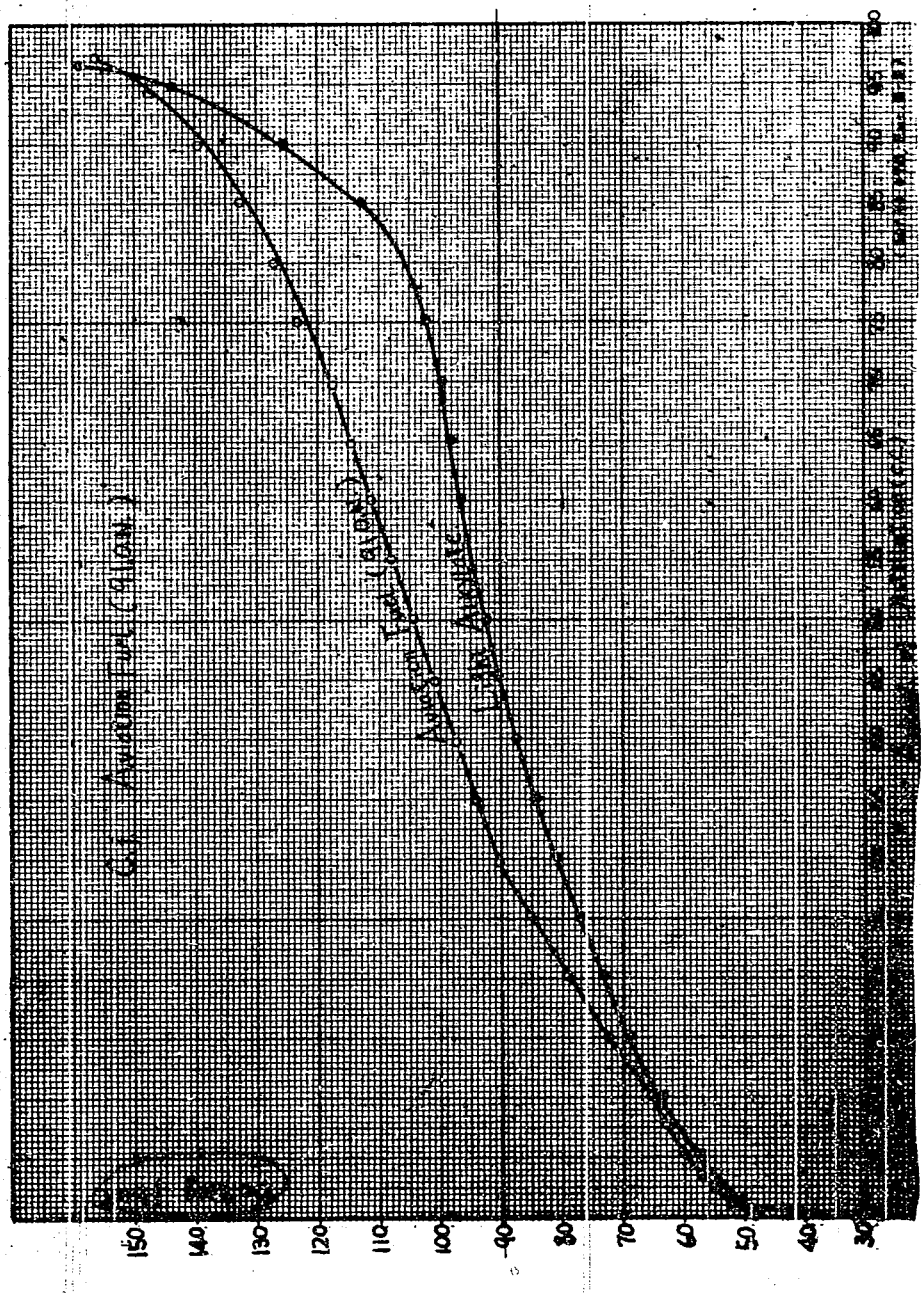
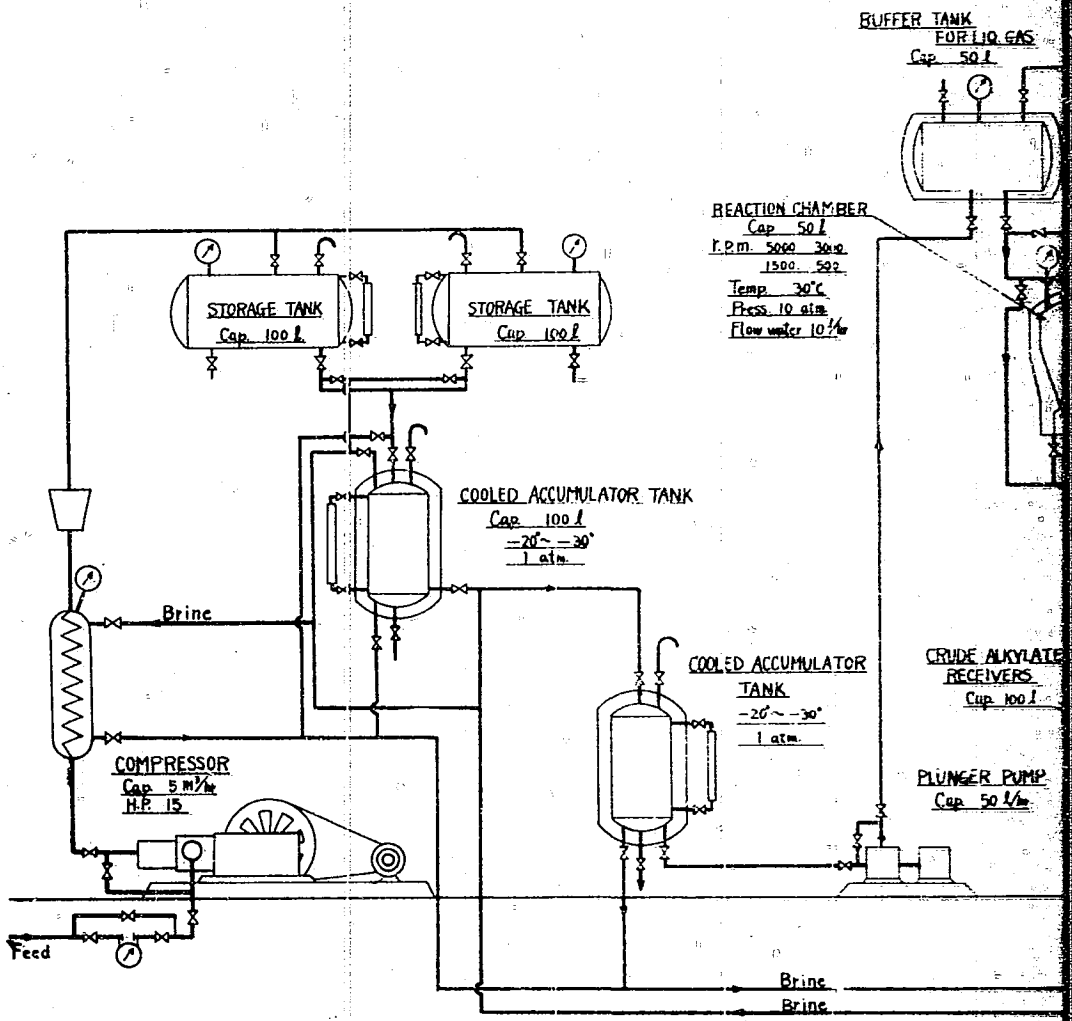
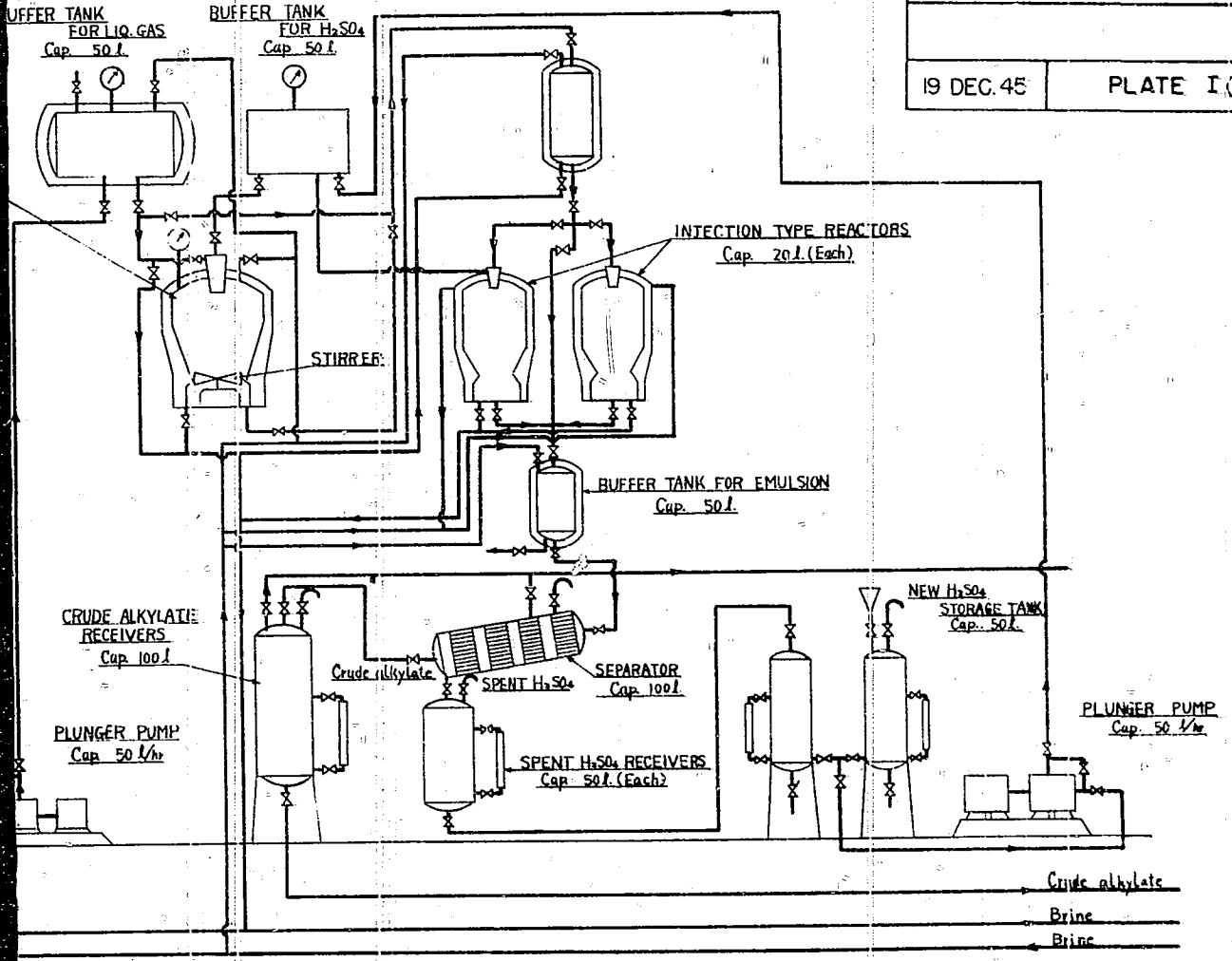


Figure 12(B)8
DISTILLATION CURVE


BUFFER TANK
FOR LIQ. GAS
Cap. 50 l
REACTION CHAMBER
Cap. 50 l
r.p.m. 5000 3000
1500. 500
Temp. 30°C
Press. 10 atm.
Flow water 10 l/hr
STORAGE TANK
Cap. 100 l.
STORAGE TANK
Cap. 100 l
COOLED ACCUMULATOR TANK
Cap. 100 l
-20°~-30°
1 atm.
Brine
COOLED ACCUMULATOR
TANK
-20°~-30°
1 atm.
CRUDE ALKYLATE
RECEIVERS
Cap. 100 l
COMPRESSOR
Cap. 5 m³/hr
H.P. 15
PLUNGER PUMP
Cap. 50 l/hr
Feed
Brine
Brine

U.S. NAVAL TECHNICAL MISSION TO JAPAN	RESTRICTED
REACTION SECTION ALKYLATION PILOT PLANT	
19 DEC. 45	PLATE I (B) 8	X-38(N)-2



ENCLOSURE (B) 9

STUDIES ON THE DESULPHURIZATION OF GASOLINE

by

CHEM. ENG. LIEUT. N. SAKODA

Research Period: 1943

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

December 1945

ENCLOSURE (B)9

LIST OF TABLES AND ILLUSTRATIONS

Table I(B)9 Experimental Results ..... Page 126

Figure 1(B)9 Experimental Apparatus for Desulphurization ..... Page 127

ENCLOSURE (B)9

SUMMARY

Cracked gasoline from midway petroleum, with 0.032% total sulphur content, was desulphurized over a catalyst named "Redgel" in a small continuous-type apparatus, and 50-60% of the total sulphur was removed. The catalyst life was greater than 10 days. The catalyst showed no selectivity with regard to type of sulphur compound removed.

I. INTRODUCTION

A. History of Project

It is a well known fact that sulphur in gasoline retards the catalytic activity of nickel hydrogenation catalyst and also reduces the antidetonating effectiveness of tetraethyl-lead. Among many investigations on the desulphurization of gasoline, that of Chem. Eng. Lieut. FURUYA is worthy of mention. He used an Fe-Si catalyst named "Redgel" which had remarkable adsorptive capacity for sulphur compounds in gasoline. The present investigation was undertaken to confirm these results using a small continuous-type apparatus.

This work was carried on from April to September 1943.

B. Key Research Personnel Working on Project

Eng. Chem. Capt. S. YAMAGUCHI

Eng. Chem. Lieut. N. SAKOTA

II. DETAILED DESCRIPTION

A. Test Apparatus and Procedure

The apparatus used in the experiment is shown in Figure 1(B)9. The reaction tube (B) contains 30 iron dishes, of dia. 10cm and depth 3cm, holding the catalyst "Redgel". The preheater and reaction tube were both heated electrically.

The gasoline to be desulphurized was heated to 200°C in the preheater and the vaporized gasoline came into contact, at a rate of 7 l/hr, with 10 kg of catalyst heated to 200°C. The reaction product was tested for sulphur content each 24 hours.

B. Catalyst Preparation

One molar ferrous sulphate solution was poured slowly into one molar sodium silicate solution and the gelatinous precipitate formed was filtered, water-washed, and dried for six hours at 105-106°C.

The dried catalyst was formed into pellets 3mm in height and 5mm in diameter.

C. Experimental Results

The experimental results are summarized in Table I(B)9.

By processing midway cracked gasoline, which contained 0.032% total sulphur (ASTM lamp method), over "Redgel" catalyst, 50-60% of the sulphur was removed. The approximate amounts of elementary sulphur, mercaptans,

ENCLOSURE (B)9

Table I(B)9
EXPERIMENTAL RESULTS

	Feed Stock	Day									
		1	2	3	4	5	6	7	8	9	10
Total Sulphur (%)	0.032	0.015	0.014	0.015	0.013	0.013	0.015	0.014	0.014	0.013	0.014
H_2S	0.005		0		0		0		0		0
Elementary Sulphur	0.002		0.001		0.001		0.001		0.001		0.001
Mercaptan	0.007		0.003		0.003		0.004		0.003		0.003
Disulphide	0.006		0.004		0.003		0.003		0.003		0.003
Thiophene	0.012		0.006		0.006		0.007		0.007		0.007
Percent of Desulphurization		53	56	53	59	59	53	56	56	59	56

ENCLOSURE (B)9

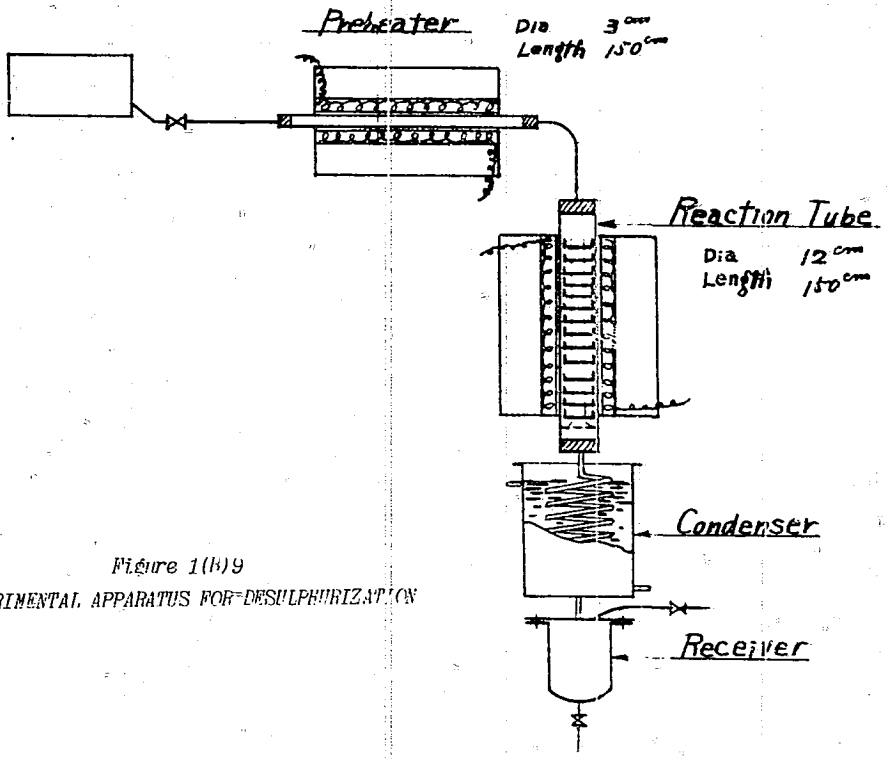


Figure 1(B)9
EXPERIMENTAL APPARATUS FOR DESULPHURIZATION

disulphides and thiophenes removed, were 50%, 40%, 70%, and 50%, respectively.

No commercial application has been made of this process, and to the author's knowledge, no large-scale gasoline catalytic desulphurization units of any type have been installed in Japan.

ENCLOSURE (B) 10

STUDIES ON THE SYNTHESIS OF ISOOCTANE FROM ACETYLENE

by

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CHEM. ENG. LT. COMDR. S. SETO

Research Period: 1940 - 1945

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

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ENCLOSURE (B)10

SUMMARY

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

I. INTRODUCTION

A. History of Research

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

B. Key Research Personnel Working on Project

Chem. Eng. Capt. Dr. FUJIO

Chem. Eng. Lt. Comdr. T. YAMAMOTO

Chem. Eng. Lt. Comdr. S. SETO.

II. DETAILED DESCRIPTION

A. On the Synthesis of Acetaldehyde from Acetylene

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

1. Procedure

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

2. Results

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

ENCLOSURE (B)10

Table I(B)10
EFFECT OF REACTION TEMPERATURE

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

Composition of Cat. Sol ..... 4 gm of $HgSO_4$ in 100cc of 25% H_2SO_4
Vol. of Cat. Sol. taken 260cc
Vol. of C_2H_2 absorbed ..... 1 lit.

Above data are plotted in Figure 1(B)10

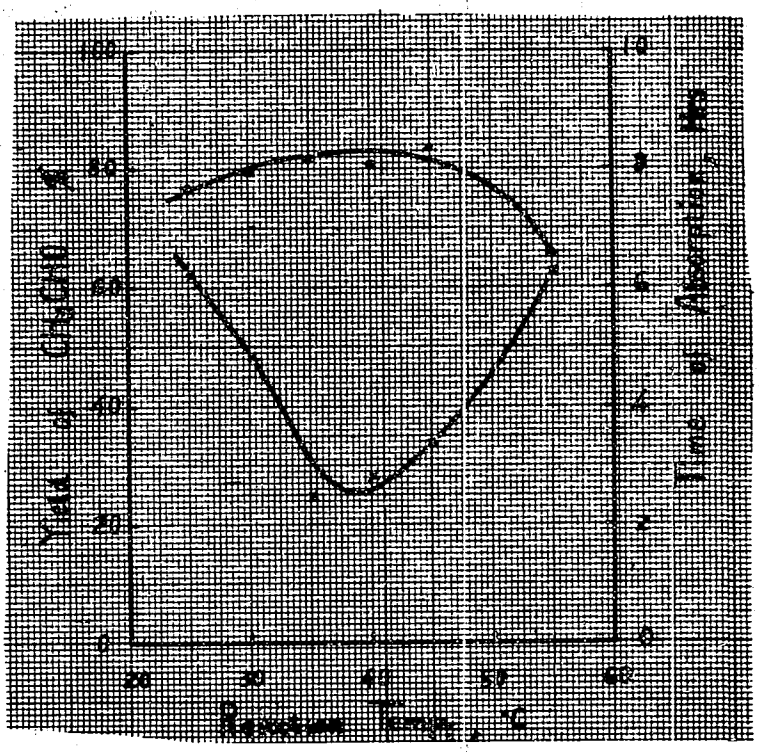


Figure 1(B)10
REACTION TEMPERATURE, °C

ENCLOSURE (B)10

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

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

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

Above data are plotted in Figure 2(B)10

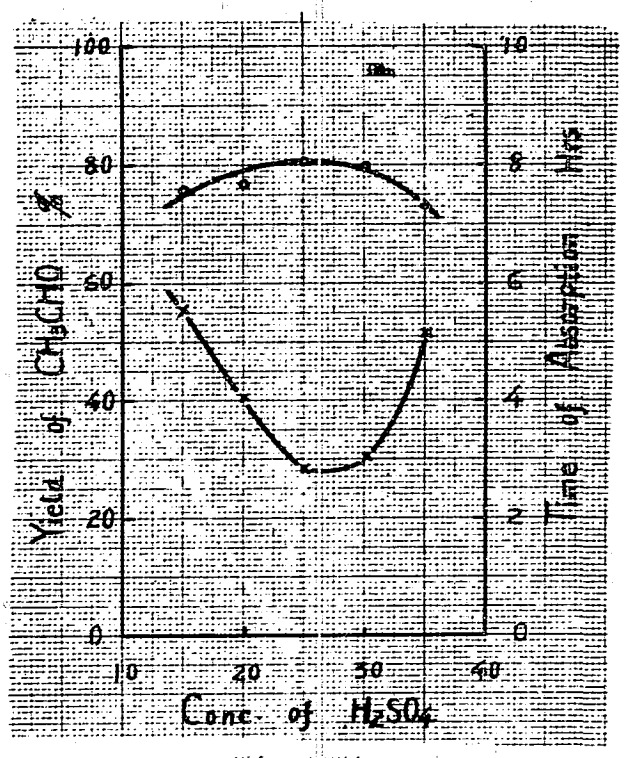


Figure 2(B)10

EFFECT OF CONCENTRATION OF H_2SO_4

ENCLOSURE (B)10

Table III(B)10
EFFECT OF CONCENTRATION OF H_2SO_4 IN CAT. SOL.

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

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

Above data are plotted in Figure 3(B)10

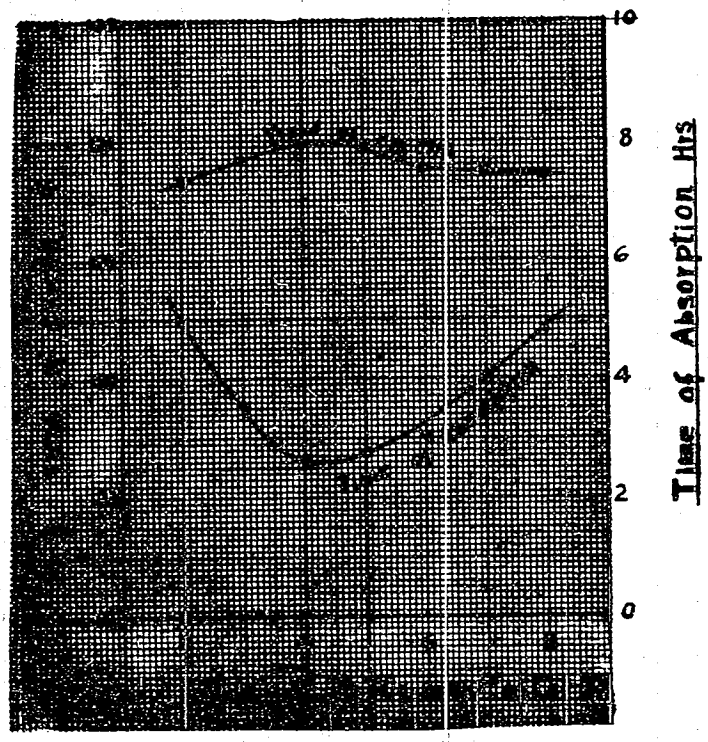


Figure 3(B)10
EFFECT OF CONCENTRATION OF $HgSO_4$ IN CATALYTIC SOLUTION

ENCLOSURE (B)10

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

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

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

Above data are plotted in Figure 4(B)10

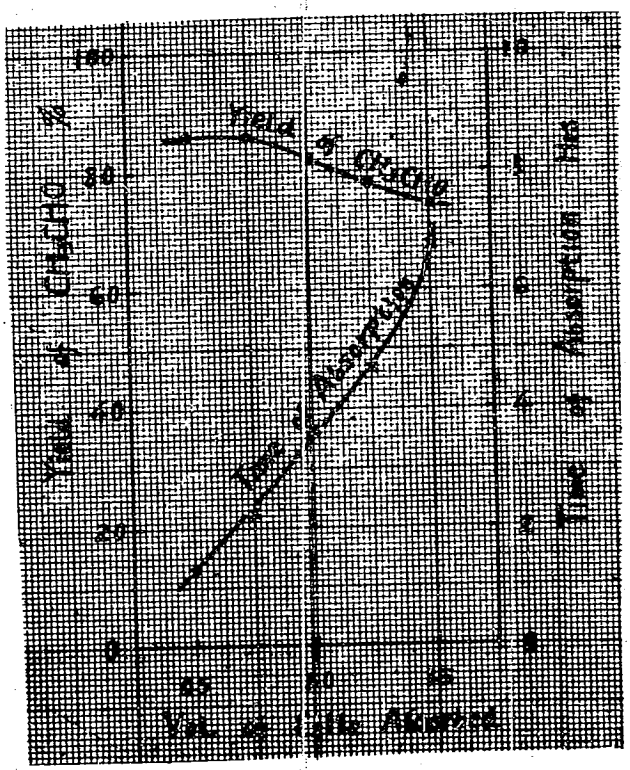


Figure 4(B)10
EFFECT OF VOLUME OF C_2H_2 ABSORBED

ENCLOSURE (B)10

Table V(B)10
EFFECT OF ADDITION OF CH_3COOH

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

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

Above data are plotted in Figure 5(B)10

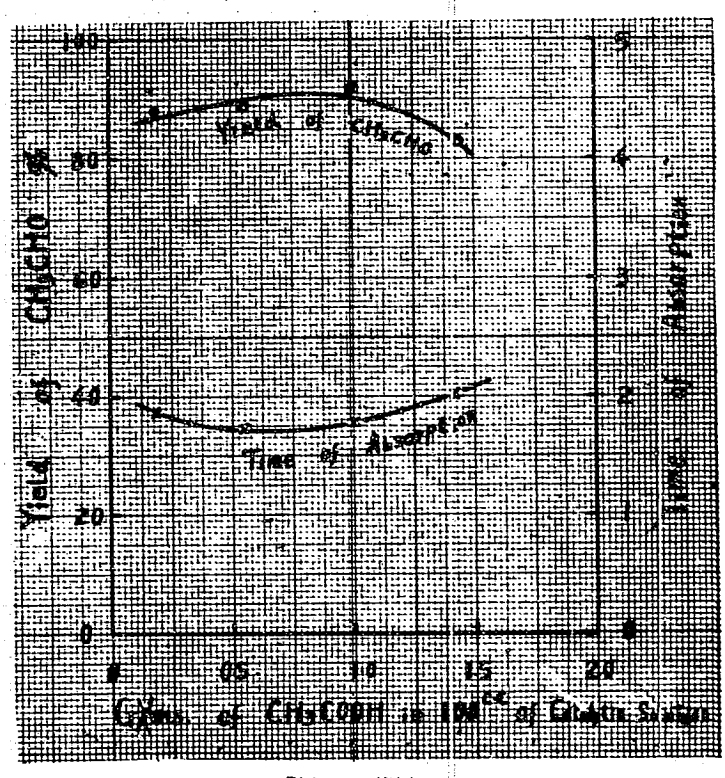


Figure 5(B)10
EFFECT OF ADDITION OF CH_3COOH

ENCLOSURE (B)10

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

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

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

Above data are plotted in Figure 6(B)10

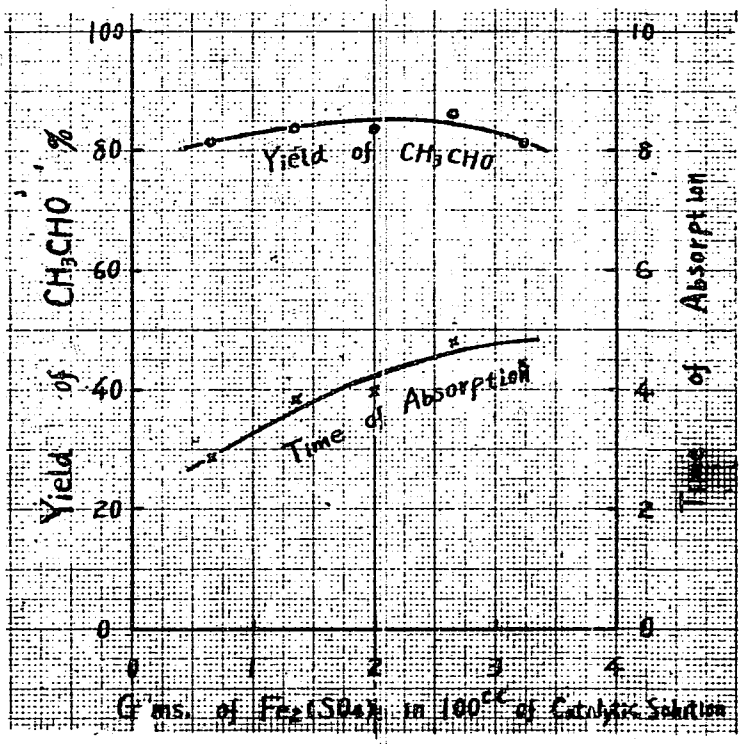


Figure 6(B)10
EFFECT OF ADDITION OF $Fe_2(SO_4)_3$

ENCLOSURE (B)10

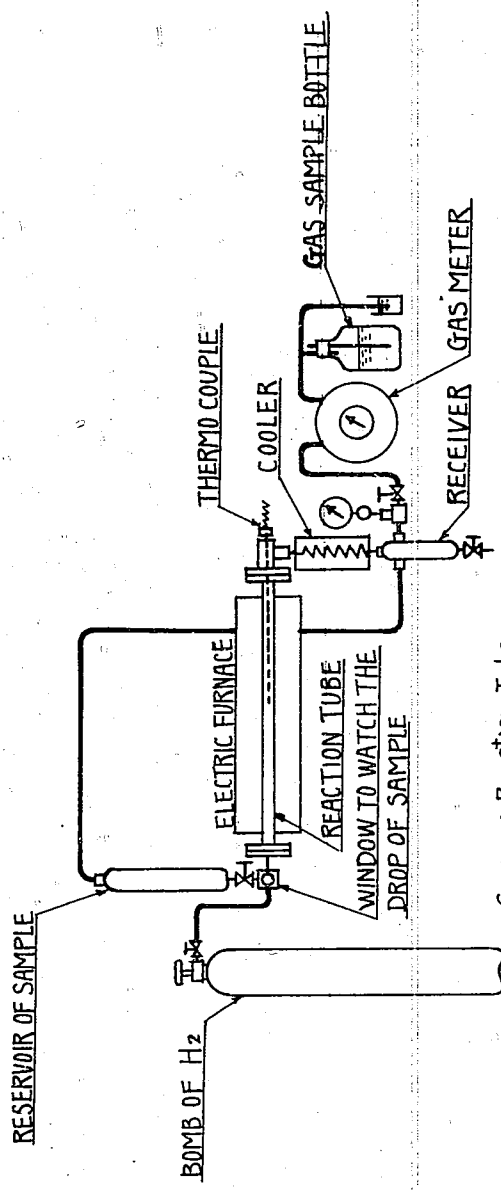


Figure 7(B)10

HIGH PRESSURE HYDROGENATION APPARATUS FOR CROTONALDEHYDE TO BUTANOL

ENCLOSURE (B)10

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

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

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

3. Conclusions

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

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

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

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

e. The optimum reaction temperature is 40°C.

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

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

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

B. On the Synthesis of Crotonaldehyde from Acetaldehyde

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

ENCLOSURE (B)10

1. The Experimental Procedure was as Follows

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

2. Experimental Results

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

3. Conclusions

From these experiments the following conclusions were made:

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

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

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

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

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

ENCLOSURE (B)10

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

	Experiment No.						
	1	2	3	4	5	6	7
Vol. of NaOH sol. added (cc)	6	8	10	12	16	20	25
Time required for addition (min.)	6	8	35	37	47	45	50
CH_3COH reacted (%)	8.0	38.0	68.5	72.0	74.4	76.0	75.6
Wt. of Crotonaldehyde obtained (gm)	9.5	113.4	230.6	242.9	253.9	268.3	256.6
Yield of crotonaldehyde to theoretical (%)	29.5	78.3	82.1	84.8	85.5	86.8	85.3
Residue and loss. (%)	19.0	7.9	6.6	7.3	8.3	10.8	5.2

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

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

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

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

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

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

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

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

C. On the Hydrogenation of Crotonaldehyde to Butanol

1. Hydrogenation at Ordinary Pressures

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

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

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

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

2. Hydrogenation under Pressure

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

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

a. For hydrogenation at ordinary pressures:

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

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

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

b. For hydrogenation at 10 atmospheric pressure:

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

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

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

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

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

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

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

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

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

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

ENCLOSURE (B)10

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

Catalyst	React. Temp. °C	Time of Exp. hr.	Wt. of Crotonaldehyde Used (gm)	Vel. of Crotonaldehyde gms. per gm of Cat.	Vel. of H_2 in l. per H_2	Consumption of H_2 in l.	Ratio of H_2 used to Theoretical	Wt. of product in gms.	% of Fract. below 105°C	% of Fract. of 105 - 120°C	% of Loss and Residue	d_4^{20} of Fract. of 105 - 120°C	n_D^{20} of Fract. of 105 - 120°C	% of CO in Waste H_2	% of CH_4 in Waste H_2
Cu 3, Ni 1, Diatm. Earth 4 Reduced at 180°C	160	5	59	0.78	29	31.2	4	54.0	17.4	78.0	4.6	0.828	1.3940		
	180	6	73	0.81	29	40.7	4	65.0	13.4	85.0	1.6	0.823	1.3940		
	210	6	66	0.73	29	44.5	4	64.0	13.4	86.5	0.1	0.822	1.3918	1.1	2.5
	230	4	44	0.73	29	23.7	4	42.3	17.0	81.0	2.0	0.824	1.3200	3.0	4.2
	250	4	44	0.73	29	24.6	4	42.0	16.4	74.5	9.1			10.3	9.7
Cu 2, Ni 2, Diatm. Earth 4 Reduced at 180°C	130	4	46	0.77	29	25.0	4	42.0	14.4	82.0	3.6	0.815	1.3973		
	160	4	50	0.83	29	27.9	4	46.0	11.3	85.0	3.7	0.843	1.3970		
	180	3	36.5	0.81	29	20.8	4	35.0	12.6	83.5	3.9	0.823	1.3928	0.7	
	200	4	47.0	0.79	29	24.8	4	44.0	16.2	82.0	1.8	0.829	1.3930	2.4	3.6
Ni 1, Diatm. Earth 4 Reduced at 300°C	100	4	44.0	0.73	28	25.2	4	43.0	26.1	72.0	1.9				
	130	4	46.0	0.77	28	25.5	4	44.0	15.2	82.5	2.3				
	160	4	44.0	0.73	28	24.9	4	43.0	13.6	86.0	0.4				
	180	4	44.0	0.73	28	24.0	4	43.0	13.7	84.5	1.8			3.5	6.1
	200	4	43.0	0.72	28			10.0	9.0					15.7	19.1
Cu 1, Ni 3, Diatm. Earth 4 Reduced at 180°C	100				29				27.4	71.0					
	130				29				22.8	75.5					
	160				29				16.7	82.0					
	180				29				15.1	81.5				3.6	5.8
	200				29									12.1	10.2
Cu 3, Ni 1, Diatm. Earth 4 Reduced at 300°C	180	5	85.0	1.13	32.0	39.5	3	80.0	38.7	60.0	1.3				
	180	6	73.0	0.81	30.0	40.7	4	65.0	13.4	85.0	1.6	0.8232	1.3940		
	180	4	47.0	0.78	35.0	26.3	5	44.0	4.9	91.5	3.6				
	180	4	48.0	0.80	42.0	29.1	6	44.0		91.0	9.0				
Cu 1, Ni 1, Diatm. Earth 2 Reduced at 180°C	180	3	36.5	0.81	28	20.8	4.0	35.0	12.6	83.5	3.9	0.8227	1.3928		
	180	4	32.0	0.53	28	18.3	5.5	32.0	5.4	90.9	3.7	0.8244	1.3905		
	180	7	42.0	0.40	28	25.8	7.0	42.0	4.5	93.0	2.5	0.8244	1.3920		

ENCLOSURE (B)10

Table XI(B)10

EXPERIMENTAL DATA ON HYDROGENATION OF CROTONALDEHYDE UNDER PRESSURE

Composition of Catalyst	Temp. of Reduct. of Catalyst °C	React. Temp. °C	Vol. of Liq. Croton per Vol. of Cat. per hr.	Time of Exp. hrs.	Wt. of Croton-aldehyde gms.	Vol. of Hydrogen l. per hr.	Vol. of Hydrogen l.	Wt. of Product gms.	% of Fract. In Product duct below 105°C	% of Fract. 115 - 120°C in Product	% of Loss and Residue	Vol. of Waste Hydrogen l.	% of CO in Waste Hydrogen	% of CH_4 in Waste Hydrogen	% of crotonaldehyde in Product	Note: Wt. of Cat. Used was 20 gms. Press. of Hydrogen was 10 atms. gauge. Anhydrous Crotonaldehyde was Used.	Note: Croton. Sat. with Water was Used. The others, Same as Above
Cu 3 Ni 1	140	140	0.40	7	120.3	19.4	135.8	121.2	19.8	77.3	2.9	61.5	0.7	3.2	0		
Cu 3 Ni 1 MgO 8	180 160 140 120	180 160 140 120	0.47 0.47 0.46 0.64	7 7 7 5.7	112.0 112.5 109.0 123.5	24.7 28.6 19.0 18.6	172.8 200.0 133.4 104.4	60.0 70.5 91.9 113.5	17.5 17.0 17.1 68.0	74.0 66.0 79.6 21.0	12.5 17.0 3.3 9.0	124.0 128.0 69.2 50.7	4.2 8.5 1.2	7.1 4.0 4.2	0 0 0 36.6		
Cu 3 Ni 1 Clay 16	140	130	0.46	7	111.0	18.5	129.7	90.0	26.0	59.0	12.0	65.8	3.6	6.5	1.0		
Cu 3 Ni 1 MgO 8	180 180 180	160 140 140	0.32 0.36 0.49	6 7 7	93.4(1) 122.0 123.5	23.6 24.6 24.0	141.3 172.2 168.2	83.0 114.0 116.5	6.0 5.0 7.2	91.5 92.0 89.7	2.5 3.0 8.1	89.5 100.5 93.3	3.1 2.2 1.6	4.5 2.5 2.0	0 0 5.7		
Ni 65 Diatm. Earth 30 Graphite 3 a.o.p. type	180 180 180 180 180	100 110 160 120 130	0.22 0.32 0.31 0.34 0.43	6 6 6 6 5	85.0 93.0 89.5 98.5 104.0	26.3 28.8 18.0 28.0 33.3	157.5 172.8 108.0 168.0 166.7	81.0 91.5 17.0 80.0 91.0	12.4 9.2 90.0 13.1 10.5	79.0 83.0 0.0 83.0 84.0	8.6 7.8 10.0 3.9 5.5	116.0 120.0 106.0 111.0 111.5	1.2 0.8 1.1 0.1 1.7	4.9 2.0 53.1 3.9 6.2	0.04 0.03 0 0 0		
Cu 3 Ni 1 MgO 8	180 180 180 180 180 180 180	160 160 160 140 140 140 140	0.38 0.55 0.80 0.40 0.63 0.77	6 4 3 6 4 3	106.5 106.0 115.5 115.5 120.0 111.0	31.4 42.5 57.0 33.2 47.0 62.0	188.0 169.5 176.5 197.0 189.0 186.5	105.5 94.5 94.5 127.0 125.0 123.0	* 83.6 83.1 76.8 96.8 64.1 50.8	** 5.4 4.8 10.9 10.5 20.0 28.1	# 8.2 10.4 11.6 11.1 11.6 7.3	127.0 119.5 119.0 127.0 120.0 120.5	1.6 5.7 7.4 0.5 1.5 1.1	1.0 6.9 10.0 0.5 2.1 1.2	## No Slightly Slightly Slightly Faint Slightly		

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

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

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

ENCLOSURE (B)10

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

a. Apparatus and procedure.

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

b. Experimental results.

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

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

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

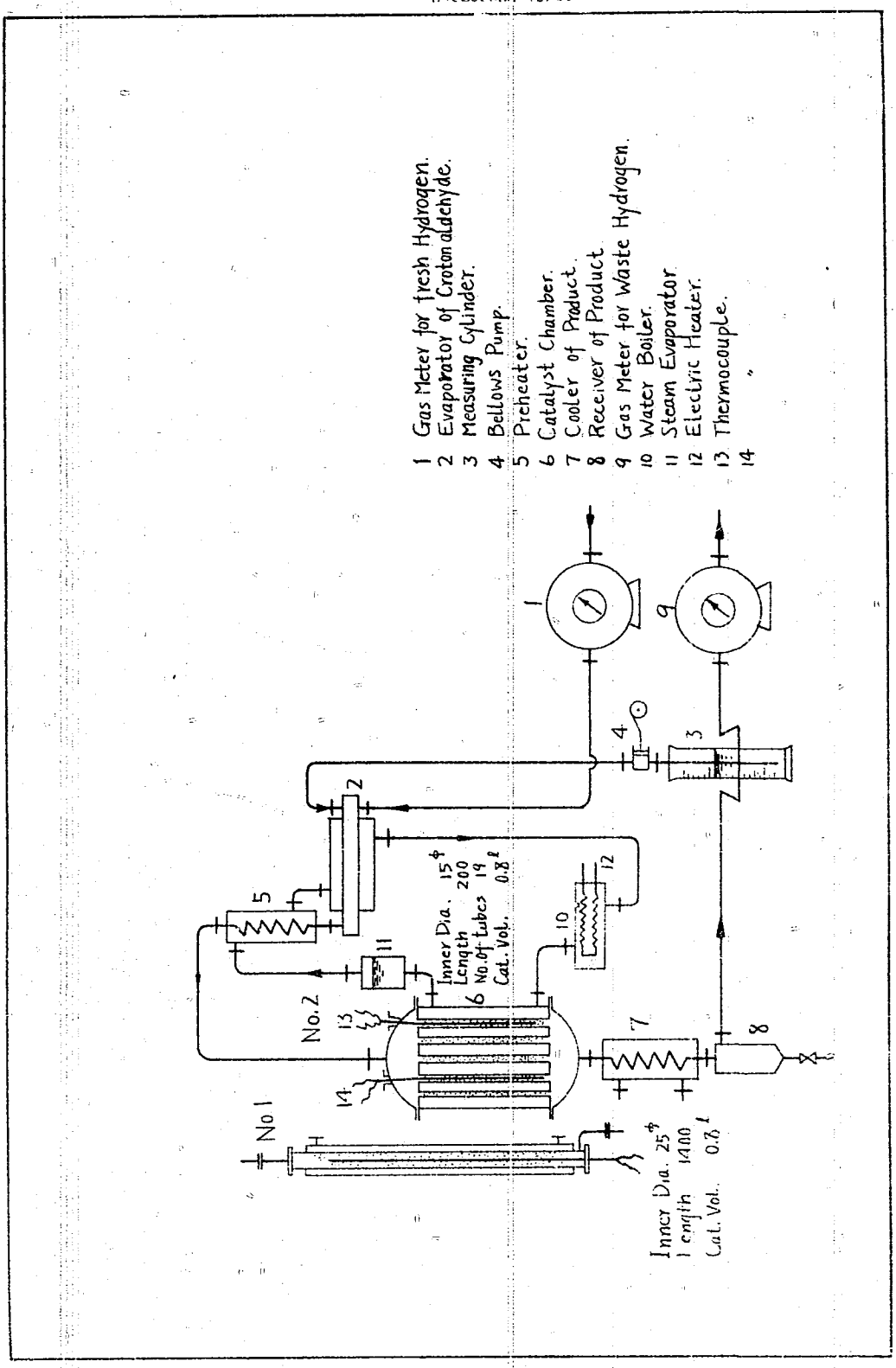
(3) The velocity of crotonaldehyde was 0.25 litre (liquid) per one litre of the catalyst per hour.

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

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

CO_2 ..... 0.0	CO ... 9.0	C_2H_{2n-2} ... 10.7
O_2 ..... 0.4	H_2 ... 78.4	N_2 ..... 1.1
C_nH_{2n} ... 0.8		

ENCLOSURE (B) 10



ENCLOSURE (B)10

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

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

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

Time Elapsed (hr)	Vel. of Liq. Croton-aldehyde in Lit./hr	Vel. of Hydrogen in Lit./hr	Purity of Hydrogen (%)	Vol. of Hydrogenated Product in Lit./hr	% of Butylaldehyde Fract. in Product	% of Crotonaldehyde Fract. in Product	Vel. of Waste Hydro-gen in Lit./hr	Purity of Waste Hydrogen (%)	Temp. of Upper Part of Reac. Tube	Temp. of Lower Part of Reac. Tube
4	1.148/4	2696/4	78.0	0.980/4	0.0	0.0	2242/4	73.3	160	145
28	2.296/8	5392/8	85.4	2.133/8	0.9	0.4	4490/8	79.2	170	150
68	2.296/8	5392/8	86.0	2.280/8	0.0	0.9	4556/8	79.0	165	150
100	2.296/8	5392/8	84.6	2.215/8	0.0	0.6	4467/8	74.1	165	150
140	2.296/8	5392/8	80.7	2.220/8	0.3	0.4	4022/8	72.9	165	150
186	2.296/8	5554/8	80.7	2.100/8	0.0	1.2	4613/8		170	160
234	2.296/8	5462/8	88.0	2.240/8	0.0	0.9	4652/8	87.0	175	155
314	2.296/8	5605/8	83.0	2.345/8	0.0	0.9	4387/8	80.3	170	160
335	2.296/8	4044/8	91.6	2.250/8	0.0	1.5	4487/8		170	165
399	2.296/8	4044/8	98.6	2.370/8	0.0	0.6	2780/8	93.0	170	160
431	2.296/8	4147/8	95.3	2.500/8	0.3	1.2	2933/8	90.0	170	160
471	2.296/8	4065/8	90.6	2.320/8	0.3	0.9	3048/8	83.3	170	160
503	2.296/8	4257/8	90.6	2.448/8	1.8	2.1	3313/8	83.3	178	160

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

c. Conclusions.

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

D. On the Preparation of Butene from n-Butanol

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

1. Apparatus and Procedure

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

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

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

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

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

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

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

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

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

The butanol used had the following constants:

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

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

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

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

2. Experimental Results

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

3. Conclusions

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

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

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

ENCLOSURE (B)10

1. Experimental Procedure

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

The composition of gas produced was as follows.

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

The catalyst was prepared by the following method.

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

2. Experimental Results

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

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

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

F. On the Catalytic Polymerization of Butene under Pressure

1. Apparatus and Procedure

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

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

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

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

ENCLOSURE (B)10

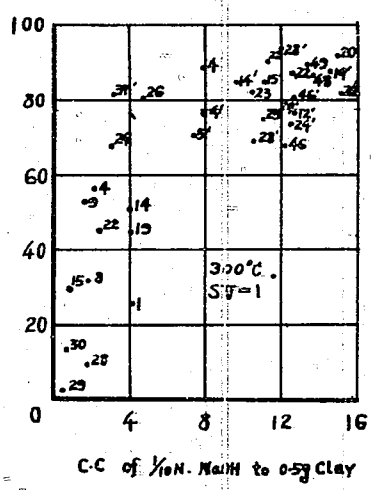


Figure 9(B)10
Yield of Butene to Theoretical

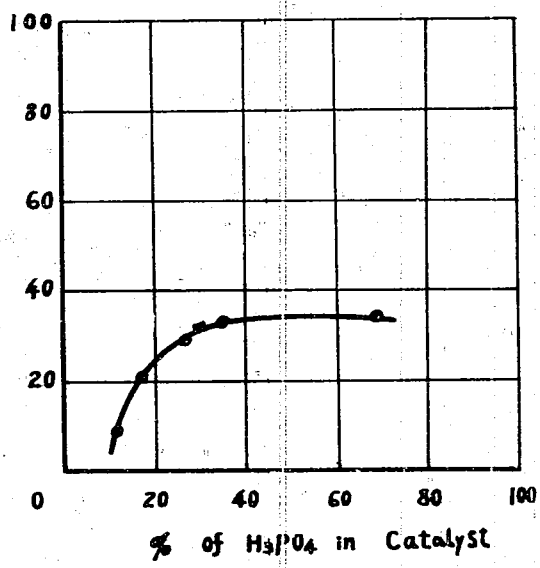


Figure 10(B)10
% of i-C_4H_8 in Gas Produced

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

2. Experimental Results

a. The effects of the pressure on the polymerization.

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

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

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

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

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

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

ENCLOSURE (B)10

Table XIX(B)10
POLYMERIZATION UNDER VARIOUS PRESSURES

(Reaction Temperature 120°C)

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

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

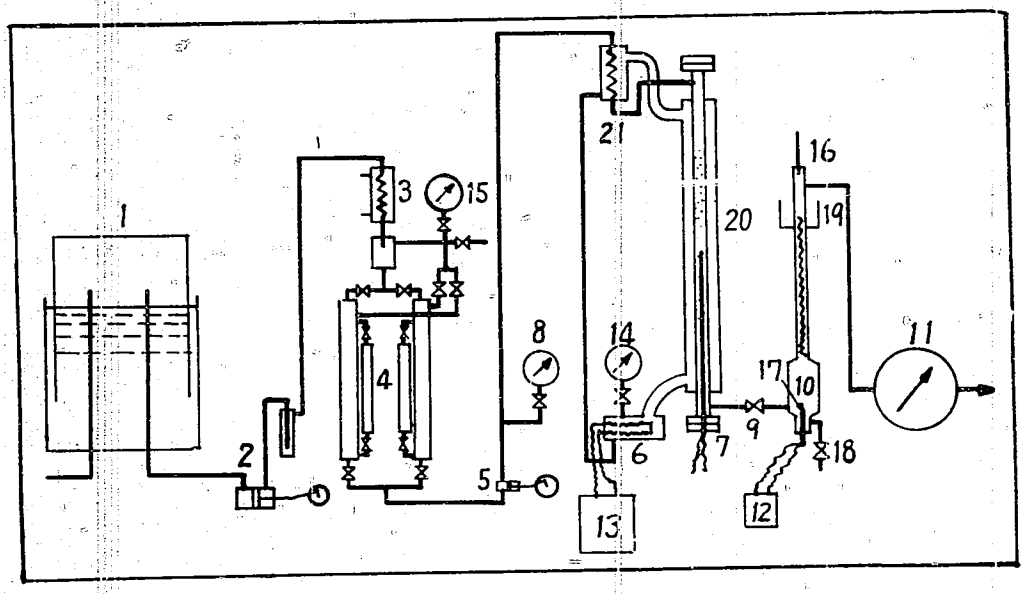
Table XX(B)10
POLYMERIZATION UNDER VARIOUS PRESSURES

(Reaction Temperature 150°C)

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

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

ENCLOSURE (B) 10



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

Figure 11(B)10

APPARATUS FOR PRESSURE HYDROGENATION OF BUTENE TRIMER

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

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

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

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

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

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

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

ENCLOSURE (B)10

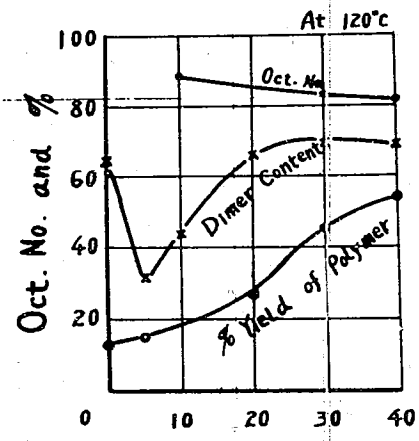


Figure 12(B)10

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

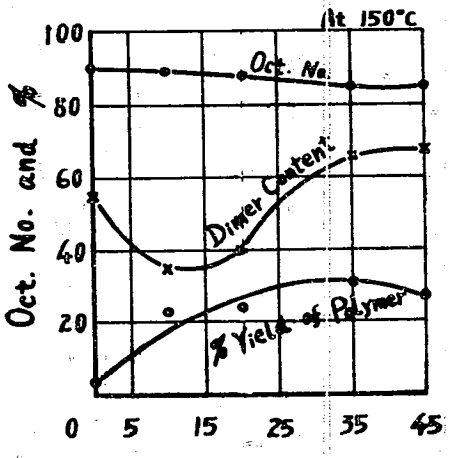


Figure 13(B)10

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

ENCLOSURE (B)10

Table XXI(B)10
POLYMERIZATION UNDER VARIOUS PRESSURES

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

Table XXII(B)10
POLYMERIZATION AT VARIOUS SPACE VELOCITIES

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

ENCLOSURE (B)10

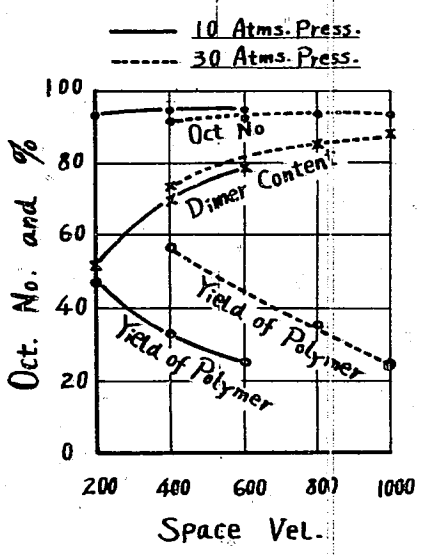


Figure 14(B)10
OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

Table XXIII(B)10
POLYMERIZATION AT VARIOUS SPACE VELOCITIES

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

ENCLOSURE (B)10

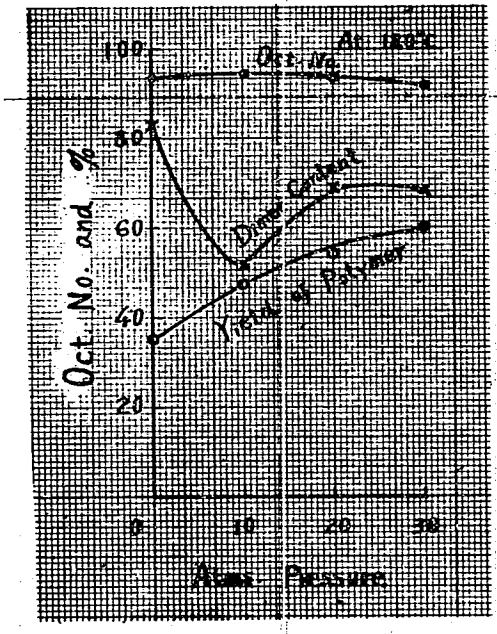


Figure 14

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

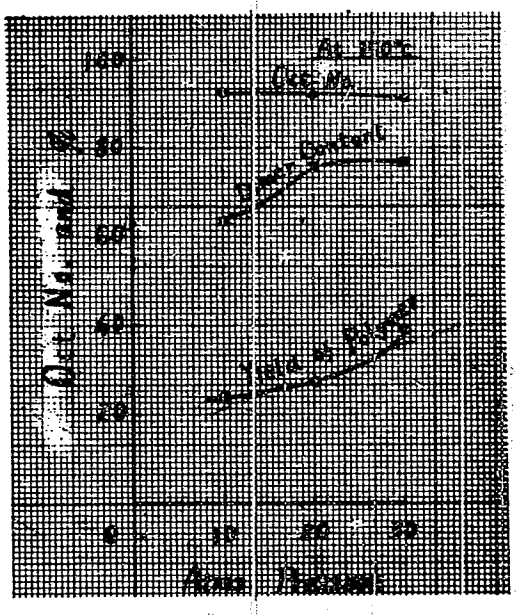


Figure 15

OCTANE NUMBER AND POLYMERIZATION AT VARIOUS TEMPERATURES AND PRESSURES

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

3. Conclusions

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

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

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

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

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

G. The Hydrogenation of Isooctene

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

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

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

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

2. Activities of Various Hydrogenation Catalyst

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

a. Cu-Ni.

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

b. Cu-Ni-Acid clay.

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

c. Cu-Ni-MgO.

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

d. Ni-diatomaceous earth.

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

e. Reduced nickel.

Prepared in usual manner.

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

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

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

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

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

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

ENCLOSURE (B)10

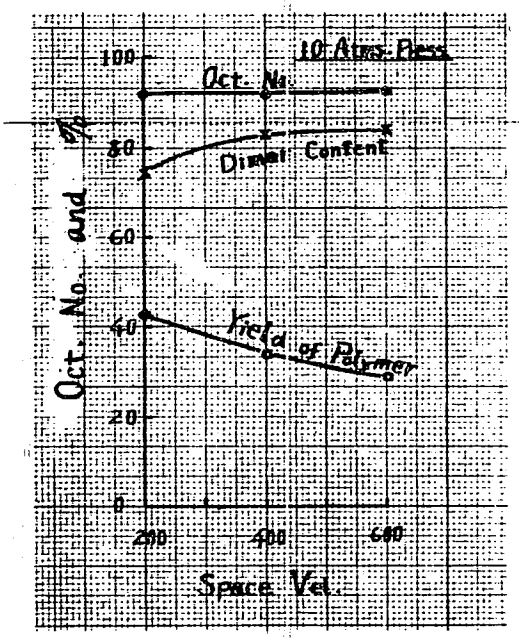


Figure 16

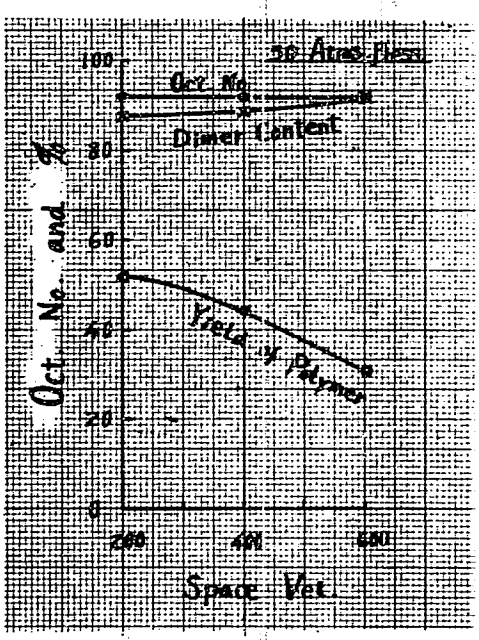


Figure 17

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

3. Pressure Hydrogenation of the Dimer by the Flow Method

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

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

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

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

5. The Pressure Hydrogenation of Butene Trimer

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

ENCLOSURE (B)10

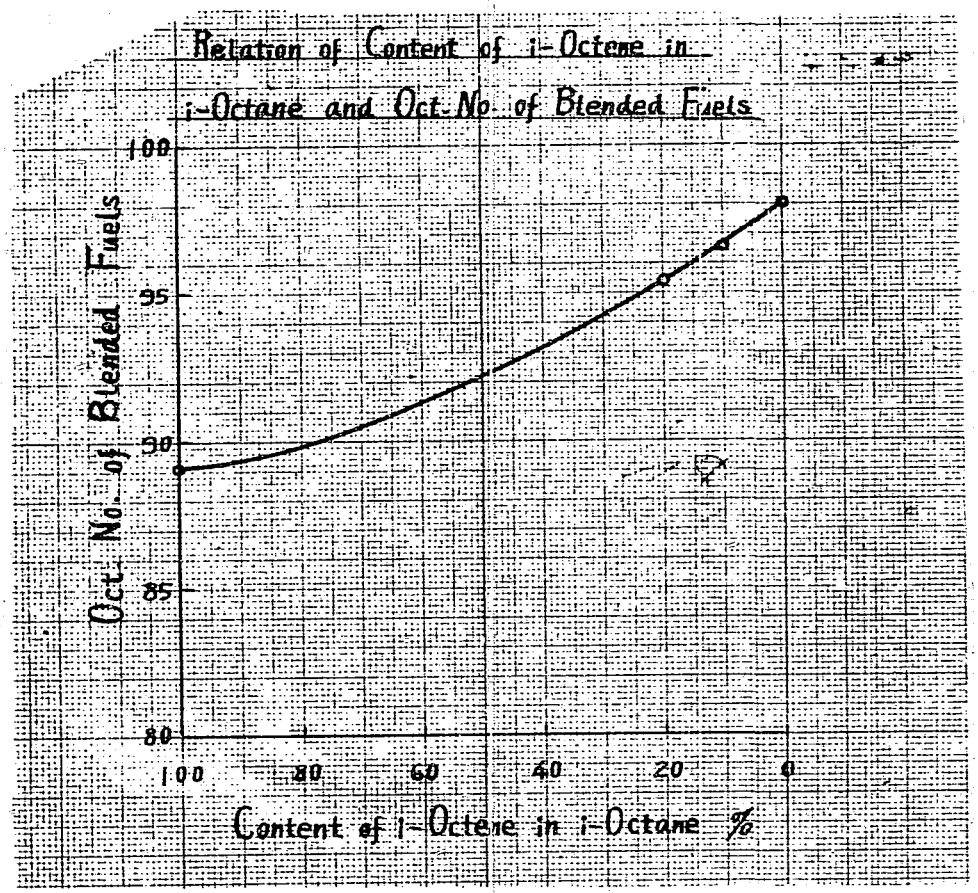


Figure 18

was completed at a temperature or 160 - 180°C, a pressure of 10 - 20 kgs/cm^2 and space velocity of the trimer of 0.5 - 1.0. It may be concluded that the hydrogenation of the trimer can be done under nearly the same conditions as the hydrogenation of the dimer.

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

Time of Exp. (hr)	Wt. of Iso-octane used (gm)	Wt. of Iso-octane Produced (gm)	Purity of Waste Hydrogen (%)	Exp. Loss (gm)	Iodine No. of Product	Vol. of Isooctane per Vol. of Cat. per hr
2.5	87.5	29.0	98.5	8.5	1.3	
2.5	72.5	64.5	97.8	8.0	1.6	0.71
1.25	92.5	84.5	98.0	8.0	(1.0)	1.8
1.5	109.0	102.5	98.0	7.5	1.9	3.1
1.0	91.0	81.5	98.0	9.5	8.7	4.5
0.83	91.5	84.5	98.9	7.5	11.4	5.4

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

Mix. Ratio of Hydro. trimer	Distillation Characteristics						Peid Vapour Press kg/cm^2	Octane Number 0.1% leaded
	I.b.p.	10%	50%	90%	97%	Sum. of 10+50+90%		
0	50.0	63.3	94.0	122.5	145.0	285.8	0.56	92.6
10	49.0	72.0	96.0	135.0	170.0	293.0	0.50	93.3
20	51.0	74.0	103.0	151.0	184.0	328.0	0.43	93.6
30	51.0	74.5	110.0	161.0	182.0	345.5	0.41	94.0

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

Trimer Used (l)	Time of Exp. in (hrs.)	React. Temp. (°C)	Vol. of Trimer (vol./vol. of Cat./hr (hr)	Press (kg/cm2)	Product (l)	Iodine Number of Product
2.210	6	180	0.5	20	2.205	3.7
2.160	6	180	0.5	10	2.059	3.3
2.140	6	160	0.5	10	2.255	4.9
4.320	6	180	1.0	10	4.465	4.0

ENCLOSURE (B) 11

SYNTHESIS OF BUTENE FROM ACETYLENE

by

CHEM. ENG. LT. COMDR.
T. YAMAMOTO

Research Period: 1942-1943

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

December 1945

ENCLOSURE (B)11

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ENCLOSURE (B)11

SUMMARY

Butene was synthesized from vinyl acetylene by partial hydrogenation. Palladium and nickel catalysts for this reaction were compared, and the exact conditions for obtaining high yields of butene and suppressing the formation of butadiene and butane were investigated.

I. INTRODUCTION

Isooctane is synthesized from acetylene through eight steps, acetylene, acetaldehyde, aldol, crotonaldehyde, butanol, butene, isobutene, isooctene and isooctane. This method is troublesome not only because of the long course but also the loss of mercury is unavoidable during the synthesis of acetaldehyde from acetylene. Hence, the manufacture of butene from acetylene through vinyl acetylene was investigated. Butene was prepared by the hydrogenation of vinyl acetylene which was obtained by the catalytic polymerization of acetylene. The catalytic polymerization of acetylene was reported by Niewland, J.A.C.S. 4197 (1931); Klebbanskii, India Rubber J., 10, 16; and Schmidt, Z. Elect. Chem., 45, 503 (1931). Since no additional data of importance were obtained in regard to the preparation of vinyl acetylene from acetylene, this report is only concerned with the partial hydrogenation of vinyl acetylene to butene.

II. DETAILED DESCRIPTION

A. Apparatus and Procedure

A mixture of vinyl acetylene and hydrogen was passed through a glass tube which was heated in an electric furnace. The catalyst was placed in the reaction tube and the temperature was measured at the center of the reaction tube. Vinyl acetylene used was prepared by the catalytic polymerization of acetylene using a well-known cuprous chloride complex salt solution and was purified by redistillation.

B. Analytical Method

The hydrogenated product which contains vinyl acetylene, butadiene, butene, ostane, hydrogen, oxygen, and nitrogen was analyzed by the following method. Vinyl acetylene in 100cc of the sample gas was measured by absorption in an alkaline mercurous cyanide solution. A 25cc portion of the remainder was mixed with 500cc of pure hydrogen and was repeatedly passed through a capillary tube packed with palladium asbestos maintained at 120°C until there was no volume change. The volume of the hydrogen consumed by the hydrogenation of butadiene and butene, and by the combustion with oxygen was measured. Separately, butene and butadiene in another 25cc portion of the remainder from the vinyl acetylene analysis was passed through bromine water, and then the bromine vapor mixed in the sample was removed by a caustic potash solution. The oxygen content was then determined on this sample by absorption in pyrogallol. The percentages of butene, butadiene and oxygen were calculated from the results of the hydrogenation, the bromine absorption and the absorption of oxygen in the pyrogallol solution. Hydrogen was determined by the ordinary combustion method on palladium asbestos. Since the vinyl acetylene used was well purified and the air in the apparatus was replaced carefully by the charging gas, it was regarded that the oxygen and nitrogen in the product came from the atmospheric air after the hydrogenation reaction. Therefore, the amount of the nitrogen in the product was calculated as four times that of the oxygen in the sample. Butane in the product was calculated by the difference of the total volume of the sample taken and the volume of the other components previously measured. These methods were checked exactly with mixed gases having known compositions.

ENCLOSURE (B)11

C. Experimental Results

1. Partial Hydrogenation of Vinyl Acetylene to Butene by Palladium Catalyst

The palladium catalysts, supported on diatomaceous earth having various compositions, were prepared by Willstatter's method.

a. Effect of the concentration of palladium in the catalysts

Table I(B)11 shows the effect of varying concentrations of palladium in the catalysts on the yield of butene

TABLE I(B)11

Pd. Conc. in Cat. (%)	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
5	17	8.0	11.7	79.8	0.5	66.3
0.66	17	3.8	10.4	79.8	6.0	65.9
0.4	11	3.1	8.8	88.1		78.2
0.3	11	7.7	20.0	72.3		64.3
0.2	15	7.0	20.5	72.5		61.4
0.1	9	10.0	11.6	78.4		71.5
0.05	15	5.6	21.7	72.7		61.7
0.025	14	4.6	15.9	79.5		68.0

Wt. of the cat. used ..... 2 grams
Reaction temperature ..... 100°C
Gas velocity .....6 lit/hr/gm of cat
Ratio of hydrogen to vinyl acetylene 2

b. Effect of the reaction temperature

Table II(B)11 shows the effect of the reaction temperature on the yield of butene.

TABLE II(B)11

React. temp.°C	C_4H_4 polymerized	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
30	0	82.8	14.7	2.5		
50	19	3.1	10.8	86.8		70.4
80	12	5.8	12.6	79.5	2.1	70.2
100	15	5.6	21.7	72.7		61.8
145	16	3.6	22.4	74.0		62.3

Pd. in cat. percent 0.05
Wt. of cat. ..... 2 grams
Gas velocity .....6 lit/hr/ gm of cat
Ratio of hydrogen to vinyl acetylene 2

c. Effect of the ratio of the amount of hydrogen to vinyl acetylene on the yield of C_4H_8

The effect of varying amounts of hydrogen to vinyl acetylene is shown in the Table III(B)11.

TABLE III(B)11

H_2/C_4H_4	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
1.2	20	39.9	40.7	14.2	11.3	11.3
2.0	9	10.0	11.6	78.4		71.5
2.3	1	2.0	2.0	88.5	7.6	87.8
2.9	23	1.1		81.9	17.0	63.5
3.9	34	0.7	4.8	69.3	25.2	48.4

Pd. content in cat. percent 0.1
Wt. of cat. ..... 2 grams
Reaction temperature ..... 100°C
Gas velocity ..... 6 lit/hr/gm of cat

d. Effect of the gas velocity

The effect of the gas velocity on the yield of butene is shown in Table IV(B)11.

TABLE IV(B)11

gas. vel. lit/hr/gm of cat.	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
12	12	33.7	33.5	32.8		28.5
6	20	12.0	18.9	69.1		55.2
3	14	4.6	15.9	79.5		67.9
1	22	3.4	6.6	83.9	6.3	65.3
0.5	26	6.8	9.6	68.5	15.1	50.7

React. temp. ..... 100°C
H_2/C_4H_4 2
Pd. conc. in cat. percent 0.05

e. From these experimental results the following conclusions were derived

(1) There was no pronounced effect of the concentration of palladium in the catalyst on the reaction within the limit of the experiments.

(2) No reaction occured below 30°C. The temperature of the reaction must be above 50°C.

(3) The unreacted vinyl acetylene could be decreased to less than 1% when approximately three times as much hydrogen as vinyl acetylene was used.

(4) The formation of butene could be completely suppressed.

(5) In view of the formation of butene at higher ratios the best ratio of the amount of hydrogen to vinyl acetylene appear s to be 0.25.

(6) At the optimum condition the concentration of butene in the C_4 hydrocarbons of the product was 80-90% and 70-75% of the vinyl acetylene was converted to butene.

2. Partial Hydrogenation of Vinyl Acetylene by Nickel Catalyst

The nickel catalyst was prepared by ignition of purified nickel nitrate at 800°C for three hours, and the catalyst was reduced in an atmosphere of hydrogen for three hours before use.

a. Effect of the ratio of hydrogen to vinyl acetylene

When the palladium catalysts were used the ratio of hydrogen and vinyl acetylene showed a pronounced effect on the yield of butene.

Therefore, the effect of the ratio of hydrogen to vinyl acetylene was first examined. The experimental results are shown in Table V(B)11.

TABLE V(B)11

H_2/C_4H_4	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
1.9	55	1.3	17.6	80.2	0.9	36.1
2.3	54	0.5	2.4	95.6	1.5	44.3
2.6	48	0.5	5.5	91.0		48.9
3.1	48	0.6	3.2	86.6	9.6	45.3
3.8	36	0.7		85.7	13.6	58.8
4.0	46	0.9	8.5	67.0	23.6	36.5
4.3	31			60.3	39.7	41.6

Wt. of cat. used ..... 5 grams
Reaction temperature ..... °C
Gas velocity .....6 lit/hr/gm of cat

b. Effect of the reaction temperature

Table VI(B)11 shows the effect of the reaction temperature.

TABLE VI(B)11

React. temp. °C	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
150	48	0.5		91.2	8.3	47.6
100	45	0.4	5.5	94.1		48.8
50	50	1.2	10.4	77.3	11.1	38.9
40	30	1.0	10.2	69.8	19.0	48.9

Wt. of cat. used ..... 5 grams
Ratio of H_2 to C_4H_4 ..... 2.5
Gas velocity .....6 lit/hr/gm of cat

ENCLOSURE (B)11

c. Effect of gas velocity

Table VII(B)11 shows the effect of the gas velocity.

TABLE VII(B)11

Gas vol. lit/hr/gm of cat	C_4H_4 polymerized (%)	Composition of C_4 fract. (%)				percent yield of C_4H_8
		C_4H_4	C_4H_6	C_4H_8	C_4H_{10}	
6	35	16.2	25.7	58.1		37.8
3	41	40.0	4.7	87.1	7.4	51.5
1.2	48	0.4	5.5	94.1		48.9
0.6	50	0.4	37.6	40.8	21.6	20.0

Wt. of cat. used ..... 5 grams
Reaction temperature ..... 100°C
Ratio of H_2 to C_4H_4 ..... 2.5

d. From these results the following conclusions were derived

(1) The unreacted vinyl acetylene was easily kept below 1%.

(2) The formation of butane was very small when the reaction temperature was 100°C and when the ratio of hydrogen to vinyl acetylene was less than 2.6. Increasing the reaction temperature and the hydrogen to vinyl acetylene ratio increases the formation of butane.

(3) At optimum conditions the gas produced contained 90 percent or more butene but half of the vinyl acetylene was polymerized and only the other half was hydrogenated to butene.

3. The Polymerization of Vinyl Acetylene, Butadiene, and Butene on the Catalysts in the Absence of Hydrogen

In order to clarify the polymerization action of the catalysts, the individual unsaturated hydrocarbons mentioned above were passed through the catalysts repeatedly in the absence of hydrogen and the volume decrease was measured at each pass. The relation between the volume decrease and the number of passes are shown in Figure 1(B)11. As the figure shows, vinyl acetylene is most apt to polymerize. The polymerization occured not only on nickel and palladium but also on the diatomaceous earth. Although the palladium-diatomaceous earth catalyst had a greater tendency to polymerize vinyl acetylene than the nickel catalyst, the hydrogenation results indicated the reverse to be true. This fact may be explained by the strong hydrogenation action of the palladium catalyst on vinyl acetylene. On this catalyst vinyl acetylene will be easily hydrogenated, therefore the polymerization of vinyl acetylene will be suppressed. Hence, catalysts having strong hydrogenation activity for the triple bond will be suitable for diminishing the polymerization loss.

4. Comparison of Palladium and Nickel Catalysts

Although from the point of view of the purity of butene in the product, the nickel catalyst is more advantageous than the palladium catalyst; the former has a stronger polymerization action on unsaturated hydrocarbons in the hydrogenation reaction than the latter.

ENCLOSURE (B)11

The polymerization action of nickel catalyst might be weakened by reducing its polymerization activity by heat, catalyst poisons, or activity deterers, and maintaining the hydrogenation activity.

III. CONCLUSIONS

This method for manufacturing butene as a raw material of isooctane is difficult to extend to commercial scale for the following reasons:

A. Butene produced contains some vinyl acetylene even when the partial hydrogenation was carried out at optimum conditions.

B. Butene produced by this method is always mixed with butadiene.

C. The elimination or the separation of the above contaminants by fractionation was difficult because of the proximity of boiling points.

D. Vinyl acetylene should be hydrogenated to a mixture of butene and butane, since there should be no butadiene or vinyl acetylene present if the product is to be used for the synthesis of isooctane.

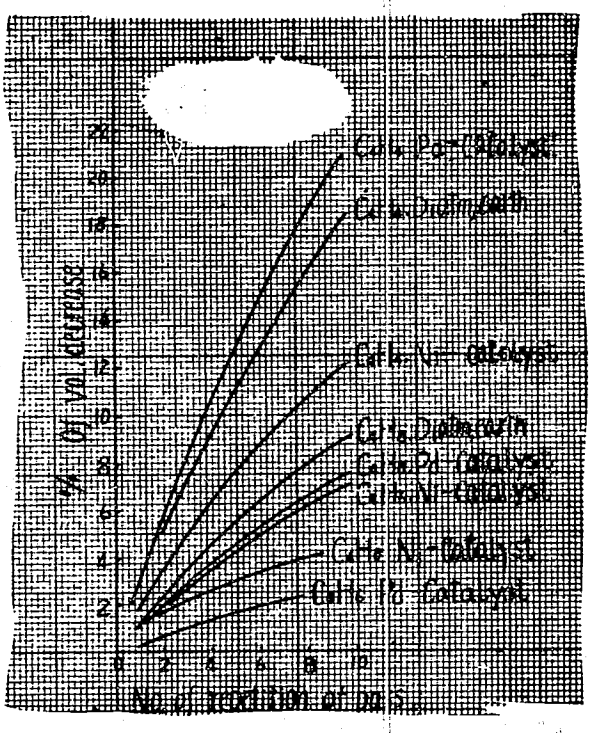

Figure 1(B)11

POLYMERIZATION OF C_4H_4, C_4H_6 AND C_4H_8 ON CATALYSTS

ENCLOSURE (B) 12

SYNTHESIS OF ACETONE FROM ACETYLENE

by

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Research Period: 1937-1940

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

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ENCLOSURE (B)12

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ENCLOSURE (B)12

SUMMARY

Acetone was synthesized from acetylene using a catalyst consisting of manganese dioxide and ferric oxide. A mixture of acetylene and steam was passed through the above catalyst at 450°C and 80 percent of the acetylene reacted and 80-85% of the reacted acetylene was converted to acetone.

The formation of acetaldehyde and acetic acid was below one percent of the acetylene reacted in each case. Pure acetone was easily separated from the product by fractionation.

I. INTRODUCTION

In general, acetone has been manufactured by the dry distillation of calcium acetate, the catalytic conversion of acetic acid and the catalytic reaction of acetaldehyde and steam. Since there was a possibility of using acetone as a raw material in the synthesis of high antiknocking iso-paraffine hydrocarbons, such as 2,3-dimethyl butane or neohexane through pinacone utilizing the pinacoline rearrangement, this research was undertaken.

Although the synthetic method of preparing acetone by the catalytic reaction of acetylene and steam has been known previously, it has not been practiced commercially due to the lack of a good catalyst. Therefore, the effects of many catalysts in this reaction were tested, but the most simple mixed catalyst consisting of manganese dioxide and ferric oxide showed the best results.

Experiments were made using a pilot plant having a capacity of $5m^3$ acetylene per hour. Although the results obtained were satisfactory, the difficulty of the local overheating of the catalyst zone was encountered. While the plant was being reconstructed, it was ordered that the research be stopped because of the success of another method at the laboratory of Chosen Chisso Hiryo Co.

The catalyst used was prepared by the following procedure:

To a solution of manganous chloride an excess of caustic soda solution was added and, separately, to a solution of ferric chloride, a solution of ammonium hydroxide was added. The amounts of manganous chloride and ferric chloride were taken according to the weight ratio of $MnO_2:Fe_2O_3=1:4$.

The precipitates were mixed mechanically, filtered, washed, dried, and ignited at 500°C. The cake of catalyst was crushed, powdered, and shaped into cylinders 6mm x 6mm.

The research was begun in 1937 and stopped in 1940 by Naval Engineer G. ISHIDA.

II. DETAILED DESCRIPTION (See Figure 1(B)12)

In laboratory scale tests, catalysts having a composition of one part of manganese oxide and four parts of ferric oxide, with small added amounts of the oxides of zinc, cadmium, vanadium, molybdenium, tin, calcium or chromium, etc., were tried as catalyst promotors.

None of these promotors showed appreciable effects on the basic catalyst of $MnO2-Fe_2O_3$. Hence, the use of the promotors was abandoned.

B. Apparatus and Procedure

A diagramatic sketch of the apparatus is shown in Figure 1(B)12. Purified carbide acetylene was introduced by a steam injector (1) through a gas

meter (2) into a preheater (3) which was heated by an electric furnace.

The amount of steam was measured by a steam flow meter (4). The mixture of acetylene and steam, heated to the reaction temperature, was passed through the catalyst layer of one of two reactors,(5) and (6). From the product the greater part of water was separated by an dephlegmeter (7). Acetone and steam were condensed by a condenser (8) and collected in a receiver (9). The waste gas escaped through a gas meter (10). The weakened catalyst activity was recovered by passing hot air heated by an electric heater (11) into the reactor through a blower (12).

C. Analytical Procedure

Acetaldehyde was determined by an ammoniacal silver nitrate solution followed by weighing the deposited silver. Acetone was measured after the determination of acetaldehyde by the Messiger's method, and acetic acid by the titration of the original sample.

D. Calculation of the Experimental Results

The percentage yield of acetone was calculted from the following equation.

$$2C_2H_2 + 3\ H_2O = C_3H_6O + 2\ H_2$$

The percentage conversion of acetylene was calculated from the concentration of acetylene and the volume of the charge and the waste gas.

E. Experimental Results

Composition of the catalyst	1 MnO_2+4 Fe_2O_3
Volume of the catalyst	30 liters
Reaction temperature	420°C - 450°C
Velocity of acetylene	3m^3/hr
Time of experiment	120 hours
Amount of steam used	10 times that of acetylene

Results Obtained

	The first day	The last day
Total volume of C_2H_2 used	71.298m^3	75.621m^3
Average concentration of C_2H_2 charged	95.4 %	96.2 %
Total volume of waste gas	65.798m^3	69.221m^3
Average composition of waste gas		
CO_2	20.8 %	17.9 %
C_2H_2	6.8 %	15.3 %
CO	7.9 %	8.2 %
H_2	48.6 %	51.2 %
CH_4	8.5 %	9.1 %
Average conversion of C_2H_2	93.4 %	88.3 %
Total yield of acetone	73.09 kg	70.71 kg
Yield of acetone based on converted C_2H_2	83.0 %	87.9 %
Total yield of acetaldehyde	1.25 kg	1.15 kg
Average yield of acetaldehyde	1.0 %	0.9 %
Total yield of acetic acid	0.65 kg	0.39 kg
Average yield of acetic acid	0.4 %	0.4 %

F. Discussion

Since the catalyst activity decreased after five days, the catalyst was aerated at 450°C for 12 hours. The mean results obtained after restarting

showed partial but not complete recovery of the catalyst activity. In repeating the reaction after recovery of the catalyst activity the yield and the percentage conversion decreased gradually.

After about 500 hour's use the average conversion of acetylene decreased to 70 percent even when the aeration had been continued for a day. It seemed that this was caused by the over heating of the catalyst during the reaction and the aeration, since no cooling device was installed to overcome the effects of the exothermic reaction.

III. CONCLUSIONS

This method is not yet successful because of the short life of the catalyst activity. Hence, additional improvements of the catalyst and the reaction apparatus are required for commerical operation.

ENCLOSURE (B)12

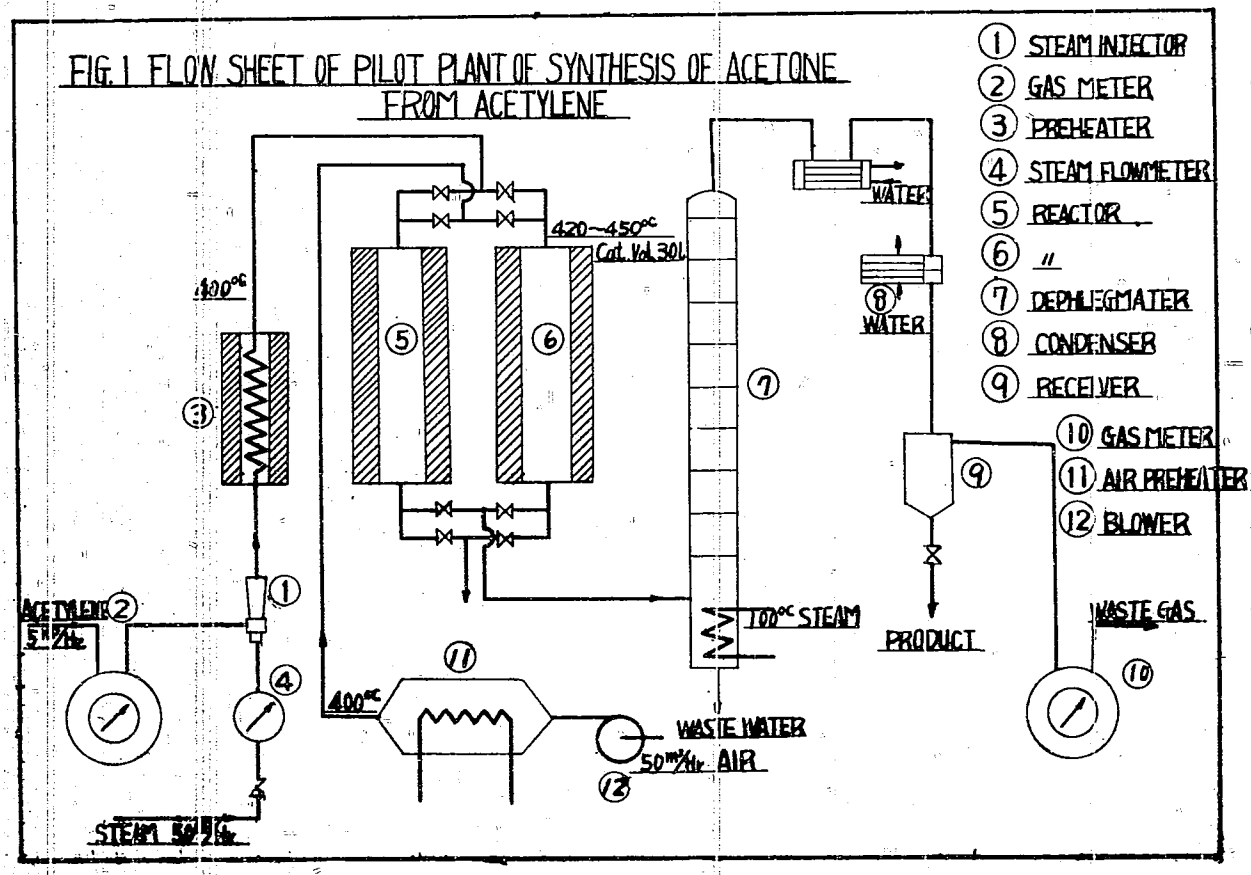

Figure 1(B)12

FLOW SHEET OF PILOT PLANT OF SYNTHESIS OF ACETONE FROM ACETYLENE

ENCLOSURE (B) 13

STUDIES ON THE SYNTHESIS OF ACETALDEHYDE WITHOUT THE USE OF MERCURY CATALYST

by

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Research Period: 1940-1945

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

Dec. 1945

ENCLOSURE (B)13

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Figure 5(E)13 Synthesis Plant of Vinyl-Methyl-Ether by Means of Methylation of Acetylene ..... Page 198

ENCLOSURE (3)13

SUMMARY

Acetaldehyde was synthesized from acetylene without mercury catalyst by three methods.

1. A dilute hydrochloric acid solution of a complex salt of cuprous chloride and ammonium chloride, which was a modification of the catalyst used in the synthesis of vinylacetylene from acetylene, was used as the catalyst for the liquid phase reaction. At the optimum conditions nearly 10 % of the acetylene used reacted and 9 % of the reacted acetylene was converted to acetaldehyde.

2. The vapor phase hydration of acetylene using a solid catalyst consisting of a mixture of cadmium phosphate and calcium phosphate was tested. Acetylene and steam were passed through the catalyst heated at 350-400°C. Nearly 40 % of the acetylene charged was hydrated, and a 90 % yield of acetaldehyde was obtained. The activity of the catalyst was maintained for 60 hours. The activity was recovered by aeration for five hours. The results obtained was satisfactory.

3. Acetylene was methylated by methanol using caustic soda as a catalyst, then the vinyl methyl ether obtained was hydrolysed to acetaldehyde and methanol. The yield of vinyl methyl ether was 94 %. Although, the investigation of the hydrolysis of vinyl methyl ether was not completed, a very high yield of acetaldehyde was obtained on the preliminary test.

I. INTRODUCTION

Isooctane is synthesized from acetylene commercially. However, the synthesis of acetaldehyde from acetylene, the first step of the isooctane synthesis, requires the use of mercury as the catalyst. Since some of the mercury is lost in the process and since the production of mercury in Japan is small, research on the synthesis of acetaldehyde from acetylene without using a mercury catalyst was ordered in 1940 for the isooctane synthesis. The research was begun by Chem. Eng. Capt. Dr. C. FUJIO and Chem. Eng. Lt. Comdr., T. YAMAMOTO and several other collaborators, and continued until the end of the war. The data in this report was collected from the notes of the above investigators by the author.

II. DETAILED DESCRIPTION

A. Liquid Phase Hydration of Acetylene Using the Complex Salt Solution of Cuprous Chloride and Ammonium Chloride as the Catalyst

1. Introduction

In the synthesis of vinylacetylene from acetylene using a cuprous chloride complex salt solution, the formation of acetaldehyde as a byproduct was observed. In order to increase the yield of acetaldehyde, the relation between the composition of the catalyst solution, the yield of acetaldehyde, and the conditions of reaction were studied.

ENCLOSURE (B)13

2. Apparatus and Procedure

Purified acetylene from a pressure vessel was introduced continuously into a reaction vessel containing about 100cc of the catalyst solution placed in a thermostat. The gas volume was measured with a gas-meter. The gas from the reaction vessel was first cooled with an ice-cooled condenser, then by contact with crushed ice, and finally with a condenser cooled by dry ice. The reaction product from each condenser was analysed. The volume of the unreacted acetylene was measured with another gas-meter. The reaction products collected from the two ice coolers were fractionated exactly and acetaldehyde was determined as the fraction distilling from 19°C to 25°C. The product separated from the dry ice cooler was fractionated with the Podbielniak's apparatus into two fractions -20°C to -10°C and 0 to 10°C. The former was regarded as vinyl chloride and the latter as vinyl acetylene. When no vinylchloride was formed the product from the dry ice cooler was evaporated and vinyl acetylene was determined by absorption in 91 % sulfuric acid. The acetylene concentrations in the charging gas and the unreacted gas were determined by absorption in alkaline mercurous cyanide solution.

3. Experimental Results

a. Acetaldehyde formation in the manufacture of vinyl acetylene

A catalyst solution having the following composition was used. This composition was obtained from the literature.

Cuprous chloride	40 grams
Ammonium chloride	23 grams
Water	45 grams
Hydrochloric acid (38%)	5 grams

The experimental results are shown in Table I(B)13, II(B)13, and III(B)13. In these tables, the difference between the quantity of acetylene reacted and the acetylene converted to acetaldehyde is considered as being due to loss and the formation of higher polymers.

Table I(B)13
EFFECT OF THE VELOCITY OF ACETYLENE

Vol. of C_2H_2 lit /hr	Reacted C_2H_2 (%)	Yield of CH_3COH_2 (%)	Yield of C_4H_4* (%)
2.0	18.6	2.0	38.2
4.3	13.5	9.5	34.3
6.5	11.1	10.8	35.0
8.7	5.3	15.5	34.8

*C_4H_4 is vinyl acetylene.

Note. The percent of reacted C_2H_2 and percent yield was calculated as follows:

Percent yield = 100 x measured wt. of CH_3OH/ vol. of reacted C_2H_2 x 44/22.4

Percent of reacted C_2H_2 = 100 x (vol. of C_2H_2 used - vol. of unreacted C_2H_2)/vol. of C_2H_2 used

The gas volume was indicated as that at N.T.P.

Table II(B)13
EFFECT OF THE REACTION TEMPERATURE

React. temp. °C	Reacted C_2H_2 (%)	Yield of CH_3OH (%)	Yield of C_4H_4 (%)
90	6.3	7.0	28.1
78	11.1	10.8	35.0
70	13.6	9.9	36.1
60	14.0	3.1	29.3

Wt. of the catalyst solution used ..... 113 grams
Vol. of acetylene .....6 lit/hr
Time of experiment ..... 5 hrs

Table III(B)13
EFFECT OF THE CONCENTRATION OF HYDROCHLORIC ACID

Vol. of 38% HCl added cc	Reacted C_2H_2 (%)	Yield of CH_3COH (%)	Yield of C_4H_4 (%)	Yield of C_2H_3Cl* (%)
	19.0		44.4	
5	11.1	10.8	35.0	2.3
10	5.0	25.6	23.3	10.0
15	4.3	14.5	10.6	13.5
20	2.8	9.5	8.1	14.1

*C_2H_3Cl is vinyl chloride.

Wt. of the catalyst solution used ..... 108 grams
Vel. of acetylene .....6 lit/hr
Reaction temperature ..... 78 °C
Time of the experiment ..... 5 hrs

From these data it is concluded as follows:

(1) Increase of the velocity of acetylene lowers the quantity of reacted acetylene and increases the percentage yield of acetaldehyde.

(2) The maximum percentage yield of acetaldehyde was obtained at 78°C.

(3) Increasing reaction temperature increases the rate of the reaction.

(4) The percentage yield of vinyl acetylene did not vary with changes in temperature and gas velocity.

(5) Though the high concentration of hydrochloric acid suppressed the rate of the reaction, the formation of vinyl chloride increased.

(6) For the production of acetaldehyde there is an optimum concentration of hydrochloric acid, which is nearly 10% of 38% HCl in the catalyst solution.

b. Effect of the addition of leucine hydrochloride

Many kinds of additives to increase the yield of acetaldehyde in this reaction were tried, among them the best results were obtained when leucine hydrochloride was used.

The leucine hydrochloride was separated from the waste of glutamic acid manufacture which is the raw material of the Japanese seasoning "Ajinomoto". The experimental results are shown in Table IV(B)13. As shown in Table IV(B)13, the maximum yield of acetaldehyde was obtained and the formation of vinyl acetylene and vinyl chloride was minimized when 10 % of leucine hydrochloride was present in the catalyst solution. The effect of leucine hydrochloride in the catalyst solution was considerable.

c. Effect of the concentration of the catalyst solution

Various catalyst concentrations were tested maintaining constant acidity by dilution with dilute hydrochloric acid.

Table IV(B)13
EFFECT OF THE ADDITION OF LEUCINE HYDROCHLORIDE

Composition of Catalyst Solution				HCl (38%) (g)	C_2H_2 Reacted (%)	Yield of Product		
Cu_2Cl_2 (g)	NH_4Cl (g)	Leu-HCl (g)	H_2O (g)			CH_3OH (%)	C_4H_4 (%)	C_2H_3Cl (%)
30	15	10	45	10	5.3	75.7	8.1	8.3
30	15	12	45	10	5.1	79.0		
30	15	14	45	10	6.5	52.0	5.5	10.2
30	15	16	45	10	7.6	49.0	2.3	11.0

Reaction Temperature ..... 78 °C
Velocity of acetylene ..... 6 l/hr
Time of experiment ..... 5 hrs

The catalyst composition ratio which showed the best results in previous experiments was maintained constant. The results obtained are shown in Table V(B)13.

Table V(B)13
EFFECT OF THE CONCENTRATION OF THE CATALYST SOLUTION

Cu_2Cl_2 (g)	NH_4Cl (g)	Leu-HCl (g)	H_2O (g)	HCl (38%) (g)	Reacted C_2H_2 (%)	Yield of CH_3CHO (%)
15	7.5	6	45	10	4.2	45.4
22.5	11.25	9	45	10	5.3	47.5
30.0	15.0	12	45	10	6.1	79.6
37.5	18.75	15	45	10	8.0	91.3
52.5	26.75	21	45	10	5.7	85.8
56.25	28.12	22.5	45	10	4.7	53.2

Reaction Temperature ..... 78 °C
Velocity of charged acetylene ..... 6 lit/hr
Time of the experiment ..... 5 hrs

8.0 % of the acetylene used was reacted and 91 % of the reacted acetylene was hydrated to acetaldehyde by the catalyst having the following composition.

Cuprous chloride	37.5 grams
Ammonium chloride	18.75 grams
Leucine hydrochloride	15.0 grams
Water	45.0 grams
Hydrochloric acid (38%)	10.0 grams

When the concentration of the catalyst is too high, a part of the constituents are deposited as solids even at 80°C. The above composition is the maximum concentration which is completely soluble at 80°C.

d. Durability of catalyst solution

In order to determine the life of the catalyst a continuous experiment was carried out at 80°C and 60 lit/hr velocity of acetylene. Though the apparatus used was larger, the principle was the same as before. The catalyst solution consisted of:

Cuprous chloride	495 grams
Ammonium chloride	240 grams
Leucine hydrochloride	189 grams
35% hydrochloric acid	128cc
Water	600cc

The product was collected at 5 hour intervals, and the concentration of water and hydrochloric acid in the catalyst was maintained constant. The results, calculated from the 130 hours experimental data, were as follows:

The percentage of acetylene reacted was 13 % and 80-90 % of the reacted acetylene was converted to acetaldehyde. After 130 hours the rate of the reaction decreased due to the diminishing of the catalyst volume by withdrawing for analysis.

e. Conclusions

The optimum conditions are as follows:

(1) The best reaction temperature is 70-80°C.
(2) The best catalyst composition is:

Cuprous chloride	38 grams
Ammonium chloride	19 grams
Leucine hydrochloride	15 grams
38% hydrochloric acid	11 grams
Water	45 grams

(3) The velocity of acetylene must be controlled as 10% of the used acetylene is reacted.

(4) During the operation water and hydrochloric acid must be supplied to replace that which has been consumed and evaporated.

(5) The life of the catalyst solution is at least 7 to 10 days. Accumulation of resinous higher polymers may interfere by decreasing catalyst activity if used for longer periods.

B. Vapor Phase Hydration of Acetylene on a Solid Catalyst

1. Introduction

A mixture of acetylene and steam was passed through the catalyst heated 300° to 400°C. Although many kinds of catalysts were tried, catalysts having strong activity such as phosphoric acid supported on diatomaceous earth lost their activity in a short time, and the activity could not be recovered. It was found that some phosphates, such as cadmium phosphate, also have good activity which could be easily recovered. This report is on the experiments using the mixed catalyst of cadmium phosphate and calcium phosphate which showed the best results.

2. Catalyst

The catalyst used was prepared as follows: A solution containing 0.1 mol of cadmium nitrate and 0.3 mol of calcium nitrate was warmed to 85°C, and a solution of sodium biphosphate ($_{p}H$. adjusted to 7) was added until the precipitation was complete. Separately, the precipitate prepared from 0.3 mol of calcium nitrate solution by the same method was mixed with the above precipitate, washed, dried and shaped into 4mm x 1mm cylinders. This catalyst had an activity as shown below.

Diameter of the reaction tube	20mm
Volume of catalyst taken	50cc
Reaction temperature	350°C
Space velocity of acetylene only	250
Amount of steam used	6 times of the theoratical
Reacted acetylene	65% of charge
Yield of acetaldehyde	97.8% to reacted acetylene

This catalyst was used and a durability test was carried out on the apparatus shown in Figure 1(B)13.

3. Apparatus and Procedure

Purified carbide acetylene was introduced through a gas meter (1) with a blower (2) and was mixed with steam at an evaporator (3). Water was pumped from a measuring cylinder (5) by a small bellows pump (4) and evaporated in the evaporator, which was heated by steam. The mixture was heated in the preheater (6) and passed through the catalyst tube of the reactor (7). The product was condensed by a condenser (10) and unreacted acetylene was separated from the product at a receiver (14). Acetaldehyde vapor remaining in the gas was washed with water in a washing tower (11). The volume of the unreacted acetylene was measured with a gas meter (15).

The recycling pump and the receiver of the dilute solution of acetaldehyde are indicated by (12) and (13), respectively.

The catalyst tubes of the reactor were immersed in a liquid mixture of diphenyl and diphenyl oxide known as "dowtherm" which was heated with a heater (8) and a regulating transformer (9). The reaction

ENCLOSURE (B)13

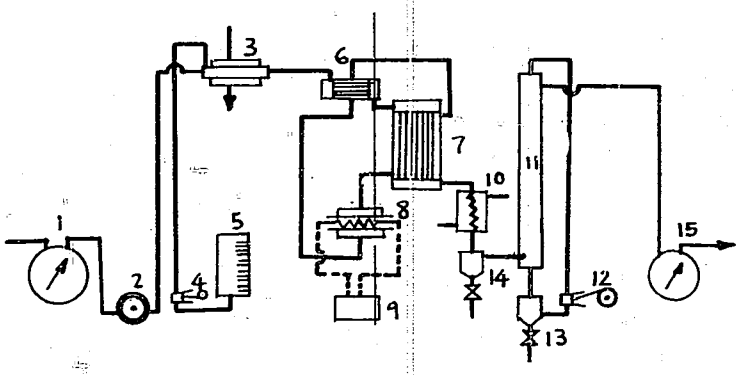

Figure 1(B)13

FLOW SHEET OF VAPOR PHASE HYDRATION OF ACETYLENE

heat was conducted from the catalyst to the dowtherm, and the evaporated vapor of the dowtherm at the outside of the catalyst tubes was condensed at the preheater (6) and the condensate returned to (8). The reactor had 19 catalyst tubes, 500mm in length and 25mm in dia. The temperature was measured at the top and the bottom of one of the catalyst tubes and the inlet of the reactor by three thermocouples.

The catalyst was reactivated in the reactor by aerating at 350°C for 10 hours. After the air was expelled by steam, water and acetylene were introduced. The reaction product from each 12 hour interval was collected and analyzed.

4. Experimental Result

A durability test of the catalyst was carried out for 480 hours. The reaction conditions were as follows:

The space velocity of acetylene only 250
The velocity of steam used ..... 6 times theoretical
The reaction temperature at the top of the reactor ..... 340-390°C

The results obtained during the first 66 hours are shown in Table 6(B)13. After 66 hours the reaction temperature necessary for maintaining 30% conversion of acetylene reached 400°C.

The reaction was stopped and the activity of the catalyst was recovered by aeration at 350°C for five hours. At the beginning of the aeration the temperature at the top of the reactor rose suddenly to 500°C and then the catalyst zone indicating the maximum temperature gradually descended to the bottom of the reactor. After recovering the catalyst activity the reaction was resumed as before. For 60 hours there was but little change over the previous results.

After the 60 hours of reaction followed by the five hours of recovering the catalyst activity had been repeated eight times, the catalyst was removed and its activity was tested in a glass tube as had been done originally.

The result obtained showed no change in the catalyst activity. The reacted acetylene was 58.8% of the used acetylene and 91.3% of the reacted acetylene was hydrated.

Table VI(B)13
VAPOR PHASE HYDRATION OF ACETYLENE

Time elapsed, hours	Reaction temp. (°C)		A C_2H_2 used, l	B C_2H_2 consumed lit	B/A	Yield of CH_3COH (%)
	top	bottom				
	357	359				
12	385	376	13.725	5.192	37.0	
24	390	380	14.840	4.787	32.2	99.3
36	390	380	13.280	4.629	34.9	90.0
48	400	390	13.700	4.512	33.0	81.0
60	395	390	13.408	4.304	32.1	96.2
66	400	400	7.293	2.247	30.9	99.6

5. Conclusions

In the vapor phase hydration of acetylene using the mixed catalyst of cadmium phosphate and calcium phosphate at reaction temperatures of 350° to 400°C, space velocity of acetylene 250, and a quantity of of steam six times the theoratical, 30 to 40% of the acetylene used reacted and 90% of the reacted acetylene was converted to acetaldehyde. The catalyst activity continued for about 60 hours, and the loss in activity of the catalyst could be recovered by aeration at 350°C for five hours.

Repetition of the running and the recovering of the catalyst activity six times over a period of three weeks shows no change in the catalyst activity.

C. Synthesis of Acetaldehyde by the Hydrolysis of Vinyl Methyl Ether and Synthesis of Vinyl Methyl Ether from Acetylene

1. Introduction

Previously the possibility of the synthesis of acetaldehyde by the hydrolysis of vinyl methyl ether and the synthesis of vinyl methyl ether from acetylene and methanol were known.

Experiments were carried out to clarify the reaction conditions. Since there were many difficulties in the use of high-pressure acetylene and methanol at high temperatures on the laboratory scale. A pilot plant having a capacity of several cubic meters of acetylene was erected without exact preliminary tests. Though the experiments on the synthesis of vinyl methyl ether were carried out successfully, the experiments on the hydrolysis of vinyl methyl ether had not yet been started.

2. Apparatus and Procedure

The flow sheet of the pilot plant is shown in Figure 2(B)13. Carbide acetylene purified by a mixture of ferric chloride, cupric acetate, mercuric chloride and diatomaceous earth, was introduced through a gas meter and compressed with a specially designed acetylene compressor in a reactor containing a caustic soda solution of methanol.

The methanol solution was circulated from the bottom to the top of the reactor through a heater heated by steam.

Acetylene was absorbed in the methanol solution under pressure and forms vinyl methyl ether by the catalytic action of caustic soda. The methanol solution containing ether was introduced through a cooler to a fractionating tower by releasing the pressure. Vinyl methyl ether was separated and condensed in a receiver. The methanol solution at the bottom of the fractionating tower was returned to the bottom of the reactor.

The methanol consumed by the reaction was supplied from a tank, and serves to dissolve caustic soda at the beginning of the run.

ENCLOSURE (B) 13

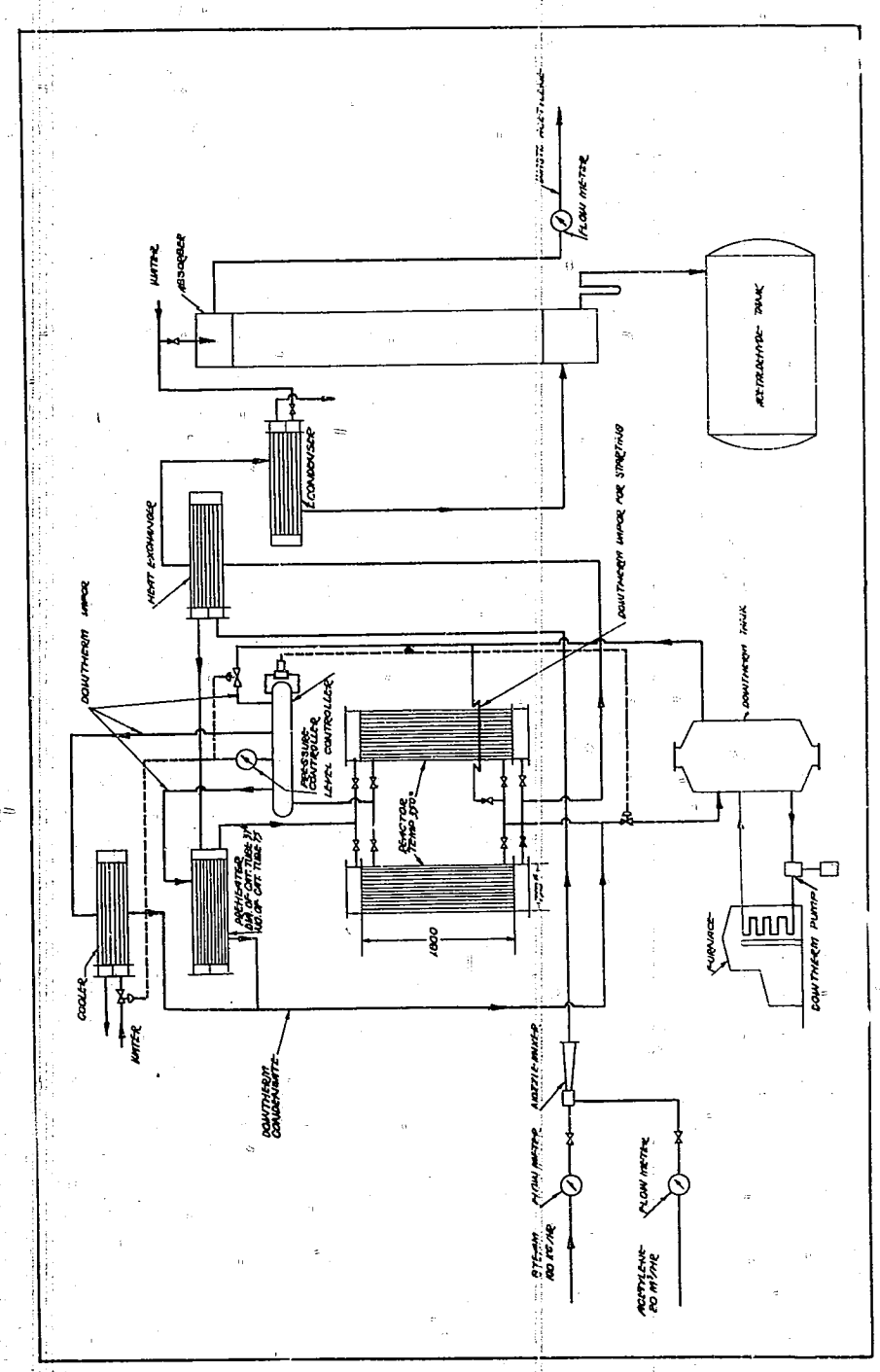

FIG. 4 SHEET NO. 1 APPARATUS FOR MAKING VINYL ACETYLENE

ENCLOSURE (B) 13

3. Experimental Results

Reaction temperature at the bottom of the reactor ..... 150°C
Pressure of the reaction tower ..... 15 atms
Velocity of acetylene charged 7.7m3/hr
Circulating velocity of methanol solution from the bottom to the top of the reactor 2m3/hr
Circulating velocity of methanol solution from the reactor to the fractionating tower 0.5m3/hr
Pressure of the fractionating tower ..... 2.5 atms
Temperature of the distilling tower, top ..... 50°C
bottom ..... 120°C
Vinyl methyl ether obtained per hour 235kg
The purity of the product 96.4%
The percent yield of the product to theoretical 94.4%

The product contained no impurities except methanol and there were no side reactions. The releasing value at the top of the reaction tower was prepared for the inert gas contained in acetylene which might be accumulated in the reaction tower, but the opening of the valve was not neccessary during 50 hours of running. It seemed that the inert gas contained in acetylene was dissolved in methanol and was ejected at the releasing valve of the receiver.

There is but little data pertaining to the properties of vinyl methyl ether in the literature. Redistilled vinyl methyl ether had the following properties.

Sp. gr. 15/4 ..... 0.783 (under pressure)
B.P. ..... 5.7°C
Solubility ..... partly soluble in water

It has no tendency to polymerize on standing under pressure in a glass pressure bottle at room temperature.

Vinyl methyl ether was easily hydrolysed by mixing with an equal volume of 0.1 N. sulphuric acid and heating in a pressure bottle at 80°C for five minutes. After neutralizing the acid, the acetaldehyde produced was determined by the hydroxylamine method. The hydrolysis was completed under the above conditions.

4. Comparison of Three Methods and Conclusions

There is but little difference in the yield of acetaldehyde by the three methods.

In the author's opinion, the first method is difficult to expand to a commercial scale because of the low rate of the reaction and the necessity of using material resistant to hot hydrochloric acid. The second method may be practiced when the design of the reactor for elimination of the reaction heat is perfected. The last method is suitable only for a small scale commercial plant because of the difficulty of the use of an acetylene compressor having a large capacity.

ENCLOSURE (B) 13

Figure 5(b)13

FLOW SHEET OF SYNTHESIS OF VINYL ETHER

ENCLOSURE (B)13

Figure 4(B)13

VAPOUR PHASE HYDRATION PLANT OF ACETYLENE TO ACETALDEHYDE

This plant was erected for semi-commercial use but was never operated.

ENCLOSURE (B) 13

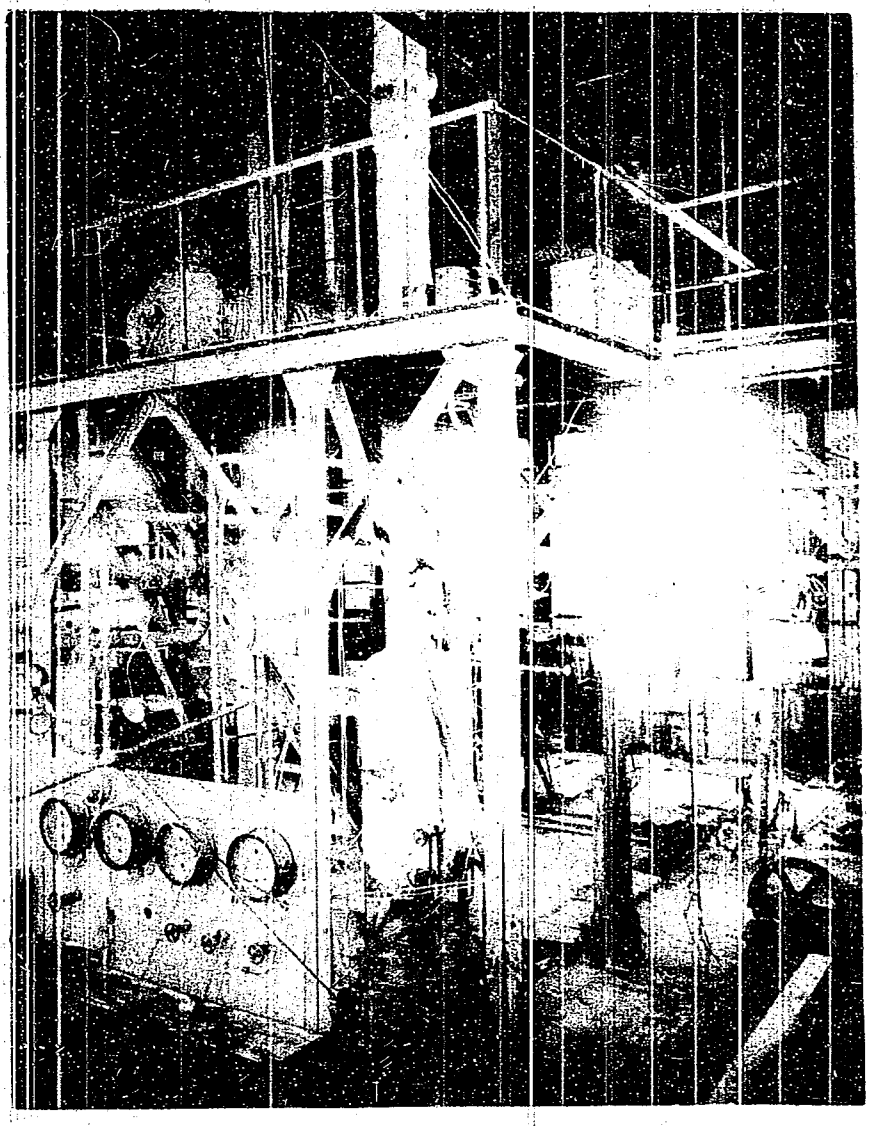

Figure 5(B)13
SYNTHESIS PLANT OF VINYL-METHYL-ETHER BY MEANS OF METHYLATION OF ACETYLENE

ENCLOSURE (B) 14

STUDIES ON THE MANUFACTURE OF ACETYLENE FROM HYDROCARBON GASES BY ELECTRIC ARC

by

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Research Period: 1943-1944

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December 1945

ENCLOSURE (B)14

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ENCLOSURE (B) 14

SUMMARY

Gas produced by petroleum cracking, which was composed of the lower hydrocarbons, methane, ethane, propane, ethylene and propylene etc., was subjected to cracking by an electric arc of 1000 kilowatts discharge. The cracked gas thus obtained was composed of 20% acetylene and 50% hydrogen. The construction of the cracking apparatus and the accessories of the plants were investigated to obtain data for design of the commercial plant.

I. INTRODUCTION

This research was begun by Eng. Capt. Dr. C. FUJIO in 1928 in the chemical laboratory of Tokuyama Fuel Depot. Methane, ethane, and ethylene were cracked with a high tension spark, under atmospheric pressure, to acetylene and hydrogen. In 1930, a pilot plant (15 kilowatts, 150,000 volts) for the utilization of the natural gas was erected in the research laboratory of SHINCHIKU, Formosa. In 1935, to avoid the injurious effect on the insulation of the electric circuit caused by a high frequency oscillating current due to the spark, cracking of the gas under diminished pressures such as 100mm Hg was studied, and an apparatus was constructed having a capacity of 40 kilowatts and 40,000 volts. It seemed that the characteristics of the discharge with this apparatus were not spark but glow. Though the power consumption per cubic meter of acetylene was 10 kilowatts, the concentration of acetylene was only 8%.

Finally, in 1940 a 1000 kilowatt plant was designed. The apparatus, as will be seen in Figure 1(B)14, consists of a cracking tube made of iron and a carbon electrode. 800 volts direct current was used instead of the alternating current previously used, and the gas was cracked at 200mm Hg pressure. This pilot plant was transported from Formosa to TOKUYAMA and was operated there from 1940 to 1941 with a cracked gas from the gyro plant. This report is a record of the experiments at TOKUYAMA.

Six commercial plant sets, each having a capacity of 3,000 kilowatts, were erected in 1943 on the basis of these data at the Second Fuel Depot of YOKKAICHI to prepare acetylene as the source of butanol.

II. DETAILED DESCRIPTION

A. Description of Apparatus

The flow sheet of the plant is shown by Figure 1(B)14. The gas from the gyro plant was stored in a gas holder and introduced to one of two cracking units made of steel, and shown in Figure 2(B)14. The cracked gas was cooled by passing it through two water coolers, and carbon particles were removed with a Cottrell precipitator and a cyclone dust catcher. To protect the wall of the reaction chamber from the heat of the arc, the gas was introduced in a high speed swirling motion. The electric circuit of the apparatus consists of an induction regulator to control the voltage, a reactor to stabilize the arc, a transformer, and a mercury rectifier. The plus terminal of the rectifier was connected to the upper electrode of the cracking apparatus, and the minus terminal, connected to the body of the cracking apparatus, was grounded. The upper electrode was composed of carbon insulated from the body. The inspection holes were covered with a cobalt glass plate to permit observation of the arc flame. Charged gas was introduced tangentially into the reaction chamber through the holes surrounding the electrode and was given a spinning motion. The starting electrode was moved by hand. The electrode and the cracking chamber were cooled by a strong flow of cold water. Twenty tons per hour

ENCLOSURE (B)14

FIGURE 10(1)4
WORKSHEET FOR ARC CRACKING

ENCLOSURE (B) 14

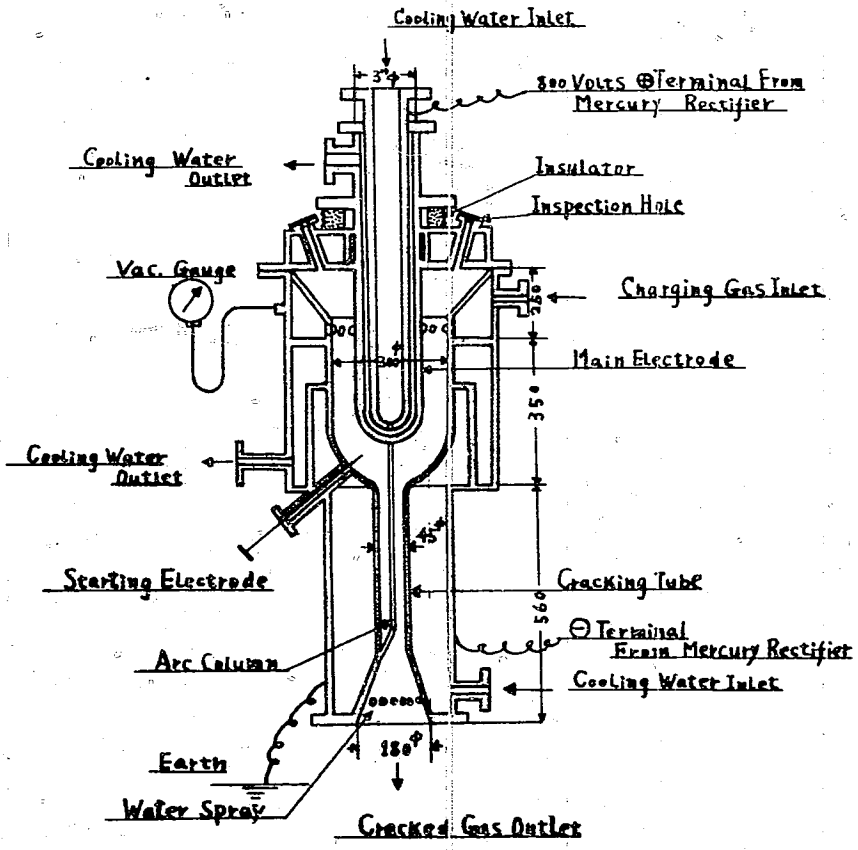

Figure 2(B) 14
ARC CRACKING APPARATUS

of cooling water was required for the copper electrode. The carbon electrode was not cooled.

B. Test Procedure

To start the apparatus, it was evacuated with a pump and the gas was introduced. This process was repeated for several times to expell all of the air from the apparatus. After controlling the gas velocity and gas pressure, the arc was started with the starting electrode. The arc between the electrodes was blown down by the gas flow to the bottom of the reaction tube. The cracked gas, quenched to about 400°C with water spray, passed into two coolers in which the temperature was kept at 30°C, and then into the Cottrell dust catcher. Gas was analyzed by the Hemple and Podbielniak methods.

C. Experimental Results

As will be seen in the experimental results shown in Tables I(B)14, II(B)14 and III(B)14, the composition of the cracked gas was not affected by the charging gas. Considerations as to the conditions for the smooth running operation of the apparatus were as follows:

1. Gas Pressure

A lower pressure is better for maintaining arc stability and avoiding a complexity of reaction products.

2. Arc Current

The stability of the arc and the capacity of the apparatus will be increased with increasing arc current, but the later is limited by the cooling temperature of the electrode.

3. Composition of the Charged Gas

Although the composition of the charged gas has no serious effect on the acetylene concentration of the cracked gas or on the arc stability, gas with high olefine content forms excessive carbon dust.

4. Arc Stability

The stability of arc is mainly dependent on the gas velocity. When the velocity is too rapid to have a smooth spinning motion, the arc is unstable.

D. Operating Difficulties

1. The Electrode

When the reaction started, carbon formed by cracking of hydrocarbons was deposited on the upper carbon electrode and consequently, the current was decreased and the voltage became irregular. To maintain smooth running for a long time the deposited carbon had to be eliminated by breaking mechanically or by lifting the upper electrode by means of a gear. The use of these devices to remove deposited carbon was not successful. Consequently, when the current became irregular, the gas was changed to another apparatus. The interval of continuous running through each arc by this method was about seven hours.

TABLE I(B)14

DATA OF CRACKING WITH CARBON ELECTRODE

No. of Exp.	Gas Pressure in mm. Hg.	Arc Current in Amp.	Voltage at Electrode in Volt	Dia of Cracking Tube in mm.	Length of Cracking tube in mm.	Properties of Upper Electrode	Vel. of Gas Charged in m^3/Hr	Vel. of Gas Produced in m^3/Hr	Time of Exp. in min.	Voltage Drop of Arc in (%)	Conc. of C_2H_2 in Cracked Gas in (%)	Production of C_2H_2 in m^3/Hr	Total Power Consumption in K.W.H.	Power Consumption per m^3 of Pure C_2H_2
1	150	650	890	53	440	+	110	253	43	46	25.5	64.5	580	9.0
2	200	650	863	53	400	+	120	262	24	40	23.5	61.7	560	9.1
3	110	600	784	53	600	+	140	306	100	47	24.4	73.5	470	6.4
4	120	600	750	53	600	+	145	250	250	49	24.4	68.0	450	6.6
5	200	600	741	53	600	+	185	407	120	50	20.4	83.1	445	5.4
6	200	650	720	53	975	−	185	315	90	50	22.5	71.0	467	6.6
7	200	680	719	53	975	−	175	338	100	50	23.5	79.4	482	6.1
8	200	650	750	50	600	+	170	307	90	53	22.0	67.4	487	7.2
9	200	620	610	50	420	+	100	231	200	59	24.4	56.4	372	6.7
10	200	650	590	52	400	+	100	230	350	60	23.5	54.2	380	7.0
11	200	650	600	53	600	+	150	293	370	48	21.6	63.2	385	6.1

ENCLOSURE (B) 14

TABLE II(B)14 ANALYTICAL DATA OF GAS CHARGED

Exp. No.	CO_2	O_2	CO	H_2	N_2	C_2H_2	CH_4	C_2H_4 + C_3H_6	C_3H_6 + C_3H_8	C_4H_8 + C_4H_{10}
1	1.0	0.5	1.0	0.8	0.8		30.4	22.3	26.2	14.1
2	0.9	0.5	2.9	4.5	2.4		7.7	12.2		5.7
3	1.0	0.3	0.3	7.2	1.4		42.0	35.0	12.5	
4	0.7	0.1	0.2	7.2	0.5		36.1	33.5	18.5	
5	0.7	0.1	0.1	7.2	0.5		36.1	33.5	18.5	
6	1.4	0.2	0.1	6.7	0.7		36.4	36.0	16.3	
7	1.5		0.2	4.7	4.7		32.7	43.6	15.2	
8	0.7	0.1		4.5	0.7		35.2	34.8	18.4	3.4
9				3.9	0.4		24.5	19.6	30.7	18.5
10		0.2	0.2	2.3	0.9		24.2	26.2	30.9	20.6
11		0.1	0.1	8.1	1.6		42.6	33.3	11.0	

TABLE III(B)14 ANALYTICAL DATA OF GAS CRACKED

Exp. No.	CO_2	O_2	CO	H_2	N_2	C_2H_2	CH_4	C_2H_4 + C_3H_6	C_3H_6 + C_3H_8	C_4H_8 + C_4H_{10}
1		0.8	2.7	60.7	5.2	24.8	4.8	0.9	5.7	
2	0.7	0.4	2.2	57.2	1.8	23.3	5.9	7.1	12.1	
3	1.0	0.1	2.5	55.4	0.3	24.0	6.8	7.5	8.5	
4	1.1	0.4	0.9	43.5	3.0	23.8	14.0	7.2	15.3	
5	0.4	0.5	0.8	41.3	4.6	20.4	11.7	9.8	10.7	
6	0.8	0.2	1.0	43.5	3.4	22.4	15.8	11.6	19.8	
7	0.5	0.7	0.6	47.4	4.3	23.5	12.4	9.4	15.0	
8	0.2	0.9	0.9	46.7	3.5	22.0	5.6	16.9	15.1	
9	1.9	0.3	0.9	38.6	3.2	24.4	7.4	17.8	15.5	
10	1.5	0.5	1.1	41.5	3.0	23.5	4.5	19.5	16.1	
11	0.6	1.8	0.6	39.6	9.0	21.5	14.2	10.3	49.4	

2. Arc Stability

In order to obtain concentrated acetylene from the cracking process, a stable arc is required. This seems to depend on the reactance of the electric circuit, the discharging current (when the discharging current is too small, the arc is apt to cut.), the gas velocity, the type of the apparatus and the electrode materials. When a copper electrode was used, though a stable arc was obtained and the carbon deposition was smaller than with the carbon electrode, the copper electrode was apt to be perforated by the arc in a comparatively short time.

3. Carbon Dust

In the cracking reaction of the hydrocarbons, acetylene was formed, but an undesirable result was the formation of carbon. This was almost completely removed by using a Cottrel precipitator. (See Appendix)

III. CONCLUSIONS

A. The apparatus used in the process consists of an iron cracking tube and a carbon electrode utilizing 1000 kilowatts and 8000 volts of direct current.

B. By the arc cracking of the gaseous hydrocarbons from the gyro cracking plant, a cracked gas composed of 20% acetylene, and 50% hydrogen was obtained.

C. The normal operation was continued for seven hours without difficulty.

D. The trouble caused by carbon deposits on the electrode could not be avoided by lifting the electrode or breaking the deposited carbon mechanically.

E. For maintenance of the stable arc, more experiments are required.

APPENDIX

The carbon caught by the Cottrell precipitator consisted of extremely fine particles. In the commercial plant the carbon dust was with drawn from the bottom of the Cottrell precipitator by the suction of a water jet. The carbon dust floating on the waste water was gathered and was tested as carbon black. Since it had absorbed oil formed by the acetylene polymerization, it was heated to 700°C for 15 minutes in a closed iron box. A test was made comparing the carbon black with that obtained by the channel method.

The carbon obtained by arc cracking was inferior to the channel method carbon in respect to ash content and blackness, but comformed to the specification of carbon black for the rubber industry and printing ink as a second grade quality material.

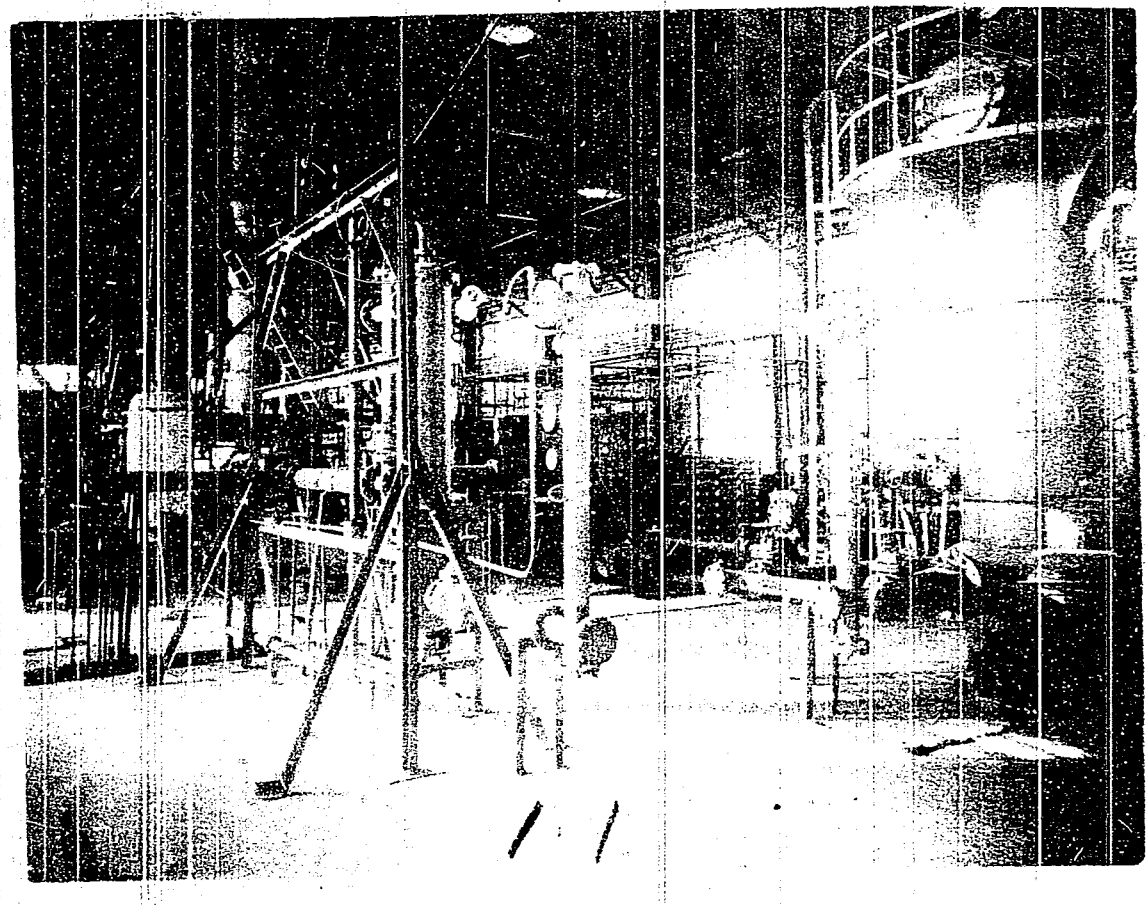

Figure 3(B)14
PILOT PLANT FOR PREPARATION OF ACETYLENE FROM
HYDROCARBON GASES BY MEANS OF ELECTRIC ARC

ENCLOSURE (B) 15

STUDIES ON THE SEPARATION OF ACETYLENE

by

CHEM. ENG. LT. COMDR.
T. YAMAMOTO

Research Period: 1940-1942

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

December 1945

ENCLOSURE (B)15

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ENCLOSURE (B)15

SUMMARY

By the extraction with water at high pressure, acetylene was separated from a mixed gas composed of 20% acetylene, 50% hydrogen, and 20% methane. The mixed gas was obtained by the arc cracking of hydrocarbon gases. The separated acetylene had a purity of 95% or more, and the amount of acetylene in the residual gas was less than 1%. This was removed by treating the gas with nickel catalyst at 350°C.

I. INTRODUCTION

Cracked gas obtained by arc cracking of lower hydrocarbon gases consists of 20% acetylene, 50% hydrogen, and 20% methane.

To use these gases as the raw material of synthesis, it was necessary to concentrate or separate acetylene. The separation of acetylene from mixed gas has not yet been done on commercial scale. As acetylene has a good solubility in water compared with methane and hydrogen, the author attempted to separate acetylene by water extraction and devised an apparatus. After several experiments improvement of the apparatus was accomplished and tests were made. On the basis of these results a commercial plant was erected at the Second Fuel Depot of YOKKAICHI. It was begun in April, 1940 and completed in September, 1942.

II. DETAILED DESCRPTION

A. The Apparatus and Experimental Procedure

The flow sheet of the apparatus is shown in Figure 1(B)15. Mixed gas from gas holder (a) is drawn through the stripping tower (m) and compressed and sent to an absorbing tower (b). Water is pumped in the absorbing tower by pump (d) from a water tank (e). The solution at the bottom of the absorbing tower is released at the medium pressure tower (f). The residual gas from the top of the absorbing tower (b) which contains scarcely any acetylene is introduced to the hydrogenation plant of the residual acetylene without releasing the pressure. This part of the plant consists of a heat exchanger (g), a preheater (h), a converter (i), and a cooler (j).

The function of the medium pressure tower is to increase the purity of acetylene. Gas is expelled by the solubility difference according to the decrease in pressure. Expelled gas which consists of almost all methane and hydrogen and a part of acetylene dissolved in water at (b) was mixed in charging gas before the compressor (c).

Water at the bottom of (f) is released to atmospheric pressure tower (k) and almost all acetylene is expelled. Acetylene from the top of (k) has a purity of 95% or more. Water at the bottom of (k) is sent by a pump (l) to the stripping tower (m). Water from the bottom of (l) which contains scarcely any acetylene, according to the solubility at the partial pressure of (m) returns to the water tank (e). The absorbing tower is 150mm in diameter and 10m in height. This plant has a charge capacity of arc cracked gas of 20m^3 per hour.

The test procedure was as follows. When the running became smooth, gas samples for the analysis were drawn from each part of the plant. Gas analysis was made by modified Hempel's method.

ENCLOSURE (B)15

B. Experimental Results

Conditions of running

Rate of charging gas	20 m^3/Hr
Rate of recycling water	5 m^3/Hr
Pressure of (b)	20 atm. p. on gauge
(f)	3 atm. p. on gauge
(k)	0 atm. p. on gauge
(m)	0 atm. p. on gauge

Analysis of charging gas

C_2H_2	18.3%
H_2	56.1%
CH_4	23.5%
CO_2, O_2 and N_2	3.1%
Temp. of recycling water	18°C
Rate of gas from to of (b)	13.5 m^3/Hr

Analysis of gas from top of (b)

C_2H_2	0.8%
H_2	70.3%
CH_4	26.5%
Rate of gas from to of (f)	23 m^3/Hr

Analysis of gas from top of (f)

C_2H_2	51.6%
H_2	11.4%
CH_4	35.4%
Rate of gas from (k)	37 m^3/Hr

Analysis of gas from top of (k)

C_2H_2	95.8%
H_2	1.0%
CH_4	2.8%

Analysis of gas at the suction of the compressor

C_2H_2	20.5%
H_2	52.3%
CH_4	25.3%

The contents of acetylene in the residual gas, if the height of the absorbing tower is sufficient, is determined by the quantity of acetylene dissolved in recycling water.

Gas from the top of the absorbing tower was introduced into the hydrogenation plant. The convertor is packed with nickel catalyst of U.O.P. type and gas, heated to 350°C. was passed through the catalyst at the space velocity of 10,000 volumes of gas per volume of catalyst per hour. Acetylene contained in gas was hydrogenated and reaction with Illosbay's reagent had shown no colouration for four weeks. As the gas treated by this method contains no acetylene, the separation of hydrogen from the residual gas can be done with Linde's machine with no danger.

III. CONCLUSIONS

From mixed gas consisting of 20% of acetylene, 50% of hydrogen, and 20% methane, acetylene having a purity of 95% or more was separated by high pressure water extraction.

The residual gas containing less than 1% of acetylene was hydrogenated on nickel catalyst at 350°C; it is possible to treat with Linde's machine for the separation of hydrogen without danger.

ENCLOSURE (B) 15

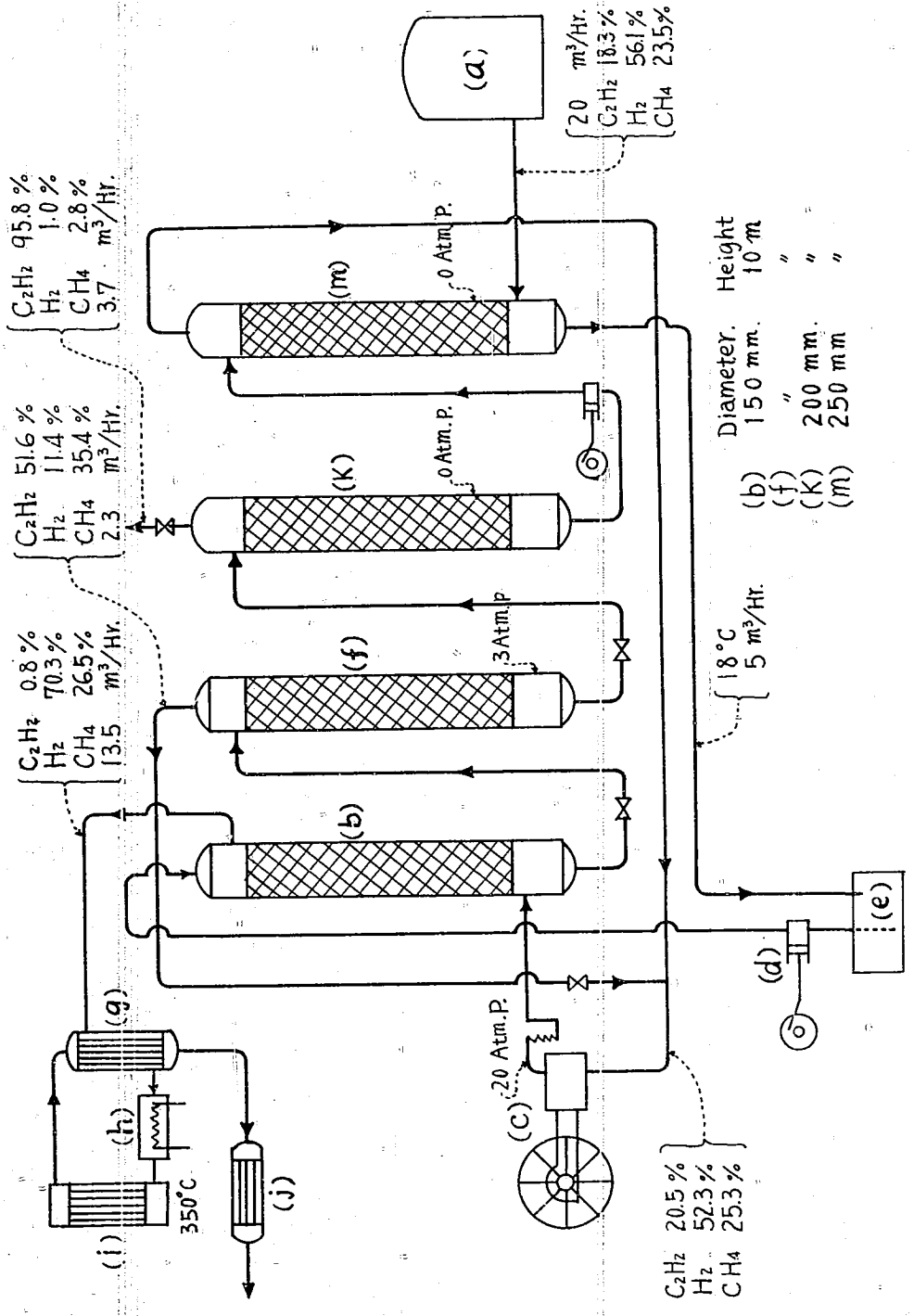

FIG. SHEET OF C₂H₂ SEPARATION

ENCLOSURE (B) 16

STUDIES ON HYDROCRACKING OF OILS AND TARS

(In Six Parts)

by

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December 1945

ENCLOSURE (B)16

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INTRODUCTION

The object of these studies was to investigate the production of high quality aviation gasoline from oils and tars by hydrocracking.

This report consists of six parts as follows:

Part 1. Studies on hydrocracking of high temperature coal tar.

Part 2. Studies on hydrocracking of low temperature coal tar.

Part 3. Studies on hydrocracking of OHA gas oil.

Part 4 Studies on hydrocracking of OMONOGAWA gas oil.

Part 5. Studies on hydrocracking of SUMATRA kerosene.

Part 6. Studies on hydrocracking OHA gas oil in a semi-commercial plant.

The results were as follows:

Raw Material	Catalyst	Reaction Temp. (°C)	Reaction Press. (kg/cm^2)	Yield of Aviation Gasoline Vol. %	Octane Number of Aviation Gasoline Leaded 0.1 %
High Temp. Tar.	MoS_3	470	200	25	92
Low Temp. Tar.	MoS_3	430	200	50	89
Sumatra Kerosene	*	420	200	70	87
Omonogawa Gas Oil	*	430	200	73	89
Oha Gas Oil	*	410	200	70	92

*Nickel-Molybdenum oxide

ENCLOSURE (B)16

PART I

STUDIES ON HYDROCRACKING OF HIGH TEMPERATURE COAL TAR

by

CHEM. ENG. LT.
K. SONE

Research Period: March 1941-December 1942

SUMMARY

The object of these experiments was to study the preparation of aviation gasoline high temperature coal tar by means of high pressure hydrocracking.

To prepare aviation gasoline of satisfactory quality, it was necessary to process in two steps, i.e. primary and secondary hydrocracking, using MoS_3 as a catalyst. In the primary hydrocracking step under conditions of 200kg/cm^2 and 420°C, a fraction boiling at 200 to 300°C (60 vol.% yield) was prepared as feed for secondary hydrocracking.

In the secondary hydrocracking step a 40 vol. % yield of aviation gasoline was obtained under conditions of 200 kg/cm^2 and 470°C. The octane value of this gasoline with 0.1 % of lead was 92.

I. INTRODUCTION

A. History of Project

A large amount of high temperature coal tar is produced as a by-product of coke manufacturing in steel works. Because of limited resources of oil in Japan, consideration was given to the use of such tar as a raw material for preparation of aviation gasoline. These hydrocracking tests on high temperature tar were started in March 1941 and completed in December 1942.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr.	K. MITSUI
Chem. Eng. Lieut.	A. MORITA
Chem. Eng. Lieut.	N. ŌWAKI
Chem. Eng. Lieut.	U. SATO
Chem. Eng. Lieut.	K. SONE

ENCLOSURE (B)16

II. DETAILED DESCRIPTION

A. Feed Stock

The creosote oil-feed stock was a brownish black, viscous liquid fractionated from crude high temperature coal tar at the Showa Steel Works. Crystals of crude anthracene had been removed from this cut by filtration.

Properties of this oil were as follows:

Properties of Creosote Oil

Ultimate Analysis

C	90.1 wt.%
H	5.6 wt.%
S	0.3 wt.%
N	0.9 wt.%
C/H	16.0 wt.%
Ash	trace
d_{20}^{20}	1.135
Free Carbon	trace

Distillation

Moisture	0.3%
First Drop	230°C
10% point	284°C
20% point	306°C
30% point	324°C
40% point	337°C
50% point	347°C
60% point	357°C
70% point	368°C
80% point	384°C
--300°C fraction	17.0%
--400°C fraction	88.5%
Phenols	4.0 vol.%
Bases	6.6 vol.%
Unsat. hydrocarbon	13.4 vol.%
Arom. hydrocarbon	76.0 vol.%
Sat. hydrocarbon	0 vol.%

B. Autoclave Tests

1. Comparison of Catalysts

200 to 300 gm of oil and 5 wt% of catalyst were introduced in a 2.4lit rotary autoclave and hydrogen was added until the pressure reached 100 kg/cm^2 at normal temperature. The autoclave was heated at the rate of 2.5°C per minute to 450°C and the reaction was continued for 30 to 60 minutes. The relative activities of catalysts were determined by comparison of the properties of oil products and analyses of the residual gases.

Experimental data are summarized in Tables I(B)16 and II(B)16.

Catalyst with good activity showed high H_2 consumption and low density of oil product. Of the various catalysts, MoS_3 demonstrated

the best activity.

2. Influence of Reaction Temperature

In these experiments 200 gm of oil and 10 gm of MoS_3 were charged to the autoclave (2.4lit Can) and H_2 was added until pressure reached 100 kg/cm2 at normal temperature.

Results of these experiments are tabulated in Table III(B)16.

On the basis of these results a temperature of 450 to 470°C was selected for the primary hydrocracking of this oil, because the yield of 200 to 300°C feed stock for secondary hydrocracking was a maximum.

3. Secondary Hydrocracking

A 200 to 300°C fraction made from creosote oil hydrogenated at 450°C over MoS_3 catalyst, was used as the feed stock. Reaction conditions and results of these experiments are given in Tables IV(B)16, V(B)16 and VI(B)16.

On the basis of these data 480° was selected as the optimum reaction temperature for secondary hydrocracking on the basis of producing maximum yield of aviation gasoline is maximum. This temperature is also regarded as the maximum allowable due to increasing coking and gasification difficulties.

C. Experiments in the Continuous Hydrocracking Pilot Plant

1. Primary Hydrocracking

A flow sheet of the pilot plant is given in Figure 1(B)16. This same unit was also used in experiments on hydrocracking of low temperature tar, Oha gas oil, pine root oil and soya bean oil.

MoS_3 was selected as the catalyst for these experiments.

Reaction conditions and results are given in Tables VII(B)16 through XI(B)16. Good yields of oil product and only a small amount of gaseous hydrocarbons were obtained in these experiments. The ratio of feed stock and hydrogen was optimum at 3 m^3/lit.oil.

Yield of the oil fraction boiling at 200 to 300°C (raw material for secondary hydrocracking) was about 60%. CS_2 was added in small amounts to maintain activity of catalyst.

2. Secondary Hydrocracking

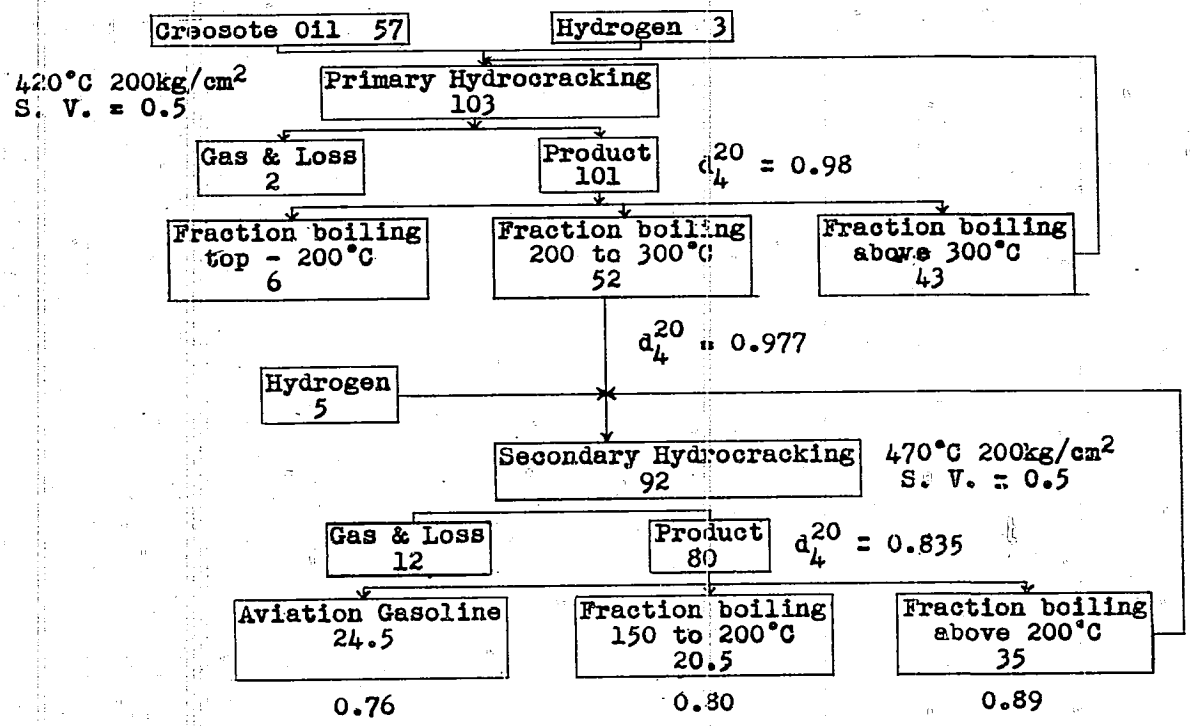
Data on secondary hydrocracking in the pilot plant, using MoS_3 catalyst, are given in Tables XII(B)16 through XV(B)16.

D. Material Balance

A material balance for the process under optimum conditions is shown in the following diagram.

ENCLOSURE (B)16

MATERIAL BALANCE



III. CONCLUSIONS

A. MoS_3 showed the best activity for hydrocracking of creosote oil in both autoclave and continuous pilot plant experiments.

B. 470°C was the optimum reaction temperature for primary hydrocracking in autoclave tests, but 420°C was optimum in the continuous pilot plant.

C. By primary hydrocracking in the continuous pilot plant, it was found that the oil product contained 10% of the fraction boiling below 200°C, 60 vol.% of the fraction boiling between 200 to 300°C.

D. By primary hydrocracking in the continuous pilot plant, the yield of aviation gasoline was 40 vol.% under conditions of 200 kg/cm² and 470°C, using MoS_3 catalyst. Octane value of this aviation gasoline was 92 with 0.1% of lead.

APPENDIX A

PROCEDURE FOR DETERMINING HYDROCARBON TYPES

A. Unsaturated Hydrocarbons

Sample used	100cc
H_2SO_4 (80% d_4^{15} = 1.732)	200cc
Temperature	below 7°C
Period	15 minutes

ENCLOSURE (B)16

Content of Unsaturated Hydrocarbons (Vol.%) = Percent of Sample Over in Engler Distillation - Percent Residual Oil Distilled Over (After Treatment by 80% H_2SO_4)

B. Aromatic Hydrocarbons

Sample (Oil with unsaturated hydrocarbon removed) used ... 50cc
H_2SO_4 (98%, d_4^{15} = 1.841) added 150cc
Temperature ..... 15°C
Period ..... 30 minutes

Content of Aromatic Hydrocarbons (vol.%) = (100-U) x $\frac{50-V}{50}$

Where: V = Oil after treatment
U = content of unsaturated hydrocarbons (vol.%)

C. Naphthenic Hydrocarbon

Sample (with unsaturated and aromatic hydrocarbons removed) used 10cc
Aniline added (b.p. 184 ± 2°C, d_4^{15} = 1.026) 10cc

Content of Naphthenic Hydrocarbon = $\frac{70-T}{30}$ (100-U-A) (Vol.%)

Where: T = Aniline point °C of sample
U = Content of unsaturated hydrocarbon (Vol.%)
A = Content of aromatic hydrocarbon (Vol.%)

D. Paraffinic Hydrocarbon

Where: Content of paraffinic hydrocarbon = 100-(U A N) (Vol.%)
N = Content of naphtenic hydrocarbon (Vol.%)

ENCLOSURE (B)16

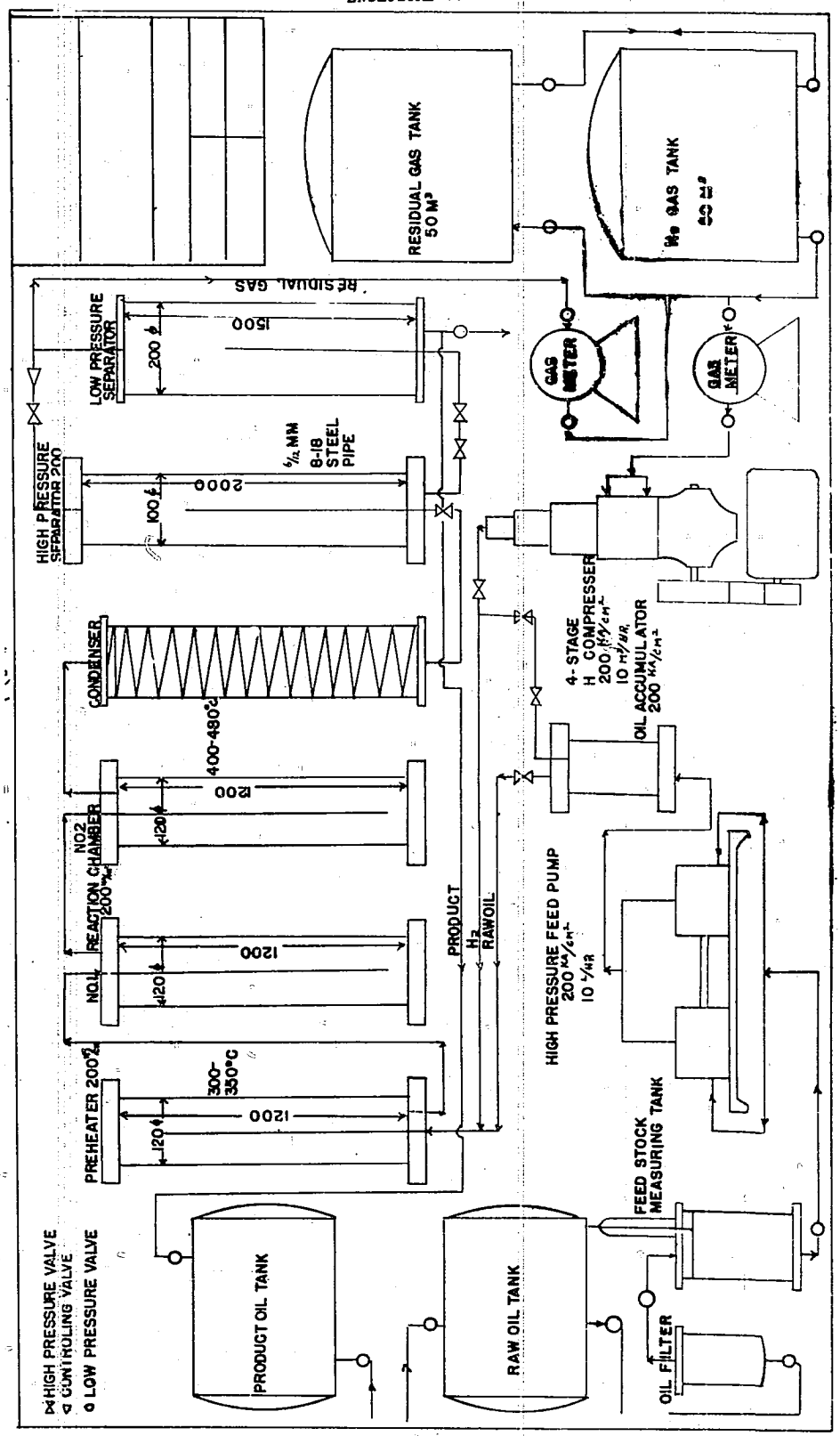


Figure 1(B)16
FLOW SHEET OF HYDROCRACKING PILOT PLANT

Table I(B)16
CATALYST TESTS IN ATUOCLAVE
REACTION CONDITIONS

Exp. No.	Catalyst	Reaction Conditions				H_2 Consumption		Analysis of Residual Gases (vol. %)							
		Oil (gm)	Catalyst (gm)	Temp. (°C)	Time (min)	Press. Drop. (kg/cm^2)	Weight (%)	CO_2	O_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	N_2	
1	No Catalyst	300		450	30	7.3	0.7	0.2	0.6	0.3	0.3	95.0		2.8	
2	No Catalyst	300		470	30	9.9	0.9	0.1	0.4		0.1	94.8		4.6	
3	$Cu\ CrO_4$	300	15	450	30	16.4	1.6	0.1	0.7	0.5	0.3	89.2	6.2	2.9	1.2
4	MoO_3	300	15	450	30	35.0	2.4			0.1	0.4	96.2		3.3	
5	MoO_3	300	15	470	30	43.0	2.9	0.1		0.7	0.4	95.5		3.4	
6	MoO_3	200	10	450	60	31.5	3.5		0.2	0.1		93.7		6.2	
7	MoO_3	200	10	470	60	37.6	3.9	0.2			0.3	96.2	2.3	1.0	3.0
8	$Al(CH_3)_3$	300	15	450	30	20.5	1.6	0.3	0.3	0.2	0.8	93.2		5.2	
9	$MoO_3 \cdot NiO \cdot SnO (3:1:0.3)$	300	15	450	30	20.4	1.4		0.2	0.2	0.5	96.5		2.6	
10	WO_3	300	15	450	30	16.6	1.4		0.1	0.3	0.3	94.0		5.3	
11	$Zn(CH_3COO)_2$	300	15	450	30	9.3	0.7			0.1	0.4	96.9		2.6	
12	$ZnCl_2$	300	15	450	30	16.4	1.3		0.2	0.2	0.4	94.6		4.0	
13	$ZnCl_2$	300	15	450	30	43.3	2.9		0.3		0.5	94.6	3.3	1.3	1.2
14	Al_2O_3	300	15	450	30	21.2	1.7	0.1		0.2	0.4	91.7	4.0	3.3	1.0
15	$SnCl_2$	300	15	450	30	24.0	1.7	0.4	0.2	0.2	0.5	95.4		3.3	
16	$MoO_3 \cdot SnO \cdot S (1:0.1:2)$	300	15	450	30	30.5	2.0	0.4		0.1	0.6	95.9		2.0	
17	$(NH_4)_2MoO_4$	300	15	450	30	23.9	1.7	0.1	0.2	0.2	0.3	95.9		3.3	
18	$ZnMoO_4$	300	15	450	30	12.3	0.9			0.4	0.5	97.1		2.0	
19	$(NH_4)_6Mo_7O_{27} \cdot S \cdot Al_2O_3$ (1 : 2 : 2)	300	15	450	30	35.5	2.4			0.2	0.4	95.8		3.6	
20	$(NH_4)_6H_4[H(MoO_4)_6]5H_2O$	200	10	450	60	31.3	3.4	0.1			0.2	94.5	2.7	2.6	1.5
21	$2(NH_4)_2O \cdot SiO_2 12MoO_3 \cdot x\ H_2O$	200	10	450	60	38.8	4.3	0.1	0.1	0.1	0.1	93.0	3.9	2.7	1.5
22	$(NH_4)_4H_6[Cu(MoO_4)_6]5H_2O$	200	10	450	60	27.3	3.0		0.1	0.5	0.2	95.9		3.3	
23	$3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3 \cdot x\ H_2O$	200	10	450	60	35.7	3.9		0.1	0.2	0.4	95.2	1.7	2.4	1.8
24	$(NH_4)_3H_6[Cr(MoO_4)_6]7H_2O$	200	10	450	60	15.7	2.0	0.1		0.5	0.6	94.2		3.6	
25	$(NH_4)_8[Sn(Mo_2O_4)_6]20H_2O$	200	10	450	60	22.3	2.5			0.2	0.2	95.6		4.0	
26	$MoO_3 \cdot WO_3 \cdot NiO (1:1:0.3)$	200	10	450	60	13.4	1.7	0.1	0.1	0.2	0.5	94.5		4.6	
27	Fe_2O_3	200	10	450	60	14.9	1.6	0.1		0.1	0.6	97.2		2.0	
28	$FeCl_2$	200	10	450	60	16.2	2.0		0.2	0.6	0.3	94.9		4.0	
29	$Na_3PO_4 \cdot 12H_2O$	200	10	450	60	13.0	1.7	0.2	0.3	0.2	0.3	95.0		4.0	
	$(NH_4)_3 \cdot PO_4(MoO_3)_{12} \cdot 6H_2O$	200	10	450	60	33.1	3.6	0.1	0.5	0.5	0.6	95.0	0.5	2.3	
31	$3\ NiO \cdot P_2O_5 \cdot 24MoO_3$	200	10	450	60	29.0	2.4	0.2	0.4	0.1	0.3	96.4		2.6	
32	MoO_3	200	10	450	60	46.1	4.8			0.3	0.5	94.6	3.0	1.4	2.3

ENCLOSURE (B)16

Table II(B)16
CATALYST TESTS IN AUTOCLAVE
PRODUCT YIELDS AND INSPECTIONS

EXP. No.	Yield of Product		Density	Fractional Distillation (°C)									Fraction boiling up to 360°C
	Wt%	Vol%	20/20 °C	I.B.P.	10%	20%	30%	40%	50%	60%	70%	80%	(Vol%)
1	100.1	101.5	1.119	220	270	292	306	315	330	342	357		75
2	99.5	105.6	1.069	215	254	294	304	321	331	342	356		75
3	98.9	101.9	1.102	215	256	287	307	317	328	342	355		78
4	102.7	110.6	1.054	104	225	262	288	299	312	325	339	355	84
5	97.6	107.5	1.042	95	221	251	269	286	302	314	332	347	88
6	93.5	102.5	1.032	118	224	254	269	290	302	315	327	342	90
7	92.8	104.3	1.010	95	182	231	248	273	289	301	317	333	91
8	98.3	102.8	1.085	114	250	281	300	311	325	336	346		81.5
9	100.1	105.7	1.085	103	255	281	298	313	323	333	345		80.0
10	97.5	100.6	1.100	193	264	284	303	314	325	336	348		79
11	97.1	101.1	1.091	127	276	298	312	320	333	355			75
12	98.0	101.8	1.093	180	262	274	298	313	326	337	349		79
13	100.5	114.0	1.045	104	225	255	278	296	311	324	339	358	83
14	99.4	103.5	1.090	165	260	277	299	316	323	333	347		78
15	96.7	101.2	1.085	145	240	272	290	305	319	330	343	358	82
16	99.8	105.8	1.071	165	242	273	293	299	317	330	343	357	83
17	98.0	102.5	1.085	145	252	273	290	308	322	334	344	359	81
18	98.5	100.8	1.109	214	265	288	307	312	335	342	357		72
19	99.0	105.7	1.063	128	239	265	284	301	315	326	338	353	85
20	96.6	105.8	1.036	116	221	253	271	291	303	315	327	340	90
21	94.1	104.8	1.019	114	216	246	264	279	292	305	318	332	92
22	96.5	104.7	1.046	142	238	268	284	291	311	320	333	348	88
23	95.1	105.4	1.024	128	225	254	271	286	299	314	325	340	90
24	96.4	100.8	1.085	193	254	279	295	313	321	334	343	358	83
25	95.4	101.6	1.065	160	248	272	288	303	316	326	338	352	85
26	96.9	100.8	1.091	188	256	284	296	314	325	334	347	359	81
27	98.4	102.2	1.093	168	252	282	298	311	321	330	342	358	84
28	97.0	102.2	1.077	140	243	267	291	306	317	329	341	356	84
29	99.1	102.7	1.095	186	252	281	298	312	324	335	346	359	81
30	96.0	105.3	1.035	109	226	249	275	292	306	318	330	347	88.5
31	95.9	103.6	1.050	174	241	268	280	296	307	317	329	342	92
32	94.9	108.1	0.9965	92	191	232	252	268	282	296	309	328	92

ENCLOSURE (B)16

Table III(B)16
EFFECT OF TEMPERATURE WITH MoS_3 CATALYST

Exp. No.	1	2	3	4	5	6
Catalyst	MoS_3	MoS_3	MoS_3	MoS_3	MoS_3	MoS_3
Reaction Temperature (°C)	400	430	430	450	470	480
Reaction Time (min)	90	60	90	60	60	60
Initial Pressure H_2 (Kg/cm^2)	100	100	100	100	100	100
Pressure Drop (Kg/cm^2)	35.5	43.3	44.2	46.1	45.6	47.8
H_2 Absorbed (Wt% of oil charge)	3.9	4.6	4.7	4.8	5.1	4.4
Analysis of Residual Gas						
CO_2	0.2		0.1			
O_2	0.3	0.2	0.2		0.1	0.1
C_nH_{2n}	0.2	0.5	0.4	0.3	0.1	0.1
CO	0.4	0.5	0.6	0.5	0.7	0.8
H_2	94.3	94.2	94.1	94.6	89.6	87.2
C_nH_{2n+2}	2.3	3.5	3.3	3.0	5.9	10.6
N_2	2.7	1.1	1.3	1.6	3.3	1.2
n	1.3	1.6	1.0	2.3	2.5	2.3
Yield of Product						
Wt %	99.2	98.5	97.7	94.9	87.7	85.0
Vol%	109.2	110.0	110.0	108.1	100.9	98.0
Density $\left(d_{20}^{20}\right)$	1.031	1.016	1.008	0.997	0.986	0.985
Fractional Distillation (Vol%)						
F.D.	168	132	106	92	85	80
10 %	241	226	222	191	152	142
30 %	282	275	267	252	225	227
50 %	305	298	294	282	259	256
70 %	332	319	316	309	295	297
90 %	358	359	353	357	336	350
Fraction Boiling						
200°C (%)	4.0	7.0	8.0	12.5	20.0	24.0
300°C (%)	47.0	52.5	55.5	63.0	72.5	71.0
360°C (%)	91.0	92.0	92.5	92.0	97.0	94.0

Table IV(B)16
SECONDARY HYDROCRACKING IN AUTOCLAVE
CONDITION OF REACTION

Exp. No.	Catalyst	Reaction Temp (°C)	Reaction Time (min)	H_2 Initial Press (kg/cm^2)	Press Drop (kg/cm^2)	H_2 Consumption (wt%)	Yield of Product (wt%)	Yield of Product (vol%)
1	MoS_3	450	60	100	25.5	2.8	96.7	103.5
2	MoS_3	470	60	100	33.8	3.9	83.9	92.2
3	MoS_3	480	60	100	41.1	6.5	75.7	85.1

Table V(B)16
SECONDARY HYDROCRACKING IN AUTOCLAVE
CONDITION OF REACTION

Exp. No.	CO_2	O_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	N_2	n
1	0.2	0.2	0.1	0.8	95.2	2.9	0.6	1.0
2	0.4	0.1	0.4	0.2	91.7	5.9	0.3	2.3
3	0.2	0.2	0.6	0.8	82.5	12.4	3.3	3.2

ENCLOSURE (B)10

Table VI(B)16
SECONDARY HYDROCRACKING IN AUTOCLAVE
PROPERTIES OF FEED STOCK AND PRODUCTS

	Feed Stock	Oil Product			A Fraction Boiling ~150°C of Product (Exp No.3)
		1	2	3	
d_{20}^{20}	0.9886	0.9241	0.9005	0.8800	0.8110
F.D. (°C)	146	96	74	60	64
10 % (°C)	208	168	116	103	82.5
20 % (°C)	222	196	142	119	87
30 % (°C)	229	206	165	137	90.5
40 % (°C)	241	218	185	155	95
50 % (°C)	250	228	200	176	99
60 % (°C)	260	236	210	193	105
70 % (°C)	272	247	220	206	111
80 % (°C)	288	260	235	219	119
90 % (°C)	305	278	263	256	131
D.P. (°C)	348	347	340	334	161
Total Distilled (%)	99.0	98.8	98.5	98.5	98.0
~150°C (%)		6.5	23.0	37.0	
~200°C (%)		22.0	50.0	65.0	
Un Sat. H.C. (%)					1.5
Arom. H.C. (%)					55.2
Naph. H.C. (%)					43.3
Para. H.C. (%)					
Octane Value Clear					83.6
Octane Value Lead					95.2

ENCLOSURE (B)16

Table VII(B)16
CONTINUOUS PILOT PLANT - PRIMARY HYDROCRACKING
REACTION CONDITION AND YIELD

Run No.		9	10	11	12	13	14
Temp of Preheater (°C)		300	300	300	300	300	300
Temp Reaction Chamber No.1		380	380	380	380	380	380
Temp Reaction Chamber No.2		430	430	430	430	430	440
H_2 Pressure (Kg /cm^2)		200	200	200	200	200	200
H_2 Charged (m^3/hr)		4	8	6	4	6	7
Oil Charged (lit/hr)		4	8	6	4	6	7
CS_2 Added (cc/lit oil)		3			3	1	1
Run Period (hr)		6	6	6	72	24	72
Yield of Product (Vol%)		114.7	112.6	118.3	115.3	115.4	116.3
Yield of Product (Wt%)		98.5	101.5	105.7	100.4	102.7	105.1
H_2 Consumption Per Hour	(m^3)	3.49	5.35	3.79	2.99	3.48	3.60
	(lit/lit oil)	845	669	630	724	573	516
	(gm/kg oil)	66.8	52.7	49.8	57.2	45.3	40.8

ENCLOSURE (B)16

Table VIII(B)16
CONTINUOUS PILOT PLANT - PRIMARY HYDROGENATION
PROPERTIES OF PRODUCTS

Run No.	9	10	11	12	13	14	Raw Material
Properties of Product							
d_4^{20}	0.9771	1.0281	1.0155	0.9897	1.0114	1.0283	1.135
First Drop (°C)	66.0	79.0	78.0	66.0	77.0	74.0	230
10 % point (°C)	156	210	201	150	207	217	284
20 % point (°C)	179	240	229	205	227	243	306
30 % point (°C)	228	264	250	218	252	271	324
40 % point (°C)	245	284	277	248	276	283	337
50 % point (°C)	260	297	290	265	287	300	347
60 % point (°C)	280	313	308	290	308	312	357
70 % point (°C)	296	331	322	310	323	326	363
80 % point (°C)	319	346.5	340	328	345	348	384
90 % point (°C)	350	373	370	366	378	370	
97 % point (°C)	390		390			390	
Dry point (°C)	397	410	395	395	395	402	
Total Distilled (%)	98.5	96.5	97.5	96.5	96.5	98.0	
Residue (%)	0.7	3.0	2.0	3.0	3.0	1.5	
Loss (%)	0.8	0.5	0.5	0.5	0.5	0.5	
~150 °C (%)	0.9						
~200 °C (%)	21.0	6.0	25	19.0	9.0	8.0	
~300 °C (%)	72.0	51.0	55.5	67.5	56.0	50.0	17.0
Analysis of residual gas							
CO_2		0.3			0.1		
C_nH_{2n}	0.2	0.3	0.2	0.1	0.2	0.5	
CO	0.6	0.3	0.6	0.9	0.5	0.4	
H_2	87.6	91.8	93.6	92.0	93.2	91.6	
C_nH_{2n+2}	11.6	6.6	6.0	7.0	5.6	5.0	
N_2		0.7			0.3	1.0	
n	1.1	1.6	1.0	1.6	1.3	2.2	
O_2					0.1	0.2	

ENCLOSURE (B)16

Table IX(B)16
CONTINUOUS PILOT PLANT - PRIMARY HYDROCRACKING
PROPERTIES OF RAW MATERIAL

Run No.	1	2	3	4	5	6	7	8
d_4^{20}	0.9423	0.9960	0.9612	0.9651	0.9842	1.0250	1.0176	1.0167
First Drop (°C)	940	104	82	92	85	95	87	92
10 % point (°C)	170	210	183	209	205	215	218	222
20 % point (°C)	212	240	223	234	235	247	245	255
30 % point (°C)	235	260	240	248	262	262	262	278
40 % point (°C)	256	276	258	263	280	283	280	290
50 % point (°C)	270	291	273	277	292	300	303	308
60 % point (°C)	285	305	284	290	305	315	313	315
70 % point (°C)	300	323	303	300	319	328	335	330
80 % point (°C)	320	338	321	315	341	344	351	343
90 % point (°C)	345	371	345	340	364	380	374	373
Dry point (°C)	378	387	385	382	385	384	395	390
Total Distilled (%)	95.0	95.0	97.0	97.0	96.5	95.0	95.0	97.0
Residue (%)			2.8	2.6	3.1			
Loss (%)			0.2	0.4	0.4			
~200 °C (Vol %)	16.5	8.5	15.0	8.0	8.0	8.0	8.0	7.5
~300 °C (Vol %)	70.0	58.0	68.5	70.0	56.0	50.0	49.5	48.0
Analysis of Residual Gas								
CO_2		0.1				0.4	0.2	
O_2		0.2	0.2		0.2	0.4	0.2	0.1
C_nH_{2n}	0.6	0.2	0.6		0.6	1.2	1.0	0.5
CO	0.6	0.4	0.4			0.6		0.1
H_2	92.0	90.0	90.9		93.9	90.9	91.5	91.3
C_nH_{2n-2}	5.3	4.0	2.0		3.4	4.2	2.0	7.2
N_2	1.5	5.1	5.9		1.9	2.3	5.1	0.8
n	1.7	1.0	1.0		1.0	1.0	1.0	1.0

ENCLOSURE (B)16

Table X(B)16
CONTINUOUS PILOT PLANT - PRIMARY HYDROCRACKING
REACTION CONDITIONS AND YIELDS

Run No.		1	2	3	4	5	6	7	8
Temp of Preheater (°C)		350	350	350	350	350	350	350	350
Temp Reaction Chamber	No.1	380	380	380	380	380	390	390	390
	No.2	420	420	420	420	420	420	430	430
H_2 Pressure (kg/cm^3)		200	200	200	200	200	200	200	200
H_2 Charged (m^3/Hr)		5	10	7	15	5	10	10	10
Oil Charged (lit/Hr)		5	10	5	5	5	10	10	10
CS_2 Added (cc/lit oil)		3	0.1	3	7	4	0.3	3	2
Name of raw material		(A)	(A)	(A)	(A)	(B)	(A)	(A)	(B)
Run Length (Hr)		6	6	6	6	12	10	6	6
Yield of Product	(Vol%)	124.5	119.5	120.2	121.8	113.9	112.7	114.2	110.4
	(Wt %)	103.4	104.9	101.8	103.6	101.8	101.8	102.4	102.0
H_2 Consumption (m^3)		403	5.50	3.78		2.24	5.71	5.01	4.79
(lit/lit vol)		803	548	747		448	571	503	479
(gm/kg oil)		63.6	43.4	59.2		36.6	45.2	39.8	39.1

ENCLOSURE (B)16

Table XI(B)16
CONTINUOUS PILOT PLANT - PRIMARY HYDROCRACKING
PROPERTIES OF PRODUCTS

Raw Material	(A)	(B)
d_{20}^{20}	1.135	1.103
First Drop (°C)	230	230
10 % point (°C)	284	295
20 % point (°C)	306	308
30 % point (°C)	324	321
40 % point (°C)	337	333
50 % point (°C)	347	343
60 % point (°C)	357	353
70 % point (°C)	368	364
80 % point (°C)	384	379
~300 °C (Vol%)	17.0	15.0
~400 °C (Vol%)	88.5	

(A) Creosote oil.

(B) Creosote oil mixed with fraction boiling above 300°C of hydrogenated product in the ratio of 4:6 by Vol.

ENCLOSURE (B)16

Table XII(B)16
CONTINUOUS PILOT PLANT - SECONDARY HYDROCRACKING
PROPERTIES OF FEED STOCK

Raw Material		(A)	(B)	(C)
d_4^{20}		0.9767	0.9574	0.9563
First Drop	(°C)	190	80.5	200.5
10 % point	(°C)	220	178	220.5
20 % point	(°C)	230	214	227
30 % point	(°C)	239	226.5	233.5
40 % point	(°C)	247	235.5	241
50 % point	(°C)	254	247	249.5
60 % point	(°C)	264	257.5	259
70 % point	(°C)	271	269.5	268
80 % point	(°C)	283	282	280
90 % point	(°C)	300	298	296.5
97 % point	(°C)	317	321.5	325
Dry Point	(°C)	323	331	346
Total distilled	(%)	98.5	99	99
Residue	(%)	1.0	0.6	0.5
Loss	(%)	0.5	0.4	0.5

(A) A 200-300°C fraction from primary hydrogenation (Table IV Run 12)

(B) A F.D ~300°C fraction from primary hydrogenation (Table IV Run 12)

(C) Mixture of raw material (A) and a fraction 200°C~ of secondary hydrogenated oil (Table VIII Run 4) in ratio of 2:1 by vol.

ENCLOSURE (B)16

Table XIII(B)16
CONTINUOUS PILOT PLANT - SECONDARY HYDROCRACKING
YIELDS AND REACTION CONDITIONS

Run No.		1	2	3	4	5	6	7
Temp of Reaction Chamber	No.1	380	400	400	400	400	450	450
	No.2	420	440	460	470	470	470	470
H_2 Pressure (kgm/cm^2)		200	200	200	200	200	200	200
H_2 Charged (m^3/hr)		5	5	5	5	5	5	5
Oil Charged (ℓ/hr)		5	5	5	5	5	5	5
CS_2 Added (cc/ℓ oil)		3.5	3.5	3.5	3.5	3.5	3.5	3.5
Name of raw material		(A)	(A)	(A)	(A)	(B)	(B)	(C)
Run Period (hr)		4	4	4	6	6	6	6
Yield of Product	(Vol%)	103.1	113.1	99.0	104.2	101.4	100.9	104.2
	(Wt %)	91.2	99.8	99.0	92.2	96.4	91.9	92.4
H_2 Consumption	(m^3)	2.42		3.42	2.80	2.55	2.73	2.26
	(ℓ/ℓ oil)	474		689	563	504	555	458
	(gm/kg oil)	43.7		63.4	51.8	47.4	52.1	42.9

Catalyst: Reaction chamber No. 1 MoS_3 + active clay 10 lit packed
Reaction chamber No. 2 MoS_3 10 lit packed

ENCLOSURE (B)16

Table XIV(B)16
CONTINUOUS PILOT PLANT - SECONDARY HYDROCRACKING
PROPERTIES OF PRODUCTS

Run No.	1	2	3	4	5	6	7
d_4^{20}	0.8661	0.8620	0.8668	0.8615	0.8655	0.8358	0.8352
First Drop (°C)	64	67	53.0	52	50	49	48
10 % point (°C)	121	150		102	100.5	91.5	90
20 % point (°C)	157	186	138	125	122	100	117
30 % point (°C)	189	204	174.5	152	148	132.5	142
40 % point (°C)	200	213	193.5	187	178	154	165.5
50 % point (°C)	209	221	204	200	198	178.5	188
60 % point (°C)	218.5	233	217	214	208	196	200
70 % point (°C)	229.5	245	228	226	221	206.5	210
80 % point (°C)	243	268	241.5	240	239	224	225
90 % point (°C)	263	300	265	263	265	244	248
97 % point (°C)	287	309	297	312	320	308.5	254
Dry point (°C)	300		375	330	330		313
Total Distilled (%)	98.5	98.5	98.0	98.5	98	98	98.5
Residue (%)	1.2	0.8	0.9	0.9	1.0	0.7	0.8
Loss (%)	0.3	0.7	1.1	0.6	1.0	1.3	0.7
~150 °C (%)	18.0	20.0	24.0	29.0	31.0	39.0	32.0
~200 °C (%)	40.0	38.5	47.0	50.0	52.0	64.5	60.0
Yield of Aviation Gasoline (%)	22.2	24.4	28.9	35.2	37.8	44.0	39.2
Analyis of Residual Gas (%)							
CO_2 (%)	0.1		0.1		0.1	0.1	
O_2 (%)	0.2		0.1	0.1	0.1	0.1	0.1
C_nH_{2n} (%)	0.3		0.4	0.5	0.5	0.6	0.2
CO (%)	0.4		0.5	0.4	0.5	0.5	0.2
H_2 (%)	93.1		89.0	89.8	89.0	86.2	89.0
C_nH_{2n+2} (%)	4.6		8.9	8.3	8.9	12.2	9.6
N_2 (%)	1.3		1.0	0.9	0.9	0.3	0.6
n (%)	1.2		1.4	1.3	1.1	1.7	1.5

ENCLOSURE (B)16

Table XV(B)16
CONTINUOUS PILOT PLANT - SECONDARY HYDROCRACKING
PROPERTIES OF AVIATION GASOLINE

Run No.		1	2	3	4	5	6	7
d_4^{20}		0.7689	0.7645	0.7755	0.7724	0.7710	0.7607	0.7534
First Drop (°C)		52	45.5	50	51	53.5	48	43.5
10 %		69.5	69	72	71	73	68	66.5
20 %		77	76	78	78.5	80	78	73.5
30 %		81.5	81.5	82.5	83.5	85	83	80
40 %		94.5	85	86	87.5	88	87	85
50 %		97.5	89	90.5	91.5	92.5	91	89.5
60 %		102	92.5	95	96.5	96.5	99	95
70 %		107.5	98	101	103.5	102	104	101
80 %		108	108	110	114	110.5	113	111
90 %		123.5	123	127	130	128	132	127
97 %		158	155	155	156.5	158	158	160
Dry Point		168.5	177.5	178	171	172	172	172
Total Distilled		98.5	99	99	98.5	98.5	98.5	99
Residue		0.5	0.6	0.5	0.5	0.6	0.6	0.4
Loss		1.0	0.4	0.5	1.0	0.9	0.9	0.6
Sum of 10 % 50 % 90 % point (°C)		280.5	281	289.5	292.5	293	291	282
Constituent Analysis								
Unsat. H.C %		1.5	2.0	2.5	1.5	4.5	3.5	4.5
Arom H.C. %		26.6	23.5	31.5	27.6	25.8	21.2	22.0
Naph H.C. %		70.7	69.5	65.2	69.7	69.7	69.0	64.9
Para H.C. %		1.2	5.0	1.1	1.1		6.3	8.6
Vapor Pressure (kg/cm^2)		0.57	0.57	0.56	0.54	0.51	0.56	0.64
Octane Value	Alone	78.6	78.4	79.0	79.2	78.2	77.7	78.6
	Leaded 0.1 %	92.1	92.2	91.9	91.7	91.6	91.5	91.7

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PART II

STUDIES ON HYDROCRACKING OF LOW TEMPERATURE COAL TAR

CHEM. ENG. LT.
K. SONE

Research Period: Aug. 1941 to May 1942

SUMMARY

The object of these experiments was to study the preparation of aviation gasoline from low temperature coal tar by high pressure hydrocracking.

MoS_3 was found to be the best catalyst, and under reaction conditions of 200 kg/cm^2, and 410 to 430°C, a 40 to 60 vol% yield of aviation gasoline with octane number (0.1% T.E.L.) of 87 to 89 was obtained.

I. INTRODUCTION

At the time of this investigation low temperature carbonization of coal had been recognized as an important source of supply of oil in Japan. In this connection plans were being made to develop hydrocracking of the tar on industrial scale. Research at the First Naval Fuel Depot was directed at determining the best catalyst and optimum conditions for the hydrocracking reaction. Key research personnel working on project were:

Chem. Eng. Lt. Comdr.	K. MITSUI
Chem. Eng. Lieut.	U. SATO
Chem. Eng. Lieut.	K. SONE

II. DETAILED DESCRIPTION

A. Test Apparatus

Tests were first made in an autoclave, and then in a continuous pilot plant. The equipment used was the same as that described in the report "Studies on Hydrocracking of High Temperature Tar."

B. Experimental Results

1. Raw materials

a. Low temperature tar oils

Middle oil and heavy oil No. 1 fractions from crude tar produced by low temperature carbonization of UBE coal at the UBE Nitrogen Works, were used. Properties of these oils are given in Table XVI(B)16.

b. Catalyst

Catalysts used in these experiments are summarized in Table XX(B)16.

c. Hydrogen

Hydrogen was prepared by electrolysis of water with purity of 99.5%.

2. Autoclave tests

a. Effect of reaction temperature

200 gm of middle oil with 10 gm of MoO_3 were put in the 2.4lit autoclave, and H_2 pumped in until a pressure of 100 kg/cm^2 at 0°C was reached.[2] The autoclave was heated at rate of 2.5°C/min and held at the reaction temperature for 60 minutes. Results are given in Tables XVII(B)16 through XIX(B)16.

b. Catalyst studies

A number of catalysts were tested in the autoclave under the following conditions:

Feed Stock	Middle oil
Amount of Feed Stock	200 gm
Amount of Catalyst	10 gm
H_2 Pressure at 0°C	100 kg/cm^2

Experimental results are given in Table XXI(B)16.

From the standpoint of yield of aviation gasoline, MoS_3 was best, MoS_3·NiS(3:1) and MoO_3 on active clay (1:1) were next best. From tests on effect of different catalyst carriers with MoO_3 catalyst, it was concluded that active clay or Al_2O_3 was more effective than acid clay or silica gel.

3. Experiments in continuous hydrocracking pilot plant

a. Hydrocracking with MoO_3 on active clay (1:1)

In this experiment, middle oil was hydrocracked using MoO_3 on active clay (ratio 1:1 by weight) tablets 6mm in diameter and 6mm in height as the catalyst. 9.5 lit(11.8 kg) of this catalyst was packed into each reaction chamber.

Test results are given in Tables XXII(B)16-a through XXII(B)16-d.

These tests gave poorer results than the autoclave tests and it is believed that contact time in the pilot plant catalyst zone was too short.

b. Hydrocracking with MoS_3 catalyst

Tablets of MoS_2 (height 6mm and diameter 6mm) were employed as catalyst. Eight lit of tablets were packed into each reaction chamber.

Reaction conditions and results are given in Tables XXIII(B)16-a through XXIII(B)16-d.

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III. CONCLUSIONS

In this research, MoS_3 was the best catalyst. It showed good activity and long life.

By hydrocracking of middle oil from low temperature tar using MoS_3 catalyst, a good aviation gasoline of 87 to 89 octane number (0.1% lead) can be obtained in yield of 40 to 60 vol%.

Table XVI(B)16
PROPERTIES OF LOW TEMPERATURE TAR

		Middle oil	Heavy oil No. 1	Recycle oil
d_4^{20}		.9681	.9740	.9371
First Drop °C		101	101	102
Engler Distillation	10% °C	195	220	210.5
	20% °C	204	226	223
	30% °C	212	234	233
	40% °C	220.5	245	242
	50% °C	239.5	255	253.5
	60% °C	242	266	263
	70% °C	258	280	278
	80% °C	275	299	294
	90% °C	300	323	325
Dry Point °C		260	330.5	336
Total Distilled Vol %		97	98.5	95
Analysis (Vol %)	Phenols	46.0	42.0	24.0
	Bases	3.5	4.5	2.5
	Neutral oil	50.5	53.5	73.5
Ultimate Analysis (Wt.%)	C	75.25		
	H	10.94	9.25	15.77
	O	12.82	10.12	6.01
	S	.58	.57	.35
	N	.41	.45	.31

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Table XVII(B)16
EFFECT OF REACTION TEMPERATURE
(Autoclave Test)

Reaction Conditions

Exp. No.	Reaction Temp. (°C)	Initial Press. of H_2 at 0°C (Kg/cm^2)	Max. Press. at Temp. (Kg/cm^2)	Final Press. at 0°C (Kg/cm^2)	Press. Drop. (Kg/cm^2)
1	350	100.8	220	73.6	27.2
2	400	100.8	224	66.0	34.8
3	410	99.5	220	62.4	37.1
4	430	99.3	238	59.3	40.0
5	450	96.5	225	52.0	44.5

Table XVIII(B)16
EFFECT OF REACTION TEMPERATURE
(Autoclave Test)

Analysis of Residual Gas (Vol %)

Exp. No.	CO_2	O_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	N_2	n
1	0.4	0.2	1.0	0.6	95.4	1.4	1.0	1.8
2	0.2		0.6	0.3	93.9	5.0		1.3
3	0.2		0.3	0.3	90.3	7.0	1.9	1.1
4	0.2	0.2	0.6	0.4	88.2	10.4		1.2
5			0.4	0.8	68.2	28.4	2.2	1.5

Table XIX(B)16
EFFECT OF REACTION TEMPERATURE
(Autoclave Test)

Yields and Properties of Product

Exp. No.	Yield (wt.%)	d_4^{15}	First Drop (°C)	10% (°C)	50% (°C)	90% (°C)	Dry Point (°C)	Fraction Boiling F.D.-150°C (vol. % per raw material)	Fraction Boiling F.D.-150°C (wt.% per product)
1	98.50	0.8669	84.5	128.5	210.5	297	341	21	46.0
2	97.00	0.8270	82.5	112.5	177.0	266	303	37.8	61.8
3	89.95	0.8214	70.5	109.0	170.0	261	297	41.5	64.0
4	78.45	0.8173	65.0	103.0	162.0	250.5	292	46.7	69.0
5	52.75	0.8103	49.0	78.5	118.5	194.5	241	75.5	91.5

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Table XX(B)16
CATALYST TESTS IN AUTOCLAVE
REACTION CONDITIONS

Exp. No.	Catalyst	Reaction Condition			H_2 Consumption		Analysis of Residual Gases (vol %)							
		Temp. (°C)	Max. Press. (kg/cm²)	Time (Hr)	Press. Drop (kg/cm²)	(wt%)	CO_2	O_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	N_2	n
1	MoO_3	450	225	60	44.5	6.04			0.4	0.8	68.2	28.4	2.2	1.5
9	WO_3	450	243	60	40.4	5.11		0.2		0.6	71.4	24.2	3.6	1.5
10	MoO_3:ZrO (3:1)	450	230	60	38.7	.86		0.2	1.6	1.0	82.0	14.0	1.2	2.0
11	MoO_3:SrO (9:1)	450	228	60	40.4	5.15	0.2		0.6	0.8	80.0	14.7	4.7	2.4
12	MoO_3:NiO:Active Clay (3:1:3)	450	232	60	42.2	5.49	0.2	0.2	0.8	0.8	77.1	17.6	3.3	1.8
13	$3(NH_4)_2OP_2O_5 \cdot 24MoO_3$	450	231	60	41.5	5.28	0.3	0.2	0.8	1.0	80.0	13.1	4.6	2.0
14	$2(NH_4)_2O\ SiO_2 \cdot 2MoO_3$	450	220	60	39.4	4.95			0.6	0.6	81.4	17.0	0.4	1.1
15	$(NH_4)_3H_6(CrMoO_4)_6$	450	231	60	40.7	5.43	0.2	0.2	0.4	0.6	76.5	22.1		1.0
16	MoO_3:SrO (9.5:0.5)	450	232	60	41.8	5.24	0.2	0.2	0.4	0.4	81.2	16.8	0.8	1.2
17	MoO_3	450	212	60	40.0	4.16	0.2		0.3	0.3	86.6	12.4	0.2	0.9
18	MoO_3:Cr_2O_3 (9.5:0.5)	450	225	60	44.6	5.44	0.2	0.1	0.7	0.8	77.3	20.6	0.3	1.5
19	H_2MoO_4	450	231	60	41.1	6.10	0.2	0.2	0.4	0.4	76.6	22.0	0.2	1.3
20	MoO_3:Acid Clay (1:1)	450	228	60	48.0	4.38	0.2	0.1	0.6	0.6	75.6	22.0	0.9	1.6
21	$CuCrO_4$	450	240	60	40.0	6.75	0.8		0.6	0.8	93.0	5.2	0.2	2.0
22	MoS_3	450	221	60	50.7	5.69	0.2		0.6		63.2	34.2	2.8	1.0
23	MoS_3	450	233	10	45.9	5.12	0.2	0.2	0.6	0.2	88.5	9.9	0.4	1.0
24	MoO_3:NiO:SnO (3:1:0.05)	450	233	60	47.2	6.15	0.2		0.8	0.6	71.8	26.0	0.6	0.9
25	MoO_3:?eO (3:1)	450	238	60	44.9	5.78		0.2	0.4	0.2	75.4	21.0	2.8	1.1
26	MoO_3:NiO:Cu_2O (3:1:0.5)	450	238	60	45.1	5.70			0.8	0.2	77.0	21.7	0.3	1.3
27	MoO_3:Active Clay (1:1)	450	230	60	47.4	5.98			0.6	0.2	72.4	26.0	0.8	0.9
28	MoO_3:SiO_2 (1:1)	450	238	60	44.3	5.03	0.3	0.1	0.4		84.6	14.6	0.1	1.0
29	MoO_3:Al-Silicate (1:1)	450	238	60	43.6	5.25	0.4	0.2	1.2	0.2	83.3	13.5	0.7	1.8
30	MoO_3:Al_2O_3 (1:1)	450	230	60	51.8	6.06	0.2	0.2	0.2		80.5	14.0	0.4	1.7
31	MoS_3:SnS (3:1)	450	238	60	40.9	5.04	0.2	0.1	1.1	0.2	76.1	18.5	0.4	1.9
32	MoS_3:NiS (3:1)	450	225	60	56.3	6.78	0.4	0.2	0.8		74.5	21.9	2.2	1.9
33	$(NH_4)_2\ MoS_4$	450	220	60	42.8	5.28	0.4		0.3	0.1	79.3	21.9	0.1	1.8
34	H_2WO_3	450	225	60	40.8	4.79	0.4	0.2	0.6		86.9	19.8	0.1	2.7
35	MoS_3	450	223	60	46.2	5.76	0.2	0.1	0.5		78.1	11.8	0.3	1.3
36	H_2WO_4:NiO:Acid Clay (3:1:3)	450	230	60	41.8	5.11	0.4	0.2	0.8	0.1	82.7	20.8	0.1	2.2
38	$(NH_4)_2\ WO_4$	450	227	60	39.8	4.26	0.2	0.1	0.5		80.6	15.7	0.7	1.9
39	$(NH_4)_2\ MoO_4$	450	231	60	44.1	5.60	0.2	0.2	0.4		78.5	17.9	0.1	1.4
40	Al-Methylate	450	255	60	23.0	3.63	0.1	0.2	1.1	0.2	83.9	20.6	0.1	2.0
41	MoS_3:SnS (3:1)	450	230	10	40.0	5.18	0.1	0.1	0.4		79.5	14.4	1.0	1.8
42	MoS_3:SnS (3:1)	430	228	60	40.0	4.85	0.1		0.7	0.2	85.0	13.9	0.1	1.4
43	MoS_3:Al_2O_3 (1:1)	450	220	60	52.2	6.35	0.2		0.8	0.4	76.2	22.0	0.4	1.8
44	MoS_3:CrS (3:1)	450	230	60	49.1	5.42	0.1	0.2	0.8	0.3	79.7	18.7	0.3	1.2

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Table XXI(B)16
PRODUCT YIELDS AND INSPECTIONS

Exp. No.	Yield of Product Vol.%	Yield of Product Wt.%	Density 15/4 °C	I.B.P.	10%	50%	90%	FBP	Fraction boiling up to 150°C Vol% Product	Fraction boiling up to 150°C Vol% Raw Mat.	Fraction boiling up to 200°C Vol% Product	Fraction boiling up to 200°C Vol% Raw Mat.	H_2O Produced (Wt%) Raw
1	64.65	52.75	0.8103	49	78.5	118.5	194.5	241.0	75.5	48.8	91.5	59.2	8.1
9	63.50	51.85	0.8140	50	82.5	120.0	204.5	253.5	71.5	45.4	89.0	56.5	10.1
10	80.00	64.60	0.8127	47.5	80.5	105.0	210.0	254.0	68.8	55.0	88.0	70.4	7.9
11	78.25	63.10	0.8116	50	83.5	124.5	178.0	259.0	67.8	53.1	87.0	68.1	8.9
12	72.50	57.50	0.8075	45.5	81.0	121.0	199.5	251.0	71.5	51.8	90.9	65.5	7.0
13	77.50	63.25	0.8175	53	88.0	130.0	217.0	271.0	64.5	50.0	85.0	65.9	7.6
14	89.50	72.35	0.8132	50	82.5	135.0	223.0	397.0	58.7	52.5	82.7	74.0	8.9
15	89.00	71.45	0.8101	52	86.0	131.0	219.0	270.0	61.8	55.0	85.0	75.7	8.9
16	82.00	67.50	0.8009	47.5	81.0	122.0	223.0	248.0	70.0	57.4	89.9	73.7	6.8
17	91.50	70.55	0.8197	52	90.5	142.5	230.0	265.5	55.3	50.4	79.9	73.1	7.9
18	82.90	66.10	0.8030	45	80.0	124.5	208.5	250.0	67.8	56.2	88.3	73.2	7.4
19	85.50	67.85	0.8056	44.5	79.0	122.0	201.5	240.0	71.0	60.7	89.9	76.8	8.6
20	77.50	61.50	0.7954	44	75.0	116.0	185.5	241.5	78.9	61.2	97.4	75.5	8.1
21	86.50	84.50	0.8095	61	97.5	147.5	238.0	289.0	51.5	44.6	75.7	65.5	8.5
22	57.75	45.60	0.7936	38.5	68.5	104.0	168.5	218.0	84.2	48.6	95.0	54.9	9.6
23	97.55	77.90	0.7987	55	87.0	135.5	221.0	266.5	60.9	59.4	84.4	82.3	7.5
24	82.00	64.95	0.7896	41	72.5	114.0	186.5	241.0	79.1	64.9	97.1	79.6	8.0
25	93.75	72.05	0.7965	47	81.0	125.0	208.5	262.0	70.0	65.6	88.2	82.7	7.7
26	80.90	64.10	0.7911	45	77.5	117.5	188.5	247.0	74.8	60.5	92.7	75.0	9.2
27	80.00	62.50	0.7846	43.5	71.5	110.0	180.0	247.5	81.9	65.5	97.0	77.5	7.9
28	85.00	67.75	0.7966	40.5	76.0	120.5	201.5	254.0	71.9	61.1	89.7	77.1	7.1
29	80.00	64.15	0.7975	44	74.5	120.5	193.5	254.5	73.5	58.8	91.9	73.5	7.2
30	79.10	61.70	0.7797	27	65.0	108.5	173.5	226.0	81.3	64.3	95.0	75.2	6.2
31	64.00	53.80	0.8332	28	65.0	128.5	210.0	281.0	64.9	41.5	88.0	56.3	9.0
32	61.00	47.99	0.7861	31.5	59.3	102.5	185.0	265.0	81.2	49.5	92.8	56.6	9.8
33	78.50	62.75	0.7898	30.5	65.0	118.0	217.0	277.0	71.0	55.7	87.7	68.9	9.5
34	70.00	58.00	0.8368	37.5	78.5	131.5	232.0	305.0	62.7	43.9	82.5	57.8	7.8
35	70.90	56.00	0.7895	30	61.5	110.0	187.0	261.0	78.0	55.3	92.0	65.2	7.5
36	75.00	60.86	0.8072	33.5	71.0	124.0	213.5	276.5	67.1	50.3	87.5	65.6	9.5
38	86.50	75.00	0.8673	41	72.5	148.5	221.0	298.0	51.5	44.5	81.5	70.5	7.8
39	75.00	59.05	0.7950	38.5	71.0	116.5	192.5	240.0	74.8	56.9	92.0	69.0	7.5
40	86.00	66.25	0.8913	37	67.5	172.5	240.0	310.0	39.0	28.9	71.8	53.1	3.1
41	90.50	76.00	0.8544	43	76.0	164.0	235.0	297.0	42.5	38.5	76.5	69.2	7.5
42	94.09	78.30	0.8311	39.5	82.0	152.5	231.0	289.0	49.5	46.5	79.5	74.7	6.0
43	80.75	62.90	0.7790	42	71.0	110.0	173.5	231.0	82.0	66.2	95.5	77.1	9.0
44	86.12	69.20	0.8060	41	70.0	126.0	181.0	236.0	69.0	58.9	81.0	69.7	8.7

ENCLOSURE (B)16

Table XXII(B)16-a
HYDROCRACKING MIDDLE OIL IN CONTINUOUS PILOT PLANT (MoS_3 ACID CLAY CATALYST)

Reaction Condition

	1	2	3	4
Temp. of Reaction chamber No. 1 (°C)	350	350	350	350
No. 2 (°C)	410	430	450	450
Reaction Pressure (kg/cm^2)	200	200	200	200
Run Period (hr)	6	6	6	6
SV. oil charged/cat.vol.	0.44	0.52	0.53	1.06
Total oil charged (lit)	25.00	27.55	30.25	60.10
Mean Value (lit/hr)	4.17	4.95	5.04	10.1
Total of Product (lit)	29.47	28.58	32.20	63.73
Yield of Product (vol%)	117.8	103.6	106.5	104.0
Total H_2 Charged (m^3)	26.8	32.60	33.2	60.1
Mean Value (m^3/Hr)	4.47	5.43	5.53	10.0
Total Residual Gas (m^3)	17.1	18.25	17.9	41.6
H_2 Consumption (wt%)	5.1	5.2	4.9	4.6
Residual Gas analysis (%)				
CO_2	0	0	0	0.7
O_2	0.1	0.3	0.1	0
C_nH_{2n}	0.1	0.6	0.2	1.8
CO	0.7	0.8	0.6	1.8
H_2	93.8	92.4	93.2	71.6
C_nH_{2n+2}	5.3	1.3	4.3	15.5
N_2	0	4.6	1.6	9.6
n	1.8	3.0	1.1	3.6

ENCLOSURE (B)16

Table XXII(B)16-b
HYDROCRACKING MIDDLE OIL IN CONTINUOUS PILOT PLANT (MoS_3 ACID CLAY CATALYST)

Product Inspection

d_4^{20}		0.9190	0.8249	0.8252	0.8549
I.B.P.	(°C)	77	55	60	63
10	"	118	98	105	113
20	"	157	112	120.5	134
30	"	176	128	131	153
40	"	192	140	145	175
50	"	208	160	168	194
60	"	221	181	191	213.5
70	"	241	203	208	227
80	"	259	232	232	247
90	"	280.5	264	262	280
97	"	344	335	315	323.5
F.B.P.	"	355	337.5	330	336.5
Total distilled	%	98.0	97.5	98	98
Residue		1.7	1.0	0.8	0.8
Loss		0.3	1.5	1.2	1.2
Fraction boiling I.B.P. 150°(Vol%)		18.0	45.5	43.5	28.5
Fraction boiling I.B.P. 200°(Vol%)		45.0	69.0	66.0	58.0
Yield of Aviation Gasoline (Vol%)		21.7	35.3	34.0	22.6

ENCLOSURE (B)16

Table XXII(B)16-c
HYDROCRACKING MIDDLE OIL IN
CONTINUOUS PILOT PLANT
(MoS_3 ACID CLAY CATALYST)

Aviation Gasoline

	1	2	3	4
d_4^{20}	0.7658	0.7625	0.7610	0.7628
I.B.P. (°C)	76	62	59	62
10% (°C)	95	82	80	66
20 (°C)	99	91	88	92
30 (°C)	104	96	95	99
40 (°C)	107	101	101	102
50 (°C)	110	105	104	107
60 (°C)	115	110	110	113
70 (°C)	120	117	118	117
80 (°C)	127	125	123	127
90 (°C)	139	138	137	138
97 (°C)	157	165	158	164
F.B.P. (°C)	177	165.5	168	178.5
Total distilled (%)	99	98.5	99	99
Residue (%)	0.5	0.7	0.7	0.4
Loss (%)	0.5	0.8	0.3	0.6
Sum of 10% 50% 90% Point (°C)	344	325	321	311
Analysis				
Unsat H.C. (Vol%)	1.5	2.5	2.5	3.5
Aromat. H.C. (Vol%)	18.7	29.3	27.3	26.1
Naph. H.C. (Vol%)	57.2	39.8	43.3	43.4
Para. H.C. (Vol%)	22.6	28.4	26.9	27.0
Octane Value Clear	68.7	74.9	72.6	71.3
Leaded 0.1%	85.7	89.0	88.5	87.0
Vapor Pressure (kg/cm^2)	0.28	0.39	0.40	0.39

ENCLOSURE (B)16

Table XXII(B)16-d
HYDROCRACKING MIDDLE OIL IN CONTINUOUS PILOT PLANT
(MoS_3 ACID CLAY CATALYST)

Topped Oil Inspection

d_4^{20}		0.8975	0.8750	0.8750	0.9004
I.B.P.	(°C)	163	151	154	151.5
10%	(°C)	192.5	175	176	180
20	(°C)	199.5	182	183	188
30	(°C)	211	190.5	191	196
40	(°C)	217.5	203.5	200.5	204
50	(°C)	228	214	211	212
60	(°C)	241	224.5	221	224.5
70	(°C)	255	241	237	238.5
80	(°C)	270.5	255.5	252	257
90	(°C)	295.5	279	278	286
97	(°C)	344	348	320	329
F.B.P.	(°C)	348.5	350	341	350.5
Total distilled	(%)	99.0	98.5	98.5	98.5
Residue	(%)	0.6	0.3	0.2	
Loss	(%)	0.4	1.2	0.3	
Aniline Point	(°C)	32.5	28.5	28.5	26.5

ENCLOSURE (B)16

Table XXIII(B)16-a
HYDROCRACKING OIL IN CONTINUOUS PILOT PLANT
(MoS_3 CATALYST)

Reaction Condition

Run No.		1	2	15	16	17	18	19
Raw Material		Middle oil	Middle oil	Middle oil	Heavy oil No.1	Heavy oil No.1	Recycle oil	Heavy oil No.1
Temp. of Preheater (°C)		300	300	300	300	300	300	300
Temp. of Reaction chamber No.1		380	380	380	380	390	390	390
Temp. of Reaction chamber No.2		420	420	420	420	430	430	450
Reaction Pressure (kg/cm^2)		200	200	200	200	200	200	200
CS_2 added (cc/lit oil)		3	0	3	3	0.5	3	3
Run Period (Hrs.)		6	12	6	6	6	6	6
S.V. of Oil oil charged/at Vol		0.50	0.98	0.50	0.50	1.0	0.46	0.49
Time passed from start (Hrs)		18-24	28-40	368-374	387-393	398-404	410 416	422 428
Total oil charged	(lit)	24.00	94.00	23.75	24.20	48.00	23.55	23.60
	(kg)	23.20	91.18	23.05	23.40	46.80	22.10	23.00
Mean Value	(lit/Hr)	4.0	7.8	3.96	4.03	8.00	3.93	3.93
Total Product	(lit)	22.86	104.76	20.59	25.68	51.84	21.25	18.36
	(kg)	21.43	89.35	17.95	21.64	43.22	17.18	14.77
Mean Value	lit/hr	3.8	8.7	3.43	4.28	8.64	3.54	3.13
Residual Gas Analysis (%)								
CO_2		0	0.2	0.2	0.3	0	0.3	70.2
O_2		0.3	0	0.4	0.2	0.1	0.1	0.2
C_nH_{2n}		0.3	0.4	1.0	0.6	0.3	0.9	1.5
CO		0.6	0.4	0.4	0.4	0.2	0.4	0.4
H_2		82.3	92.4	75.1	83.5	86.1	85.8	86.0
C_nH_{2n+2}		14.8	6.6	20.5	14.4	12.9	12.4	10.7
N_2		1.7	0	2.4	0.6	0.4	0.1	1.0
n		1.4	1.1.0	1.3	1.0	1.0	1.6	1.9

Table XXIII(B)16-b
HYDROCRACKING OIL IN CONTINUOUS PILOT PLANT
(MoS_3 CATALYST)

Yield of Product

Run No.	1	2	15	16	17	18	19
Raw Material	Middle oil	Middle oil	Middle oil	Heavy oil No.1	Heavy oil No.1	Recycle oil	Heavy oil No.
Vol %	95.0	111.5	86.6	106.2	108.0	90.1	79.6
Wt %	92.2	98.0	77.9	92.6	92.3	77.9	65.3
Total H_2 Charged (m^3)	26.2	106.7	27.2	27.6	52.70	26.20	26.80
Mean Value (m^3/Hr)	4.4	8.9	4.5	4.6	8.7	4.37	4.47
Total Residual Gas (m^3)	12.4	48.0	12.3	10.3	27.70	14.00	13.40
Mean Value (m^3/Hr)	2.7	4.0	2.5	1.7	4.6	2.33	2.23
H_2 Consumption (Wt% per product)	5.0	6.2	6.0	9.3	5.5	5.7	5.9

ENCLOSURE (B)16

RESTRICTED

ENCLOSURE (B)16

Table XXIII(B)16-c
HYDROCRACKING OIL IN CONTINUOUS PILOT PLANT
(MoS_3 CATALYST)

Aviation Gasoline

	1	2	15	16	17	18	19
d_4^{20}	0.7556	0.7597	0.7601	0.7545	0.7540	0.7616	0.7489
I.B.P. (°C)	38.0	64.5	55.0	59.0	61.0	54.5	55.0
10%	77.5	84.0	80.0	83.5	85.0	77.5	79.5
20	85.5	91.0	87.5	92.0	93.5	86.0	86.5
30	92.0	98.0	93.0	98.0	99.0	92.0	93.0
40	97.0	102.0	98.0	103.5	104.0	97.5	99.0
50	102.0	106.0	102.5	109.0	107.5	103.0	104.5
60	106.5	110.5	108.0	114.0	114.0	108.5	110.5
70	113.0	112.5	113.5	119.5	119.5	115.0	117.5
80	124.0	125.0	121.0	129.0	127.0	124.5	127.0
90	133.0	135.0	132.5	138.0	140.0	138.0	143.0
97	152.5	155.0	151.5	161.5	162.0	165.0	168.0
F.B.P.	161.5	170.0	163.0	181.0	184.0	178.0	181.0
Total Distilled %	98.5	98.5	98.0	98.5	99.0	98.5	99.0
Residue	0.6	0.7	0.7	0.4	0.3	0.4	0.6
Loss	0.9	0.8	1.3	1.1	0.7	1.1	0.4
Vapor Pressure kg/cm^2	0.45	0.39	0.42	0.40	0.42	0.42	0.33
Constituent Analysis							
Unsat. H.C. vol%	1.5	0.7	1.5	2.0	3.0	5.0	2.0
Arom. H.C. "	25.6	20.9	21.7	20.6	19.4	20.0	16.7
Naph. H.C. "	49.6	55.4	53.0	50.3	51.7	53.8	50.1
Para. H.C. "	23.3	23.0	23.8	27.1	25.9	21.2	31.2
Octane Value not leaded	73.5	771.2	73.3	69.3	67.8	74.4	68.5
Leaded 0.1%	88.8	86.7	87.4	86.2	85.8	88.5	84.9

Table XXIII(B)16-d
HYDROCRACKING OIL IN CONTINUOUS PILOT PLANT
(MoS_3 CATALYST)

Topped Oil Inspection

	1	2	15	16	17	18	19
d_4^{20}	0.8319	0.8297	0.8698	0.8522	0.8564	0.8429	0.8441
I.B.P. (°C)	153	154	160	154.5	162	159	156
10%	166	174.5	180.5	181.5	185	178	175
20	174	180.5	187.0	190	196	187	181
30	181.5	189.5	198	202	205	195	190
40	190	201.0	208	212	215	206	197
50	200.5	211.5	216.5	222	232	215	206
60	212	223	227.5	234	242	224	216
70	225	237.5	242	258	254.5	235	226.5
80	241	257.5	257	264.5	272	250	246
90	269	294	290	294.5	299	276	268
97	311	325	350	335	345	320	313
F.B.P.	323	337	360	355	362	342	343
Total Distilled %	98.0	98.0	98.0	99.0	98.5	98.5	99.0
Residue	0.9	1.4	1.4	0.7	1.1	0.9	0.7
Loss	1.3	0.6	0.6	1.3	0.4	0.6	0.3
Aniline Point °C	42.0	48.5	38.5	43.0	41.5	46.0	40.0

ENCLOSURE (B) 16

PART III

STUDIES ON HYDROCRACKING OF OHA GAS OIL

by

CHEM. ENG. LT.
K. SONE

Research Period: November-December, 1940

SUMMARY

The hydrocracking of Oha gas oil over catalyst No. 6 (NiO-MoO_3-Active clay) was studied in a continuous pilot plant. Studies were made under reaction conditions of 200 kg/cm^2, space velocities of 0.46, 0.69 and 0.92 and temperature range from 360 to 420°C. The yield of aviation gasoline at 400°C was 75.3%, and at 420°C was 81.2%. The octane number of these gasolines was 92 (with 0.1% lead).

It was concluded that this catalyst had excellent activity for hydrocracking of Oha gas oil.

I. INTRODUCTION

A. History of Project

Many autoclave tests had been made since 1935, in search of good catalysts for hydrocracking mineral oils, and it was reported that catalyst No. 6, (NiO-MoO_3-active clay) had the best activity for this purpose. This project was initiated to confirm the effectiveness of this catalyst and to obtain specific data on the hydrocracking of Oha gas oil in a continuous pilot plant.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr.	K. MITSUI
Chem. Eng. Lieut.	A. MORITA
Chem. Eng. Lieut.	U. SATO
Chem. Eng. Lieut.	K. SONE

II. DETAILED DESCRIPTION

Pilot plant and test procedures used in this investigation have been described previously in the report "Studies on Hydrocracking of High Temperature Tar".

ENCLOSURE (B)16

A. Raw Materials

Gas oil obtained from Oha crude was used as a feed stock. Its properties are as follows:

Table XXIV(B)16

Density (d_4^{20})	0.832
Distillation (°C)	
I.B.P.	154°C
10%	177
20%	183
30%	188.5
40%	195.5
50%	202
60%	209
70%	218
80%	231
90%	250
F.B.P.	298
Ultimate Analysis	
Unsaturated HC (Vol%)	2.0
Aromatic HC (Vol%)	13.7
Saturated HC (Vol%)	84.3
Aniline Point of Saturated HC (°C)	65.2
Content of Sulphur (Vol%)	0.08

Catalyst No. 6 was prepared in The Third Naval Fuel Depot. It consisted of NiO-MoO_3 and active clay (1:3:3 by weight). Its physical properties were as follows:

Tablet Diameter	6.7mm (Average)
Tablet Height	20.0mm (Average)
Density	1.74
Weight per unit volume	915 kg/m^3

8.75 liters of this catalyst were packed in each reaction chamber.

Hydrogen with purity of 99.5% was prepared by electrolysis of water.

B. Results

Experimental data are summarized in Tables XXV(B)16-XXIX(B)16 incl.

A plot of data showing the relation between reaction temperature and yield of aviation gasoline is given in Figure 2(B)16.

The yield of aviation gasoline was only 10% at the reaction temperature of 370°C but above 370°C, the yield rapidly increased until it reached 80% at 420°C. Variation of space velocity had little effect on the yield.

The relation between reaction temperature and properties of aviation gasoline is given in Figure 3(B)16.

It is seen that variation in reaction temperature had little effect on these properties.

III. CONCLUSIONS

A. Catalyst No. 6 was excellent for manufacture of aviation gasoline by continuous hydrocracking of Oha gas oil.

B. The optimum reaction temperature for a S.V. of 0.5 was 400°C, and for S.V. of 1.0, 420°C. The yields of aviation gasoline for these cases were 75.3 vol% and 65.5%, respectively.

C. Properties of the hydrocracked residual oil differed from the residual product of thermal cracking, its density being lower, and its aniline point higher. On the basis of other experiments it is known that the former could easily be hydrocracked to aviation gasoline.

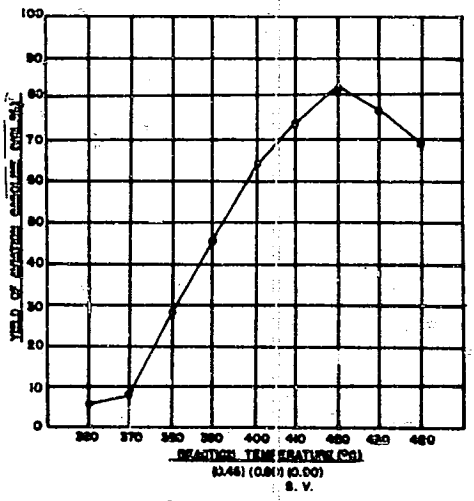


Figure 2(B)16

RELATION BETWEEN REACTION TEMPERATURE AND YIELD OF AVIATION GASOLINE

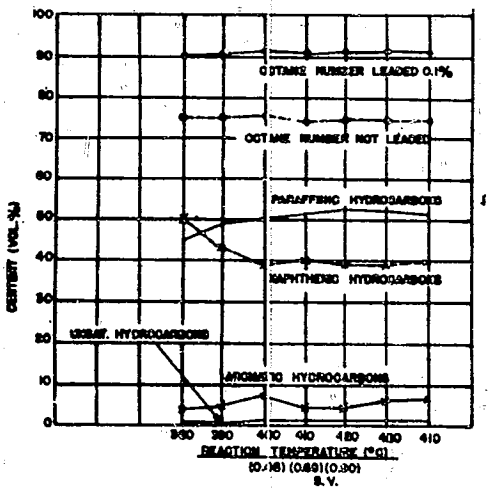


Figure 3(B)16

RELATION BETWEEN REACTION TEMPERATURE AND PROPERTIES OF AVIATION GASOLINE

ENCLOSURE (B)16

Table XXV(B)16
REACTION CONDITIONS AND YIELD

		Run Number								
		1	2	3	4	5	6	7	8	9
Reaction Press. (kg/cm^2)		200	200	200	200	200	200	200	200	200
Reaction Temp. (^oC)		360	370	380	390	400	410	420	420	420
S. V.		0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.69	0.92
Run Period (hr)		6	6	6	6	6	12	24	12	12
Oil Charged	(lit)	47.8	47.9	47.9	48.0	48.1	95.3	190.2	140.3	190.8
	(kg)	39.8	39.9	39.9	40.0	40.1	79.0	158.0	116.4	158.2
	(lit/hr)	7.98	7.98	7.98	8.0	8.0	7.94	8.0	11.7	15.9
Product	(kg)	38.4	40.6	36.2	39.8	42.5	66.5	136.0	95.7	136.2
	(lit)	47.0	49.9	46.6	51.2	57.1	91.4	189.5	131.7	183.5
H_2 Charged (m^3)		42.9	41.4	41.6	41.2	40.5	93.4	176.3	141.3	167.3
Residual Gas (m^3)		30.2	29.0	32.4	29.0	26.3	54.9	104.2		
Yield of Product	(vol%)	98.2	104.0	97.2	106.5	118.5	96.0	99.3	94.0	96.2
	(wt%)	95.6	100.2	90.6	99.5	105.0	84.0	86.1	82.0	86.0
H_2 Consumption	(wt%)	2.86	2.71	2.06	2.63	2.88	4.3	4.07		

ENCLOSURE (B)16

Table XXVI(B)16
PROPERTIES OF PRODUCTS

		Run Number								
		1	2	3	4	5	6	7	8	9
Density	d_4^{20}	0.817	0.812	0.781	0.777	0.743	0.727	0.718	0.727	0.738
Fractional Distillation	I.B.P. (°C)	72.5	71	60	50	44.5	40.5	32	32.5	35
	10% (°C)	161.5	158.5	110	86	67.5	60	52	54.5	59
	20% (°C)	174	171.5	138	109	84	74	68	68.5	77.5
	30% (°C)	180.5	180	155.5	127	99.5	90	83.5	81.5	94.5
	40% (°C)	185	187	166	144	114.5	102	96	94.5	110
	50% (°C)	193	190.5	175	156.5	128	111	106.5	109.5	127
	60% (°C)	202	198.5	182.5	170	143.5	124	120	125	143
	70% (°C)	209.5	206.5	191	180.5	160.5	144	135	145	159
	80% (°C)	220	219	202	192	177	167	153.5	166	177.5
	90% (°C)	243	238	215	207.5	198.5	192.5	186	190	201.5
	97% (°C)	270	260	246	239	234				
	F.B.P. (°C)	277	265	251	247	238	228	235	231	240.5
	Total Distilled (vol%)	98.5	97.5	98.5	98	98	96	96	97.5	96.5
	Residue (vol%)	0.7	1.3	0.7	0.8	1	0.5	0.7	0.3	0.7
	Loss (vol%)	0.8	1.2	0.8	1.2	1	3.5	3.3	2.2	2.8
Four Point Method (%)	-80 (°C)	1.5	2.8	7.0	15.8	21.3	24.0	27.5	28.5	21.5
	-105 (°C)	2.7	4.0	14.0	24.3	36.0	43.5	48.5	46.5	38.5
	-150 (°C)	7.5	10.0	28.3	42.0	58.3	73.5	78.0	74.0	64.5
	-170 (°C)	19.5	24.0	43.3	56.3	69.3	82.0	85.0	82.0	76.0
Yield of Aviation Gasoline (vol%)		5.4	8.0	28.0	46.7	63.7	74.4	81.9	77.8	68.1

ENCLOSURE (B)16

Table XXVII(B)16
PROPERTIES OF RESIDUAL GASES

		Run Number								
		1	2	3	4	5	6	7	8	9
CO_2	(vol%)	0	0	0	0	0	0	0	0	0
O_2	(vol%)	0	0	0	0	0	0	0	0	0
C_nH_{2n}	(vol%)	0.3	0.2	0.3	0.3	0.2	0.5	0.3	0.5	0.6
CO	(vol%)	0.1	0.1	0	0.1	0.1	0.3	0.1	0.1	0.1
H_2	(vol%)	95.6	91.7	92.7	92.6	90.7	92.2	89.4	92.4	92.3
C_nH_{2n+2}	(vol%)	0.9	1.9	1.9	0.5	1.9	2.9	4.3	1.9	4.9
N_2	(vol%)	3.1	6.1	5.1	5.5	6.4	4.1	5.4	5.1	2.1
n		1.5	1.0	1.5	1.0	1.5	1.0	1.4	1.0	1.0

ENCLOSURE (B)16

Table XXVIII(B)16
PROPERTIES OF AVIATION GASOLINE

		Run Number						
		3	4	5	6	7	8	9
Density	d_4^{20}	0.723	0.718	0.707	0.705	0.703	0.702	0.708
Fractional Distillation	I.B.P. (°C)	39	37	37	37.5	34	34.5	37
	10% (°C)	62	60	54.5	56.5	53	52	52
	20% (°C)	75.5	72	66	66.5	63	62.5	64
	30% (°C)	85	82	76	75.5	72.5	71.5	73.5
	40% (°C)	93	91.5	85	83	81.5	80	83
	50% (°C)	102.5	98.5	92.5	92.5	90	90	92
	60% (°C)	110	107	99.5	100	99	98.5	100.5
	70% (°C)	118.5	116	108.5	108	107.5	107	110
	80% (°C)	130	130	119	117	117	119	122
	90% (°C)	148	140	137	130	131	135	141
	97% (°C)	172	170	160	160	159	159	163
	F.B.P. (°C)	180	173	164	174	167.5	165.5	168
	Total Distilled (vol%)	98.5	98	98.5	97.5	97.4	97.2	97.5
	Residue (vol%)	0.5	0.7	0.4	0.4	0.3	0.6	0.6
	Loss (vol%)	1.0	1.3	1.1	2.1	2.3	2.2	1.9
Sum of 10%, 50% and 90% P. (°C)		312.5	298.5	284.0	279.0	273.0	277.0	285.0
Analysis	Unsaturated HC (vol%)	1.0	1.0	2.0	2.0	2.0	1.5	1.5
	Aromatic HC (vol%)	3.0	5.9	7.8	4.9	4.9	6.0	6.8
	Naphthenic HC (vol%)	50.2	43.4	39.1	40.3	39.4	39.2	39.7
	Paraffinic HC (vol%)	45.8	49.7	51.1	52.8	53.7	53.3	52.0
Octane Number	Clear	75.6	75.5	76.1	74.0	74.5	74.5	74.5
	With 0.1% Lead	90.6	91.0	92.0	91.6	92.0	92.2	92.0

ENCLOSURE (B)16

Table XXIX(B)16
PROPERTIES OF TOPPED OILS

		Run Number						
		3	4	5	6	7	8	9
Density	d_4^{20}	0.813	0.810	0.804	0.804	0.804	0.808	0.812
Fractional Distillation	I.B.P. (°C)	151	148	145	151	151	149	153
	10% (°C)	166	168	160	165	165.5	164	168.5
	50% (°C)	184	186	180	179.5	180	181	184.5
	90% (°C)	224	223	216	215	213	216.5	220.5
	F.B.P. (°C)	261	263	251	256	256	253	250.5
Analysis	Unsaturated HC (vol%)				0	1.3	2.0	0.5
	Aromatic HC (vol%)				7.0	7.9	8.8	9.0
	Saturated HC (vol%)				73.0	90.8	89.2	90.5
	Aniline Point (°C)				62.5	63.0	63.6	63.8

ENCLOSURE (B) 16

PART IV

STUDIES ON HYDROCRACKING OF OMONOGAWA GAS OIL

by

CHEM. ENG. LT.
K. SONE

Research Period: April-August 1941

SUMMARY

This study was made to investigate the production of aviation gasoline by hydrocracking Omonogawa gas oil. It was found that the fraction boiling between 160-220°C was the best feed stock for preparing high octane aviation gasoline.

INTRODUCTION

A. History of Project

Although Omonogawa gas oil had characteristics similar to Oha gas oil, yet upon hydrocracking under similar conditions a poorer quality of gasoline was obtained (see Table XXX(B)16). The conditions selected for these tests were optimum from the standpoint of yield, and catalyst No. 6 which was the best known for hydrocracking of mineral oils, was used. In view of these results, further work was centered on determining whether gasoline of higher quality could be made by hydrocracking special cuts from Omonogawa gas oil.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr.	K. MITSUI
Chem. Eng. Lieut.	A. MORITA
Chem. Eng. Lieut.	K. SONE

II. DETAILED DESCRIPTION

A. Raw Materials

An Omonogawa gas oil, boiling range of 125-298°C, was fractionated into 18 narrow boiling cuts. Properties of the gas oil and each of these cuts are given in Table XXXI(B)16 and Figure 5(B)16.

B. Test Apparatus

These experiments were made in the 1 lit/hr continuous hydrocracking unit #3. A flow chart of this unit is given in Figure 4(B)16.

One liter of used catalyst, No. 6, was packed in the preheater and one liter of new catalyst, No. 6, was paced in the reaction chamber. Afte the apparatus was examined for leakage at 300 kg/cm^2, the pressure was

reduced to 200 kg/cm^2, heating was started, and H_2 circulated at the rate of 1 m^3/hr. After temperature in the reaction chamber reached 300°C, oil was charged into the preheater by the high pressure feed pump at the rate of 1 lit/hr and mixed with hydrogen. In the preheater the mixture was heated to 300°C by electric heaters, and introduced into the reaction chamber maintained at 430°C. From the reaction chamber the mixture of hydrocracked products and gas passed through the condenser and into the high pressure separator. The gas and liquid products were separated under full pressure, the liquid being withdrawn to the low pressure separator and sent to storage. The gas from the high pressure separator was reduced to normal pressure, flow rate measured in the gas meter and then discharged to the air.

Oil was flashed into the low pressure separator intermittently (every 30 mins) and drawn off from the bottom.

The product oil was distilled to yield an aviation cut with 150°C endpoint and a residual oil.

A summary of reaction conditions follows:

Reaction pressure	200 kg/cm^2
Temperature of preheater	300°C
Temperature of reaction chamber	430°C
H_2 charged	1 m^3/hr
Oil charged	1 lit/hr
S.V. of oil	1.0
Catalyst	NiO.MoO_3.Active clay (1:3:3)

C. Yield and Properties of Products

Yields and properties of products are summarized in Tables XXXII(B)16, XXXIII(B)16, and XXXIV(B)16. In these runs there was generally a 5-20% loss of oil product in gas due to intermittent operation of the low pressure separator. Properties of aviation gasoline obtained in these runs are given in Table XXXV(B)16 and Figure 6(B)16.

On the aviation gasolines from gas oil samples No. 1, 2, 3, and 4 the 50% points were 121, 121.5, 128, and 112°C, but in the case of samples No. 5-18 it was 90-105°C. These results indicated that it was more difficult to hydrogenate the lighter boiling gas oil cuts.

Yield of aviation gasoline was best for samples No. 10-14, with the exception of samples No. 1-4 which had large amounts of material boiling up to 150°C in raw material maximum octane number was indicated for samples No. 5-9. Properties of topped oil are given in Table XXXVI(B)16. The content of aromatic hydrocarbons in the topped oil decreased and the content of paraffinic hydrocarbons increased as compared with the feed stocks.

III. CONCLUSIONS

On the basis of these experiments it was concluded that the fraction of Omonogawa gas oil boiling in the range 160-220°C was the optimum hydrocracking charge for production of high octane aviation gasoline.

In comparing the hydrocracking of Oha and Omonogawa gas oil, for a given boiling range cut these oils have similar compositions and the reaction on hydrocracking is the same.

The total Oha gas oil, however, gave a better yield of high octane gasoline since it had a narrower boiling range than the Omonogawa gas oil, and a higher content of the optimum 160-220°C components.

ENCLOSURE (B)16

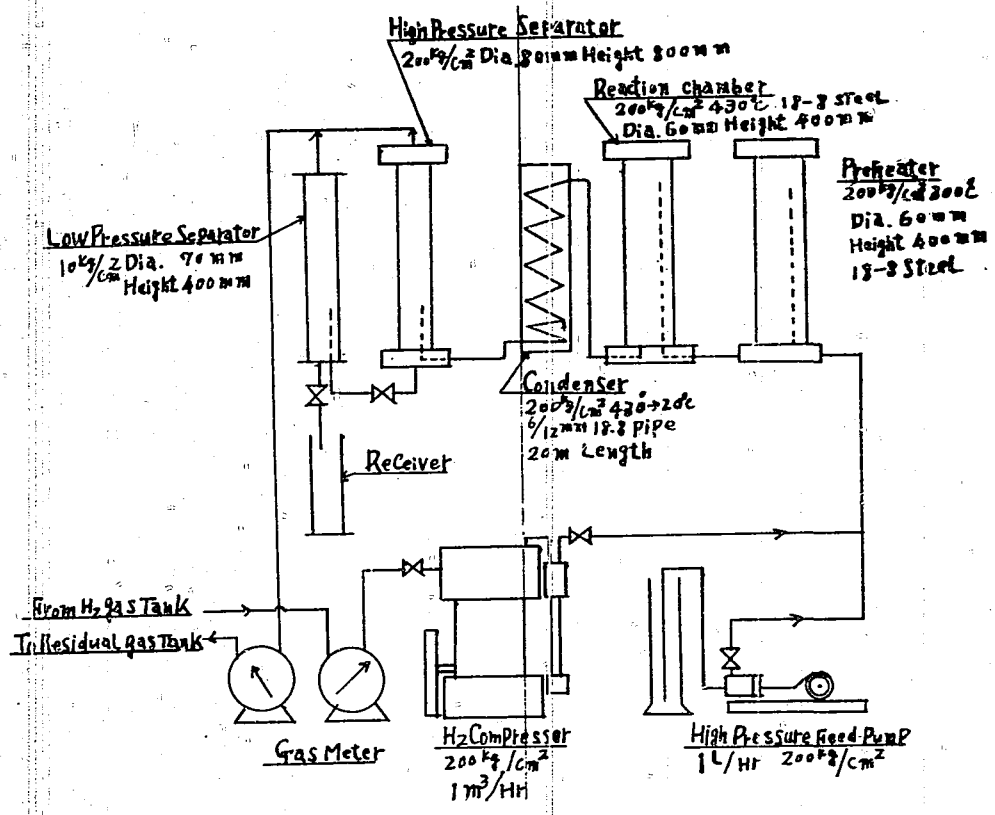


Figure 4(B)16

FLOW CHART OF THE APPARATUS

ENCLOSURE (B)16

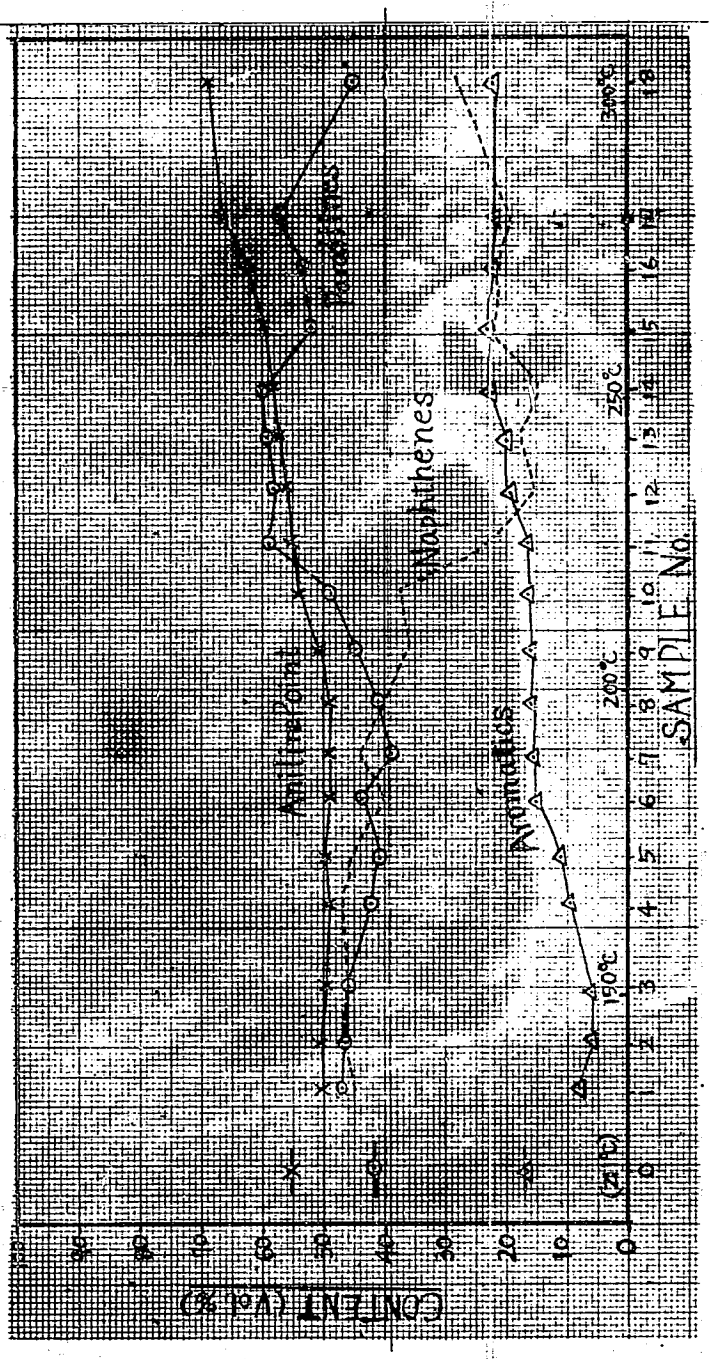


Figure 5(B)16
PROPERTIES OF RAW MATERIALS

ENCLOSURE (B)16

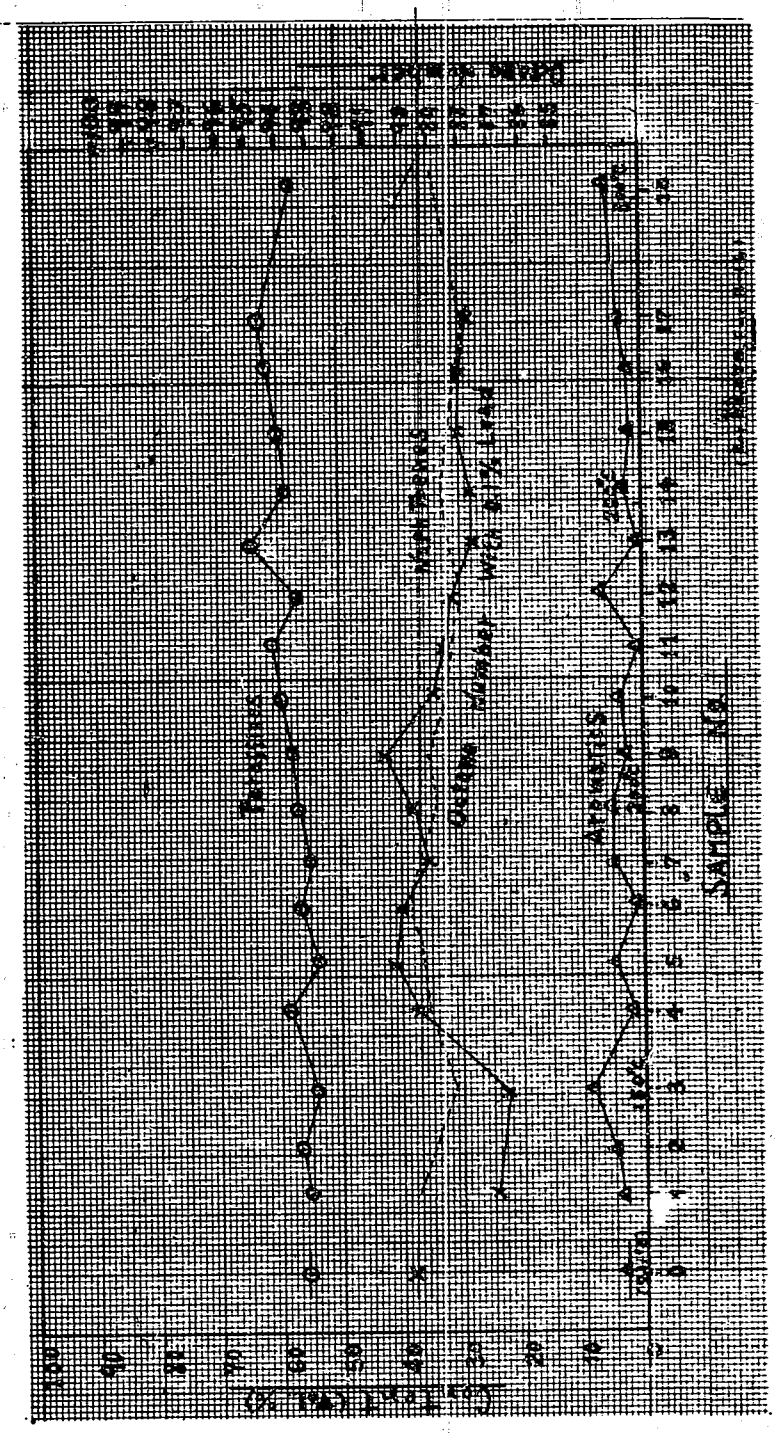


Figure 6(B)16
PROPERTIES OF AVIATION GASOLINE

Table XXXII(B)16
YIELD AND H_2 CONSUMPTION

Run No.	Sample No.	Density of Sample (d_4^{20})	Density of Product (d_4^{20})	Run Period (hr)	Oil Charged (l/hr)	Product (l/hr)	Yield (vol. %)	H_2 Charged (ml/hr)	Residual Gas (m^3/hr)	H_2 Consumption (wt. %)
1	0	0.8229	0.7663	4.5	1.2	1.1	93.8	1.7		
2	1	0.7685	0.7379	3.0	1.2	0.8	67.3	1.1	0.8	2.5
3	2	0.7766	0.7501	3.5	1.0	0.7	68.3	1.1	0.8	4.0
4	3	0.7858	0.7404	4.0	1.0	0.9	86.5	1.3	1.3	1.5
5	4	0.7967	0.7407	3.0	1.0	0.8	79.1	1.3	1.0	3.5
6	5	0.8056	0.7677	3.0	1.0	0.9	94.5	1.5	0.6	9.9
7	6	0.8127	0.7481	3.5	1.0	0.8	83.3	1.3	0.4	9.3
8	7	0.8220	0.7611	5.0	0.9	0.7	74.4	1.4	0.7	9.1
9	8	0.8301	0.7476	4.0	1.1	1.0	91.0	1.2	0.8	4.2
10	9	0.8348	0.7550	3.5	1.0	0.7	70.0	1.1	0.8	3.1
11	10	0.8370	0.7423	4.0	1.0	0.7	74.4	1.4	0.7	7.5
12	11	0.8412	0.7413	3.5	1.1	1.0	90.6	1.1	0.7	5.1
13	12	0.8455	0.7440	4.5	0.9	0.7	75.6	1.0	0.8	
14	13	0.8487	0.7393	3.0	0.9	0.8	88.9	1.1	0.7	5.1
15	14	0.8543	0.7618	5.5	1.0	1.0	97.8	1.1	0.7	4.2
16	15	0.8570	0.7570	4.5	1.0	0.9	93.7	1.1	0.9	2.3
17	16	0.8611	0.7632	2.0	1.1	1.0	90.2	1.1	0.7	3.8
18	17	0.8685		2.0	1.0	1.1	104.9	1.1	0.6	4.8
19	18	0.8724		3.0	0.9	1.0	104.2	1.1	0.7	4.7

Table XXX(B)16
COMPARISON OF HYDROCRACKING OF OHA AND OMANOGAWA GAS OIL

			Oha	Omonogawa
Boiling range of gas oil			150-250	125-298
Density of gas oil			0.832	0.823
Reaction Conditions	Catalyst		$NiO.MoO_3$-active clay	$NiO.MoO_3$-active clay
	H_2 pressure (kg/cm2)		200	200
	Temperature		420	420
Gasoline Fraction	Yield (vol. %)		70	43.6
	Density d_4^{20}		00.7118	0.7107
	Distillation	I.B.P. (°C)	29.3	31.0
		10% (°C)	53.5	55.0
		50% (°C)	97.0	97.0
		90% (°C)	141.5	142,5
		F.B.P. (°C)	165.5	164.5
Octane Number	Clear		74.0	70.3
	With 0-1% lead		91.7	89.0

Table XXXI(B)16
PROPERTIES OF RAW MATERIALS

		Sample No.																	
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Mean B.P. (°C)		211.0	133.4	141.1	151.1	164.2	172.6	182.3	189.6	198.6	207.2	216.9	225.5	234.1	243.2	251.6	261.6	271.4	280.4	303
d_4^{20}		0.8229	0.7685	0.7766	0.7858	0.7967	0.8056	0.8127	0.8220	0.8301	0.8345	0.8370	0.8412	0.8455	0.8482	0.8543	0.8570	0.8611	1.8685	0.8724
n_D^{20}		1.4869	1.4266	1.4304	1.4355	1.4408	1.4460	1.4490	1.4540	1.4581	1.4615	1.4620	1.4660	1.4690	1.4726	1.4768	1.4775	1.4798	1.4775	1.4852
Fractional Distillation	I.B.P.	124.5	99.0	122.0	140.5	149.0	158.0	170.0	177.5	189.5	199.0	210.0	218.0	228.0	237.0	246.0	257.0	266.5	276.5	284.5
	10%	149.5	117.5	129.0	143.5	153.5	163.5	173.5	183.0	193.0	202.5	211.5	220.5	230.0	239.5	245.5	259.0	267.5	277.5	296.5
	20%	161.5	123.0	131.0	144.0	155.0	164.5	175.0	184.0	194.0	203.0	213.0	222.0	230.5	240.0	249.0	259.5	268.5	278.5	298.5
	30%	174.0	126.0	133.5	145.0	155.5	165.5	176.5	185.0	195.0	204.0	213.5	222.5	231.0	241.0	249.5	259.5	269.0	279.0	300.5
	40%	201.5	127.5	136.0	147.0	167.5	167.0	178.0	186.5	196.0	204.5	214.0	223.5	232.0	241.5	250.0	260.0	270.0	279.2	301.2
	50%	219.5	131.5	138.0	148.5	159.5	168.5	179.0	187.5	197.0	205.5	215.5	224.0	232.5	242.0	250.5	260.5	270.5	279.5	302.0
	60%	233.0	136.5	141.5	150.0	161.6	170.5	180.5	189.0	198.0	206.5	216.0	225.0	233.0	243.0	251.0	261.5	271.5	280.0	302.5
	70%	244.5	140.0	144.5	152.5	163.5	172.0	182.5	190.5	199.5	208.0	217.5	226.0	234.5	243.5	252.0	262.0	272.5	281.0	304.5
	80%	255.0	143.5	147.5	156.0	166.5	175.0	184.5	192.5	201.5	210.0	219.0	228.0	236.0	245.0	253.0	263.0	274.5	282.0	308.5
	90%	269.5	151.0	156.0	162.0	172.0	179.0	189.5	197.0	205.0	213.0	222.0	230.5	238.0	247.5	255.0	265.0	274.5	283.5	312.5
	F.B.P.	298.0	173.0	174.0	174.0	213.0	215.5	215.5	215.5	217.0	224.0	233.5	241.5	250,5	255.5	263,0	271.5	282.5	288.0	324.5
Constituent Analysis H.C.	Unsat. (%)	1.0	0.0	0.0	0.0	0.5	0.0	1.0	0.5	0.5	1.0	0.0	0.0	0.5	1.0	0.5	0.0	0.5	0.0	1.0
	Arom. (%)	16.8	8.0	6.0	6.0	10.0	15.6	11.8	15.9	16.7	16.2	17.0	17.0	19.9	20.7	23.6	23.7	22.9	22.0	23.0
	Naph. (%)	40.5	44.8	47.0	47.6	47.1	40.4	45.9	44.4	40.5	36.9	33.2	23.5	21.2	18.7	15.9	23.9	22.7	20.2	29.9
	Para. (%)	41.7	47.2	47.0	46.4	42.4	44.0	41.3	39.2	41.3	45.9	49.8	59.2	58.4	59.6	60.0	52.4	53.9	57.8	46.1
Aniline Point	(°C)	55.6	49.8	50.6	49.8	49.8	49.6	49.6	49.4	49.4	51.2	54.2	55.3	57.2	58.6	58.8	60.2	62.8	67.8	69.2
	Sat. H.C. (°C)	68.2	58.2	59.8	61.2	61.2	63.2	62.2	63.6	63.8	68.6	71.0	73.4	75.3	78.4	79.6	80.0	83.2	86.2	89.3

RESTRICTED

Table XXXIII(B)16
PROPERTIES OF OIL PRODUCT

		Sample Number																	
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
d_4^{20}		0.7663	0.7379	0.7501	0.7404	0.7407	0.7677	0.7481	0.7611	0.7476	0.7550	0.7423	0.7413	0.7440	0.7343	0.7648	0.7570	0.7632		
Distillation	I.B.P.	60.0	55.0	56.0	48.0	44.0	56.0	50.5	57.5	45.5	52.0	48.5	49.5	51.0	48.0	54.0	66.0	56.0	63.0	61.0
	10%	92.0	91.2	80.0	80.5	72.8	97.0	78.0	88.5	72.8	82.2	69.0	72.5	76.5	72.0	83.0	86.0	84.0	93.0	98.0
	20%	108.0	104.2	99.0	104.0	88.2	117.0	96.0	109.5	88.5	100.3	83.5	87.0	90.0	84.8	100.5	101.0	101.0	115.0	118.0
	30%	123.5	113.0	112.0	119.0	101.0	140.0	113.5	127.5	105.2	118.0	97.0	101.0	103.0	97.0	117.0	110.0	118.0	131.59	148.0
	40%	132.3	118.8	119.5	127.5	126.0	157.7	131.5	143.5	123.0	131.5	109.0	113.0	115.0	107.0	138.0	128.0	133.0	159.0	172.5
	50%	142.7	123.0	125.0	133.7	138.8	160.5	148.7	158.0	140.0	151.0	122.0	131.5	132.6	122.0	172.0	148.2	156.0	181.0	218.0
	60%	160.0	126.5	129.0	138.5	144.5	164.0	161.0	169.0	162.0	176.0	140.0	150.0	152.0	142.0	212.0	170.0	193.0	255.5	282.0
	70%	182.0	131.0	132.3	143.2	150.0	168.2	165.0	177.0	180.5	192.0	163.0	142.0	182.0	166.5	233.0	224.0	254.0	280.0	299.0
	80%	217.0	136.0	139.0	148.5	156.0	175.0	177.0	185.0	190.0	200.8	201.5	215.0	216.0	220.0	251.0	269.0	272.0	285.0	305.0
	90%	251.0	144.0	156.2	155.5	164.0	182.8	183.0	192.0	199.0	209.0	214.0	226.0	233.0	242.0	258.0	268.0	279.0	296.0	312.0
	F.B.P.	282.0	180.7	166.5	178.4	181.0	235.1	204.2	218.5	219.5	229.0	232.5	237.0	248.8	254.0	276.5	278.5	285.0	299.0	329.0
Aniline point of Product		55.2	58.4	57.6	59.0	59.6	56.4	59.2	59.6	60.0	61.0	60.8	61.8	62.0	62.0	64.6	65.0	65.0		
Constitution (M.C.)	Unsat.	3.2	0.5		2.1	1.8	0.8	0.6	0.0	0.6	2.0	4.2	1.8	2.2	2.3	1.7	3.5	2.0	1.8	0.8
	Arom.	4.7	4.7		9.0	1.6	6.5	2.3	5.9	5.0	1.5	2.1	3.2	7.0	0.9	2.5	3.3	2.2	7.8	10.0
	Naph.	38.7	39.0		34.7	39.7	44.6	44.9	41.9	40.7	36.5	37.6	37.1	33.5	33.1	35.4	28.1	27.5	28.4	31.5
	Para.	53.4	55.8		54.2	56.9	51.9	47.8	52.2	53.7	60.0	56.1	57.9	57.3	63.7	60.4	65.1	68.3	67.0	57.7

Table XXXIV(B)16
ANALYSIS OF RESIDUAL GASES

Run No.	CO_2	C_nH_{2n}	CO	C_nH_{2n+2}	H_2	n
1	0	0.2	0	2.0	96.4	1.2
2	0.2	0.6	0.4	3.9	94.4	1.0
3	0.2	0.2	0	6.4	92.7	0.7
4	0	0.2	0	4.9	94.5	1.6
5	0	0.4	0.6	5.9	91.8	1.3
6	0	0.4	0	12.9	86.3	1.3
7	0	0.1	0	9.3	89.6	1.4
8	0	1.0	0.2	7.1	90.5	1.5
9	0	0.8	0	6.6	92.6	1.2
10	0	0.2	0	2.7	97.1	1.8
11	0	0.2	0	4.9	94.0	1.6
12	0	0.6	0.4	4.9	92.4	2.0
13	0					
14	0	0.2	0.1	3.9	95.7	2.5
15	0	0	0.3	4.9	94.4	1.0
16	0	0.2	0.2	6.0	93.3	1.3
17	0	0.4	0	5.0	94.2	1.8
18	0	0.4	0	4.3	94.3	2.3
19	0	0.2	0	5.7	93.2	2.5

Table XXXV(B)16
PROPERTIES OF AVIATION GASOLINE

		Sample Number																		
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Yield (vol. %) of oil product		54	95	93	86	70	39	51	45	55	50	64	60	58.5	63	64	52	49	36.3	33
d_4^{20}		0.7394	0.7412	0.7363	0.7418	0.7285	0.7186	0.7122	0.7169	0.7070	0.7084	0.7107	0.7132	0.7109	0.7133	0.7198	0.7149	0.7162	0.7176	0.7140
Fractional Distillation	I.B.P.	58.0	62.0	55.5	57.5	46.5	43.0	41.0	52.5	44.0	41.5	41.5	49.0	45.5	49.0	47.5	50.5	48.5	50.0	48.5
	10%	82.0	86.0	82.5	81.0	68.0	62.5	61.5	69.5	64.5	62.0	61.0	67.0	65.0	69.0	67.0	69.0	68.0	70.0	68.0
	20%	92.2	105.0	95.0	101.0	79.5	72.0	70.0	76.5	74.5	72.5	70.5	76.5	72.5	79.0	76.5	78.0	77.5	80.0	79.0
	30%	102.0	113.0	109.5	112.0	90.5	79.5	78.5	83.5	83.5	80.5	98.5	84.5	81.0	88.0	85.0	86.0	85.5	89.0	88.0
	40%	110.0	117.5	117.0	121.0	101.5	86.5	86.0	89.5	90.0	87.0	85.0	90.5	87.5	94.0	91.5	93.0	94.0	97.0	96.5
	50%	115.0	121.0	121.5	128.0	112.0	90.5	93.5	95.5	96.0	93.0	93.0	97.0	94.0	100.0	98.0	99.0	101.0	103.0	104.0
	60%	120.5	124.5	125.5	132.0	122.5	104.0	102.5	101.5	101.5	99.0	99.5	103.5	100.0	107.0	105.0	105.0	107.5	109.0	111.0
	70%	126.5	128.2	126.5	133.0	131.0	115.5	111.0	107.5	107.5	106.0	106.5	110.5	107.5	114.0	112.0	111.5	114.5	115.5	119.0
	80%	135.0	133.2	134.0	140.0	137.5	127.0	129.0	116.5	115.0	115.0	114.0	117.5	111.0	121.5	120.0	119.0	123.5	123.0	128.0
	90%	141.7	139.0	140.5	144.0	145.0	142.0	149.0	131.5	128.0	125.0	125.0	131.5	126.0	135.5	133.0	133.0	138.5	137.5	139.5
	97%	152.0	148.0	151.0	149.0	152.5	155.0	164.0	153.5	158.0	158.0	138.0	145.0	141.0	156.0	151.5	155.0	151.0	156.5	162.0
	F.B.P.	175.0	154.0	160.5	157.0	161.0	161.5	169.5	169.5	163.5	161.5	151.0	167.0	152.5	163.0	166.0	166.0	163.5	163.0	168.0
Aniline Point			57.4	58.0	58.2	58.6	56.4	58.0	57.2	58.8	58.4	59.4	59.4	58.6	58.6	58.6	58.6	58.8	58.8	58.4
Constitution (H.C.)	Unsat.	2.5	0.5	0.5	2.5	2.5	2.0	1.0	0.0	1.0	1.0	1.0	3.0	3.0	0.5	2.0	2.5	2.5	0.5	2.5
	Arom.	3.9	4.9	5.9	9.7	2.3	5.6	1.9	6.0	5.9	3.9	5.0	1.9	7.7	0.9	3.9	2.9	2.9	4.9	6.8
	Naph.	37.4	38.4	36.1	32.7	36.1	37.5	39.4	38.2	35.3	36.7	33.9	33.2	31.5	33.5	34.5	33.4	32.1	30.9	34.1
	Para.	56.2	56.2	57.5	55.1	59.1	54.9	57.7	55.8	57.8	58.4	60.1	61.4	57.8	65.1	59.6	61.2	62.5	63.7	58.6
Values	Unleaded	66.7	66.2		65.5	68.3		70.8	69.4	69.3	70.9	68.7	66.9	66.9	66.4	67.5	66.5	65.1	65.7	
	Leaded 0.1%	89.7	87.2		86.7	89.7	90.5	90.2	89.4	89.8	90.7	89.1	88.7	88.4	87.7	89.8	88.2	88.1	87.8	

Table XXXVI(B)16
PROPERTIES OF RESIDUAL OIL

	Sample Number																		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
d_4^{20}	0.8108	0.7872	0.7788	0.7792	0.7826	0.7952	0.7886	0.7964	0.8010	0.8033	0.8059	0.8058	0.8032	0.8176	0.8148	0.8118	0.8179	0.8203	0.8314
Fractional Distillation	156.5																		
I.B.P. (°C)	167.0	154.0		149.0	150.5	151.5	157.5	159.0	167.0	166.5	174.5	172.5	159.0		172.0	161.0	161.5	165.5	168.0
10%	179.5	157.0		153.0	153.0	158.0	162.5	169.5	175.0	178.5	187.5	189.55	181.5	191.5	202.0	192.5	195.5	202.5	208.0
50%	252.5	164.0		157.0	158.0	155.8	171.0	180.0	186.5	195.5	202.5	211.0	214.5	226.0	238.5	246.5	258.0	269.5	298.0
90%	381.5	211.0		169.0	169.0	182.0	183.0	193.0	200.5	208.0	217.5	225.5	233.5	143.0	254.0	262.0	272.5	281.0	317.0
F.B.P.		260.0		192.5	187.5	247.5	201.0	213.0	216.5	222.0	232.0	240.0	248.5	258.0	266.0	272.5	285.0	299.5	339.0
Aniline Point Crude Residue	55.5	61.0	59.2	59.0	60.6	57.8	61.6	61.8	63.8	64.8	65.8	67.8	68.2	70.0	70.0	72.8	73.2	74.8	74.4
Aniline Point Sat. H.C.	68.6	62.6		61.2	61.4	61.5	62.4	63.2	64.2	68.8	67.7	69.8	71.2	70.4	71.0	77.2	78.2	81.8	83.4
Constitution (H.C.) Unsat.	4.0	0.5		0.0	0.0	0.0	0.2	0.0	0.0	0.0	1.0	0.0	0.8	4.0	1.2	4.5	1.5	0.0	0.0
Arom.	5.7	0.4		4.6	1.0	10.4	2.7	5.8	4.0	2.0	5.9	5.2	5.9	0.7	0.0	3.8	8.8	12.0	11.6
Naph.	40.3	50.8		47.0	48.1	49.2	50.6	44.9	47.3	49.3	44.3	42.9	36.6	32.4	37.0	22.4	23.1	5.5	30.2
Para.		48.3		48.4	50.9	40.4	46.7	49.3	48.7	48.7	48.8	51.9	56.7	62.9	61.8	69.3	66.6	72.5	58.2

ENCLOSURE (B) 16

PART V

STUDIES ON HYDROCRACKING OF SUMATRA KEROSENE

by

CHEM. ENG. LIEUT.
K. SONE

Research Period: August-December 1941

SUMMARY

This study was made to determine the optimum boiling range of feed stock for preparation of aviation gasoline from Sumatra Kerosene by hydrocracking. It was found that the fraction boiling from 180-210°C was best for this purpose.

I. INTRODUCTION

In the study on hydrocracking of OMONOGAWA gas oil it was established that the fraction boiling from 160-220°C was best for preparing aviation gasoline. This report covers a similar study on the cracking of narrow fractions of Sumatra Kerosene since a good aviation gasoline could not be obtained by hydrocracking of the total kerosene cut.

Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr.	K. MITSUI
Chem. Eng. Lieut.	A. MORITA
Chem. Eng. Lieut.	K. SONE

II. DETAILED DESCRIPTION

A. Raw Materials

A Sumatra Kerosene cut boiling from 200-250°C was used as the raw material, and this was fractionated into 13 narrow cuts. Properties of the total kerosene and each fraction are given in Table XXXVII(B)16.

B. Test Apparatus and Procedures

The same test apparatus and procedures were used as described in the report "Studies on Hydrocracking of Omonogawa Gas Oil".

The reaction conditions were as follows:

Reaction Pressure ..... 200 Kg/cm^2

Temperature of Preheater ..... 300°C

Temperature of Reaction Chamber ..... 420°C

ENCLOSURE (B)16

H_2 Charged ..... 1 m^3/hr

Oil Charged .....1 lit/hr

Run Period ..... 3-5 hr

Catalyst ..... NiO MoO_3 Active clay (1:3:3) by wt

C. Results

Experimental data are summarized in Tables XXXVII(B)16 to XLII(B)16 and in Figure 7(B)16.

In 14 runs, the yield of product ranged from 70-90 volume%. A part of this variation was due to losses resulting from the intermittent oil gas separation operation. Hydrogen consumption was also higher than expected due to losses.

The content of aromatic hydrocarbons in the feed stocks was generally 10-20 volume%, but after hydrocracking the aromatic content dropped to about 2 volume%. Generally the topped oil became rich in paraffins, as reflected by higher aniline point compared with the feed stock.

III. CONCLUSIONS

In hydrocracking of paraffin rich Sumatra Kerosene, it is considered that the fraction boiling between 160-210°C is the most suitable for producing high octane gasoline.

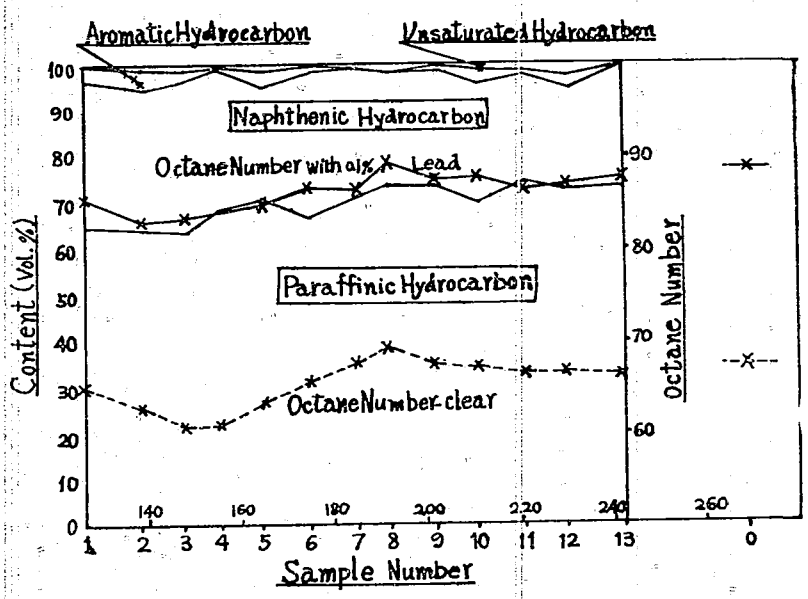


Figure 7(B)16

HYDROCRACKED PRODUCT DATA

		Sample Number													
		0	1	2	3	4	5	6	7	8	9	10	11	12	13
Yield-(Vol%)				1.0	1.1	1.9	4.7	4.4	4.0	8.0	15.0	17.0	12.0	13.2	12.8
Mean B.P. (°C)		220.2	126.7	139.0	148.0	155.7	164.5	174.5	184.5	192.3	201.7	211.2	221.0	230.4	241.7
d_4^{20}		0.8055	0.7491	0.7585	0.7647	0.7702	0.7759	0.7825	0.7808	0.7906	0.7954	0.8002	0.8049	0.8132	0.8239
Fractional Distillation	I.B.P. (°C)	159.0	80.0	78.5	106.0	121.5	132.5	134.0	169.0	182.5	193.0	203.5	214.5	224.5	236.0
	10 %	196.0	96.5	118.5	127.0	138.5	148.5	164.5	177.0	186.0	196.0	206.5	216.5	226.5	238.5
	20 %	204.5	103.5	122.5	132.0	141.5	152.0	166.5	178.0	187.0	197.0	207.0	217.5	227.0	239.0
	30 %	210.0	109.0	126.5	136.5	145.5	156.0	168.5	179.5	188.0	198.0	208.0	218.0	227.5	239.5
	40 %	216.0	113.0	130.5	141.0	149.5	159.0	170.5	181.0	189.0	198.5	209.0	218.5	228.5	240.0
	50 %	220.0	118.3	135.0	146.0	153.5	162.5	172.5	182.5	190.0	199.5	209.5	219.0	229.0	240.5
	60 %	224.0	125.5	139.5	151.0	157.5	165.5	174.5	184.0	191.5	201.0	210.5	220.0	229.5	241.0
	70 %	229.5	134.0	145.0	156.5	162.5	169.5	177.0	186.0	193.0	202.5	211.5	221.5	230.5	242.0
	80 %	238.0	145.5	152.5	163.0	167.0	174.5	180.0	189.5	195.5	205.0	213.5	223.0	232.5	243.0
	90 %	248.0	164.0	163.5	172.0	176.0	187.5	185.0	193.5	199.0	208.5	217.5	225.5	234.5	245.5
	F.B.P.	265.0	204.5	198.0	198.0	200.5	202.0	202.0	214.5	214.5	220.0	227.0	237.5	244.5	254.5
Aniline Point (°C)		65.0	52.8	51.2	51.4	51.6	52.7	54.8	57.6	60.8	63.0	66.0	68.5	69.2	68.7
Correlation Analysis	Unsat. H.C.(Vol%)	1.0	1.0	1.0	0	1.5	1.0	1.0	0.5	0.5	0	1.0	0	0.5	1.0
	Arom. H.C.(Vol%)	14.2	10.0	13.8	16.0	14.7	20.7	18.2	17.9	20.4	15.0	15.2	10.4	17.5	11.8
	Naph. H.C.(Vol%)	18.1	26.7	26.1	23.8	22.3	22.1	18.0	16.0	15.3	17.5	14.1	17.9	11.8	13.9
	Paraff.H.C.(Vol%)	66.7	62.3	59.1	60.2	61.5	56.2	62.8	65.6	63.8	67.5	69.7	71.7	70.2	73.3

Table XXXVII(B)16

PROPERTIES OF RAW MATERIALS

Table XXXVIII(B)16

YIELD AND MATERIAL BALANCE

	Sample Number													
	0	1	2	3	4	5	6	7	8	9	10	11	12	13
Run Period (Hr.)	5.0	5.0	3.0	4.5	3.5	5.0	3.5	3.5	3.5	5.0	4.5	4.5	4.5	4.5
Oil Changed (l/Hr.)	1.06	0.82	0.80	1.00	1.01	0.98	1.01	1.05	1.12	1.02	1.22	1.00	0.96	1.01
Product (l/Hr.)	0.94	0.78	0.60	0.73	0.80	0.77	0.96	1.01	1.00	0.91	0.84	0.96	0.97	0.97
Yield (Vol%)	88.7	94.6	75.0	73.3	79.2	78.4	94.8	95.8	89.2	89.2	68.6	96.0	100.7	96.0
H_2 Changed (m^3/Hr.)	1.22	1.03	0.98	1.20	1.04	1.14	1.14	1.17	1.16	1.15	1.28	1.16	1.12	1.12
Residual Gas(m^3/Hr)	0.80	0.97	0.81	1.02	0.88	0.87	0.88	0.84	0.86	0.84	0.91	0.82	0.78	0.78
H_2 Consumtion (Wt%)	5.0	1.7	5.4	2.6		5.5	3.7	4.6	3.9	4.3	3.9	4.3	4.1	3.1

RESTRICTED

		Sample Number													
		0	1	2	3	4	5	6	7	8	9	10	11	12	13
Mean B.P. of Sample		220	127	139	148	156	165	175	185	192	202	211	221	230	242
d_4^{20}		0.7190	0.7137	0.7220	0.7276	0.7335	0.7307	0.7330	0.7211	0.7146	0.7248	0.7130	0.7239	0.7197	0.7199
Fractional Distillation	I.B.P. (°C)	37.5	39.0	43.5	45.0	52.5	42.0	49.0	37.0	43.5	37.5	35.0	40.5	40.0	40.5
	10 %	59.0	64.5	73.0	78.0	81.5	76.0	78.0	60.0	62.0	63.0	65.5	60.0	59.0	50.5
	20 %	73.5	76.0	86.0	93.5	98.0	95.5	96.5	75.0	75.0	81.5	67.5	75.5	71.5	71.5
	30 %	88.5	88.5	97.5	106.5	112.5	112.0	112.0	92.0	87.0	100.0	82.0	89.0	84.0	82.5
	40 %	103.0	95.5	106.5	118.5	123.5	126.0	140.5	108.5	100.5	119.0	98.0	102.0	94.5	93.5
	50 %	116.0	103.0	114.0	127.0	131.0	136.5	151.5	130.5	115.5	137.5	115.0	116.0	107.5	106.5
	60 %	140.0	110.0	121.5	135.0	138.5	145.0	161.0	154.5	139.0	173.0	133.5	133.5	123.5	123.0
	70 %	163.0	118.0	128.5	142.0	146.5	154.0	165.5	170.0	176.0	186.0	176.0	179.0	147.5	143.0
	80 %	197.0	126.5	136.5	152.5	157.5	161.5	171.0	178.0	184.0	195.0	198.0	203.0	207.0	197.0
	90 %	213.0	149.0	150.5	164.0	167.5	170.0	177.5	185.0	190.0	201.0	206.0	211.0	222.5	230.5
	F.B.P. (°C)	235.5	198.5	192.0	200.5	204.0	194.0	192.5	203.5	201.0	228.5	217.0	232.0	232.0	251.5
	Mean B.P. (°C)	129.6	106.0	113.5	123.9	128.4	128.4	135.8	126.6	124.8	138.3	125.7	131.0	126.2	127.1
Aniline Point (°C)		65.4	60.0	59.2	62.2	61.4	62.7	64.4	65.6	66.0	66.6	66.8	67.4	66.8	65.8
Constituent Analysis	Unsat. H.C. %	1.2	0		0.8	0	0.7	0	0.9	1.8	1.2	1.8	1.3	2.7	1.2
	Arom. H.C. %	1.3	3.6		2.2	1.0	3.9	1.5	0.9	0	0.2	2.4	0.5	2.1	0.1
	Naph. H.C. %	24.1	30.1		32.6	32.8	27.0	26.8	23.2	21.9	23.0	20.8	21.1	19.9	23.8
	Paraff. H.C. %	73.4	66.3		64.4	66.2	68.4	71.7	75.0	76.3	75.6	75.0	77.0	75.3	75.4

Table XXXIX(B)16

PROPERTIES OF TOTAL LIQUID

Table XL(B)16

ANALYSIS OF RESIDUAL GAS

	Sample Number													
	0	1	2	3	4	5	6	7	8	9	10	11	12	13
CO_2 (%)	0	0.1	0.2	0.2		0.1	0.1	0	0.4	0	0	0	0.4	0.1
C_nH_{2n} (%)	0.6	0.6	0.5	0.6		0.8	0.7	0.4	0.6	0.4	0.4	0.3	0.4	0.5
CO (%)	0.3	0.1	0.1	0.1		0.1	0.1	0.8	0	0.2	0.5	0	0	0.3
H_2 (%)	94.7	93.3	67.4	73.8		73.2	93.1	92.1	87.4	93.5	90.5	90.9	93.9	91.1
C_nH_{2n+2} (%)	0.3	1.2	25.1	24.0		23.1	3.3	4.8	3.2	2.3	3.0	6.8	4.1	6.2
n	1.7	1.1	1.4	0.8		0.8	0.6	2.3	1.2	1.2	4.0	1.5	1.4	1.6

		Sample Number													
		0	1	2	3	4	5	6	7	8	9	10	11	12	13
Mean B.P. (°C)		220	127	139	148	156	165	175	185	192	202	211	221	230	242
d_4^{20}		0.6930	0.7119	0.7212	0.7204	0.7204	0.7241	0.7166	0.7142	0.6899	0.6882	0.6945	0.6874	0.6931	0.6926
Fractional Distillation	I.B.P. (°C)	45.0	51.0	44.0	51.5	52.5	49.5	50.5	43.0	41.5	45.5	44.5	41.5	41.5	46.0
	10 %	59.5	73.0	75.5	80.0	82.0	70.0	64.5	55.5	55.0	61.5	57.5	58.5	59.0	60.0
	20 %	64.5	81.5	87.5	91.0	92.5	81.0	72.0	62.0	63.0	69.0	66.5	69.5	66.5	68.5
	30 %	71.0	88.5	96.5	100.5	101.0	91.5	81.5	69.0	69.5	76.5	74.0	76.0	74.5	76.5
	40 %	83.5	95.0	103.5	108.0	108.0	102.0	91.0	75.5	75.5	83.0	81.0	84.0	82.0	84.0
	50 %	91.0	99.5	109.5	115.0	114.5	110.5	100.5	83.5	81.0	89.5	88.0	91.5	90.0	92.0
	60 %	98.5	104.5	114.5	121.0	121.0	119.0	109.5	89.5	87.0	96.0	94.5	99.5	98.5	99.0
	70 %	105.0	111.5	120.3	137.0	127.0	126.0	120.0	97.5	93.5	103.0	102.0	107.0	106.0	107.5
	80 %	114.5	118.0	125.5	134.0	134.0	133.5	135.0	107.5	101.0	111.5	110.5	116.0	116.0	116.5
	90 %	126.5	127.0	137.0	142.0	143.0	146.0	149.0	122.5	113.5	123.0	122.5	125.5	122.0	128.0
	97 %	153.5	139.5	147.0	153.0	159.5	161.0	166.5	146.0	134.0	144.5	144.0	138.5	139.5	143.5
	F.B.P.	156.0	150.5	159.5	166.5	164.0	170.5	168.5	158.0	156.0	165.5	148.0	150.5	155.5	152.5
Constituent Analysis	Unsat. H.C. %	1.0	0	0.5	1.0	0	1.0	0	1.5	2.0	1.0	2.0	2.0	3.0	1.5
	Arom. H.C. %	1.9	4.0	5.2	2.9	1.0	3.9	2.0	0	0	0.4	2.7	0.9	2.4	0
	Naph. H.C. %	24.5	31.3	30.1	32.6	31.0	24.9	31.3	25.6	24.8	24.9	25.4	23.3	21.9	25.9
	Paraff. H.C. %	72.6	64.7	64.2	63.5	68.0	70.2	66.7	72.9	73.2	73.7	69.9	73.8	72.2	72.6
Octane Value	Not Leaded	67.0	65.0	62.8	60.5	61.0	63.2	65.5	67.4	69.2	67.4	67.1	66.3	66.6	67.1
	Leaded 0.1 %	88.2	85.2	83.4	83.4		84.9	86.6	86.4	89.5	87.4	87.8	86.4	86.8	87.6
Yield of Aviation Gasoline %		82.0	90.5	89.0	79.0	76.0	65.0	49.0	56.0	62.0	43.0	64.0	62.0	72.0	73.0

Table XLI(B)16

PROPERTIES OF AVIATION GASOLINE

Table XLII(B)16

PROPERTIES OF TOPPED OIL

		Sample Number													
		0	1	2	3	4	5	6	7	8	9	10	11	12	13
d_4^{20}		0.7789	0.7618	0.7752	0.7664	0.7731	0.7641	0.7664	0.7685	0.7712	0.7792	0.7789	0.7814	0.7840	0.7880
Fractional Distillation	I.B.P. (°C)	158.0	157.0	153.5	149.0	150.0	147.5	152.0	162.0	160.0	167.0	165.0	175.0	173.0	166.5
	10 % (°C)	173.0	163.0	158.5	155.0	158.0	153.5	159.0	168.0	169.5	179.0	178.5	192.5	190.0	192.0
	50 % (°C)	198.0	173.5	168.0	164.0	165.5	162.5	169.5	176.0	181.0	192.5	197.5	210.0	217.0	225.5
	90 % (°C)	228.5	298.5	197.5	183.5	187.0	179.0	180.5	189.5	193.6	205.0	210.5	220.5	228.0	239.0
	F.B.P. (°C)	260.0	244.0	226.5	224.0	243.5	206.0	192.0	206.0	203.0	226.5	220.0	238.0	237.0	247.0
Aniline Point (°C)		72.4	66.8	64.3	67.0	65.8	65.6	67.7	69.8	71.0	70.7	73.2	75.6	76.0	75.8
Constituent Analysis	Unsat. H.C. %	1.5	0		0	0	0	0	0	1.5	1.5	1.5	0	2.0	2.0
	Arom. H.C. %	0	0		0	1.0	4.0	1.0	2.0	0	0	1.9	0	0	0.4
	Naph. H.C. %	23.1	19.6		32.6	37.9	28.1	22.4	19.9	17.1	20.9	12.6	17.3	15.3	14.1
	Paraff. H.C. %	75.4	80.4		67.4	61.1	67.9	76.6	78.1	81.4	77.6	84.0	82.7	82.7	83.5

Fractional Distillation

ENCLOSURE (B) 16

HYDROCRACKING OHA OIL IN THE SEMICOMMERCIAL HYDROGENATION PILOT PLANT

by

CHEM. ENG. LT. COMDR.
K. MITSUI

Part VI

Research Period: 1941-1942

SUMMARY

A study was made of the hydrocracking of Oha gas oil in a semicommercial pilot plant at OFUNA. Special attention was paid to the durability of the MoO_3 catalyst and the control of reaction temperature. It was found that this process was satisfactory for large scale application.

I. INTRODUCTION

A. History of Project

Up to this time many studies had been made in autoclaves and small scale pilot plants, investigating variables such as raw oil, type, reaction pressure, temperature, time, catalyst, purity of fresh H_2 and construction of reaction chamber. This investigation was made to study the process in a large semicommercial scale plant, paying special attention to the distribution of heat in reaction chamber and the durability of the MoO_3 : Ni_2O_3 : clay catalyst.

B. Key Research Personnel Working on Project

Chem. Eng. Lt. Comdr.	K. MITSUI
Chem. Eng. Lt.	R. YUMEN
Chem. Eng. Lt.	U. SATO
Chem. Eng. Sec. Sub. Lt.	M. YANAGITA
Chem. Eng. Sec. Sub. Lt.	H. NISHIKAWA

II. DETAILED DESCRIPTION

A. Catalyst

The catalyst employed in these experiments was the same as that which gave most satisfactory results in small scale pilot plant tests. It was composed of MoO_3, Ni_2O_3 and acid clay, mixed in the weight ratio of 3:1:3 and dried at 110°C. Physical properties are as follows.

ENCLOSURE (B)16

Properties of Catalyst

Diameter (mm)	6.2
Length (mm)	5.2
Density	2.06
Packed Density (kg/l)	1.34
Free Space (%)	34.9
Porosity (%)	19.3

B. Charge Stocks

The properties of the Oha gas oil used as charge stock are given below.

Properties of Oha Gas Oil

Density (20°/4°C)	0.833
Distillation	
Initial drop	160.5°C
10%	177°C
20%	183°C
30%	192°C
40%	201°C
50%	210°C
60%	221°C
70%	233°C
80%	244°C
90%	268°C
Dry point	315°C
Composition	
Unsaturates	1.0%
Aromatics	24.6%
Naphthenes	11.2%
Paraffins	62.7%
Aniline point	43.8°C

C. Hydrogen

Fresh hydrogen was prepared by electrolysis of water and purity was 99.5%.

D. Apparatus and Procedure

The semicommercial hydrogenation pilot plant was used, (Plate I(B)16) and the conditions of operation had been determined by the small scale pilot plant experiments on hydrocracking of Oha gas oil. The reaction chamber used was 200mm I.D. and 4500mm high and 6 U type heat exchanged pipes (15mm I.D. and 19mm O.D.) were inserted. The volume of catalyst was 160 liters and surface of heat exchanger was 20.8m^2 per 1m^3 catalyst for runs 1 to 37 and 110 liters and 24.4m^2/m^3 resp., for runs 38 to 47.

Raw gas oil was forced into the preheater by a hydraulic feed pump. Fresh hydrogen from the gas-holder was metered and compressed by a five-stage compressor to about 200 kg/cm^2. It was mixed with the raw gas oil and passed over the outside of the hot hydrocracking oil coil in the preheater, and then entered the reaction chamber.

From the reaction chamber the mixture of hydrogenated products and gas passed through the preheater, a cooling coil, and thence to the high pressure separator. Gas and liquid products were separated under full pressure, the liquid oil being withdrawn to the low pressure separator

(about 30 kg/cm^2) from which it passed to storage. The gas from the high pressure separator was recycled by a booster pump. This gas was about 85% hydrogen purity and it was not necessary to wash to avoid H_2S corrosion difficulties in the booster pump. Light oils contained in the low pressure release gases were removed by absorption on active charcoal.

Throughout these experiments the following conditions were maintained as closely as possible:

1. Temperature in the reaction chamber: 350°C, 400°C, and 450°C.
2. Pressure in the plant: 200 kg/cm^2
3. Space velocity: 0.5~2.0

The test was continued for 2040 hours and 47 runs were made. During these runs a special U-type heat exchange system was used to maintain uniform reaction temperature. Details of this system are given in Plate II(B)16. The relation between aviation gasoline yield and reaction temperature is given by Figure 8(B)16.

III. CONCLUSIONS

A. The average oil yield for all runs was 109.6% by volume.

B. It was concluded that the catalyst MoO_3 : Ni_2O_3 : acid clay (3:1:3) was satisfactory for use in large scale hydrocracking plants at the Second and Third Naval Fuel Depots. It was believed that 1.5 space velocity; 410°C and 200 kg/cm^2 were optimum plant operating conditions. A catalyst life up to four months was expected under favorable conditions.

C. Oha gas oil was a satisfactory charge stock for production of aviation gasoline by hydrocracking, giving a good yield of high octane product.

D. The reactor heat exchange system worked satisfactorily and a reaction temperature variation of only 1°C could be maintained.

ENCLOSURE (B)16

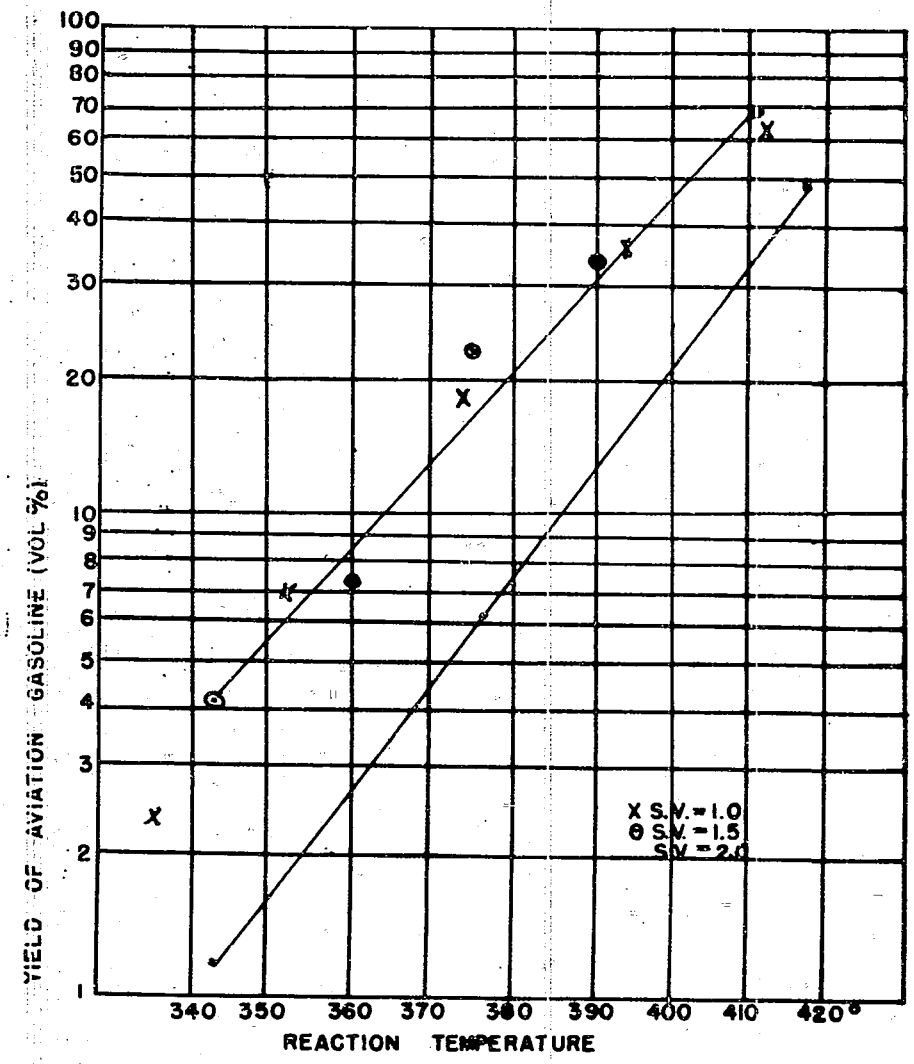
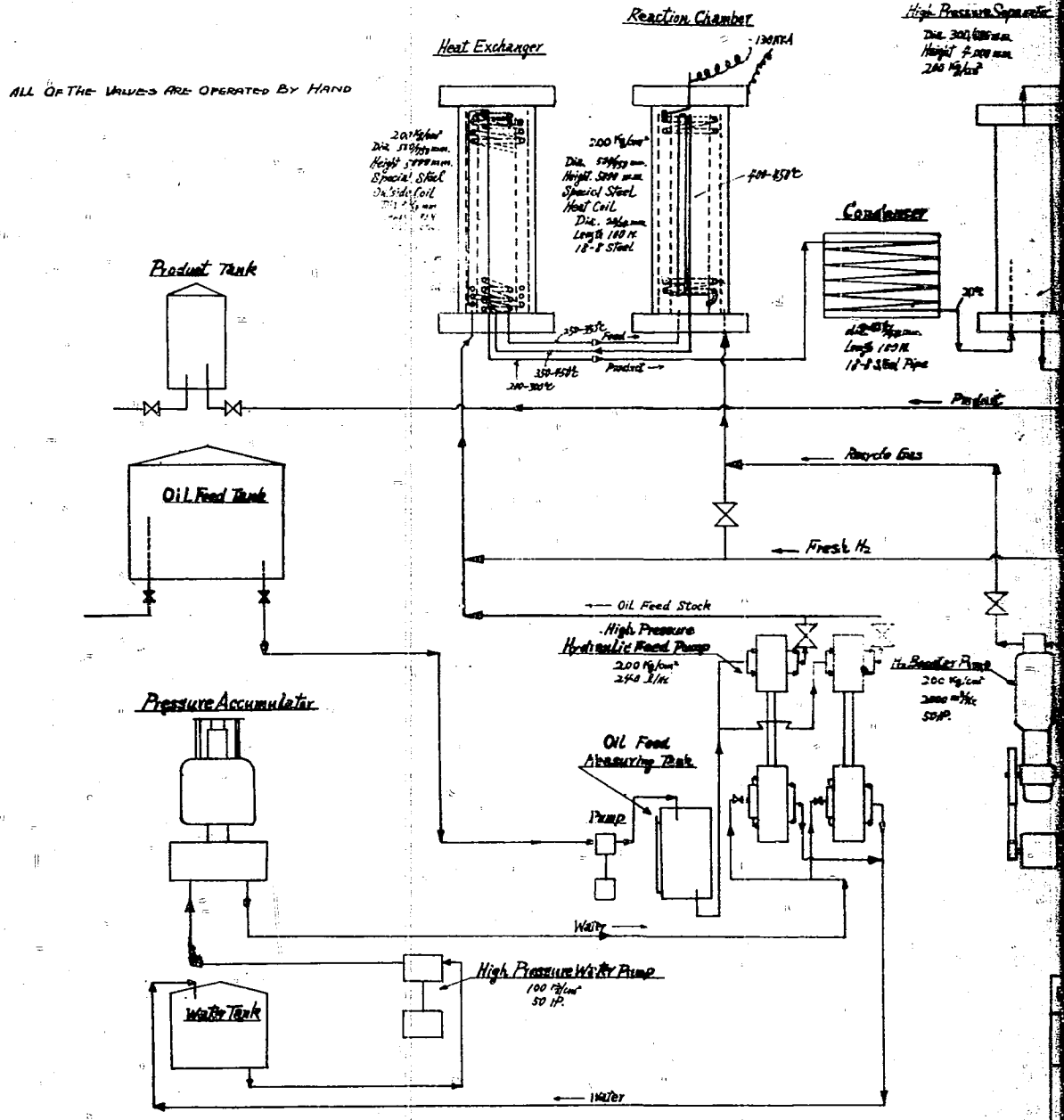
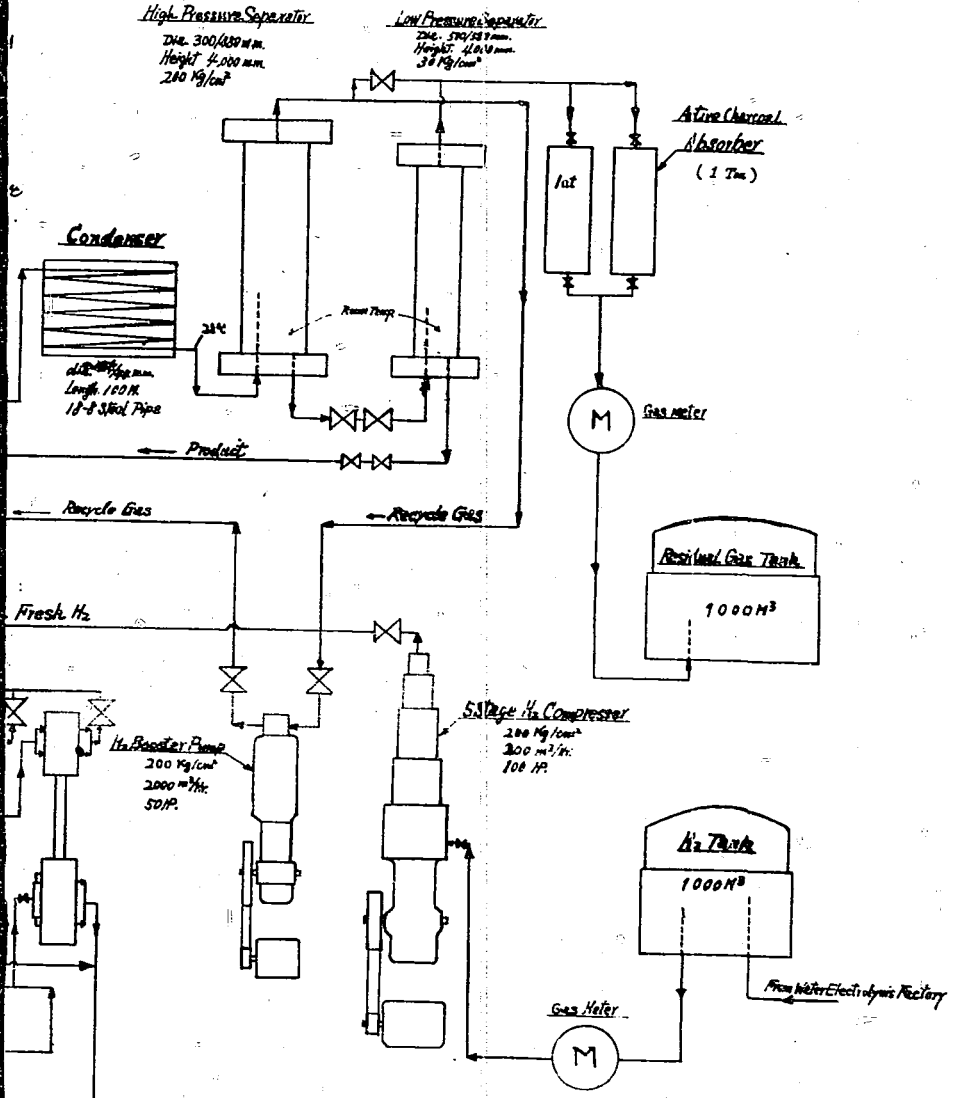


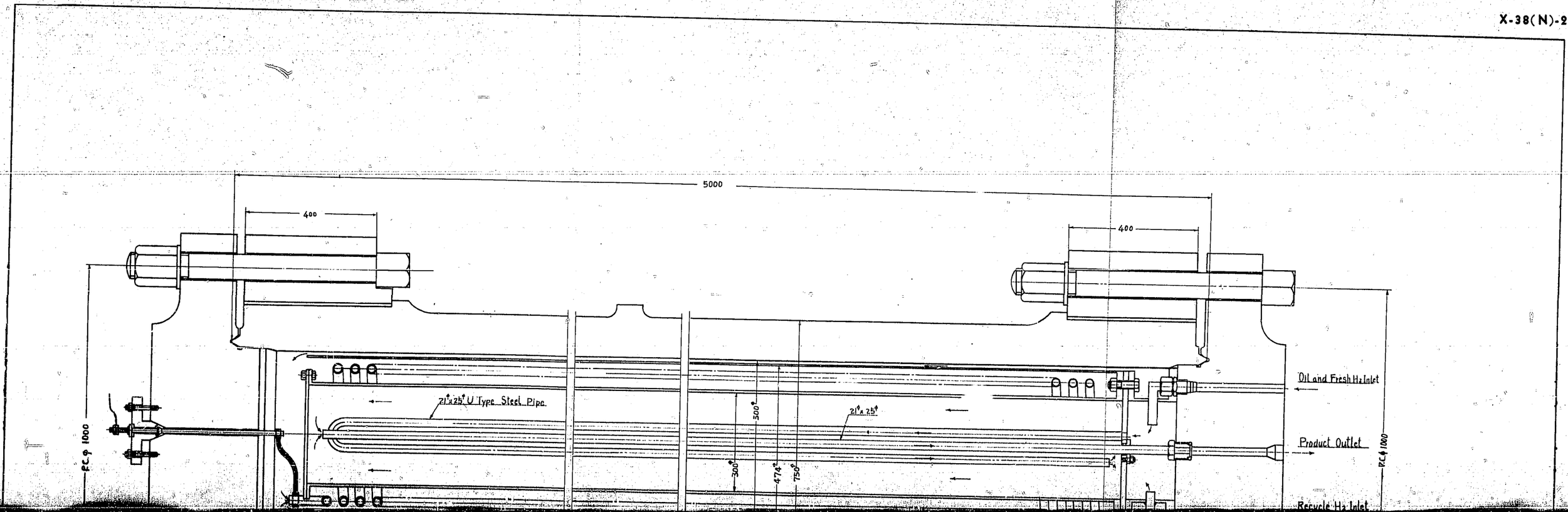
Figure 8(B)16

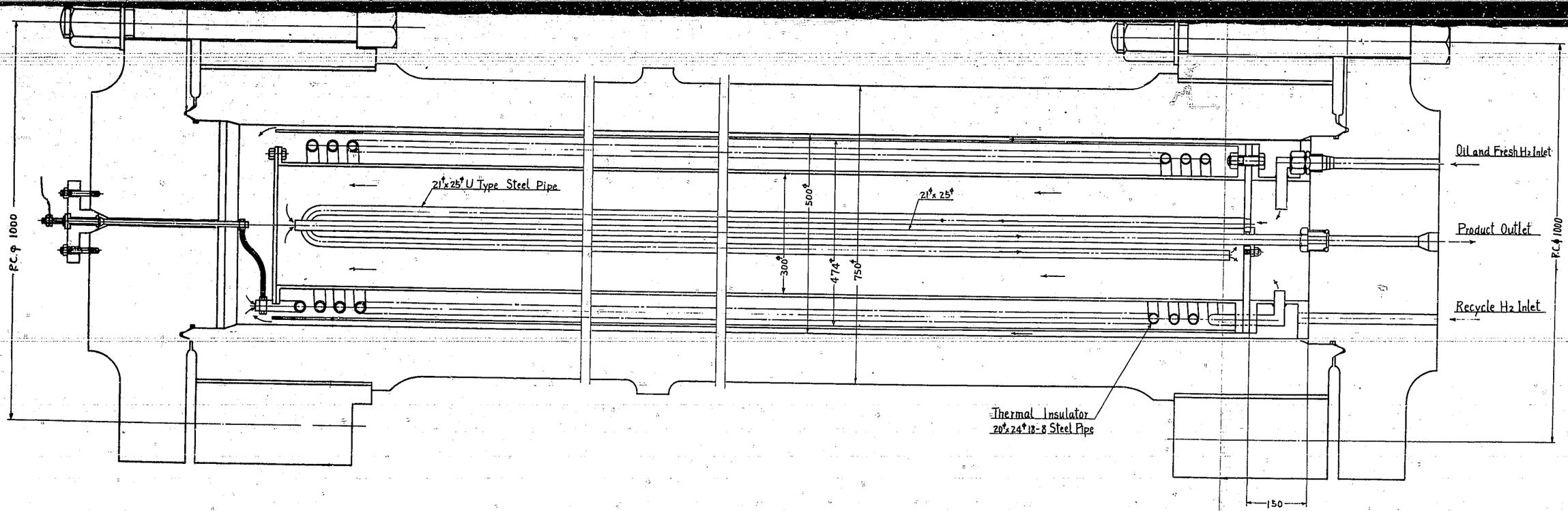
ELD OF AVIATION GASOLINE


ALL OF THE VALVES ARE OPERATED BY HAND
Heat Exchanger
Reaction Chamber
High Pressure Separator
Condenser
Product Tank
Oil Feed Tank
Pressure Accumulator
Oil Feed Measuring Tank
Pump
Water Tank
Product
Recycle Gas
Fresh H2
Oil Feed Stock
High Pressure Hydraulic Feed Pump
High Pressure Water Pump
Water

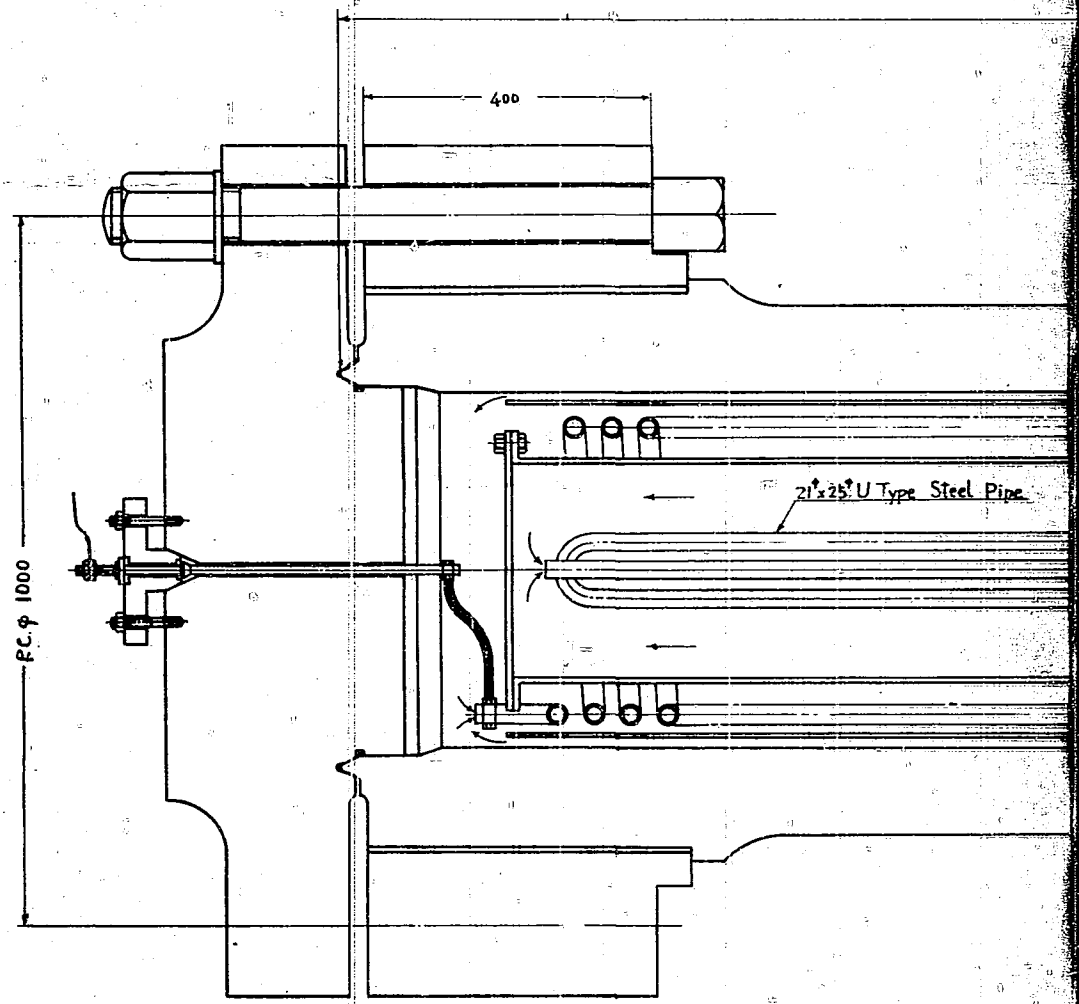


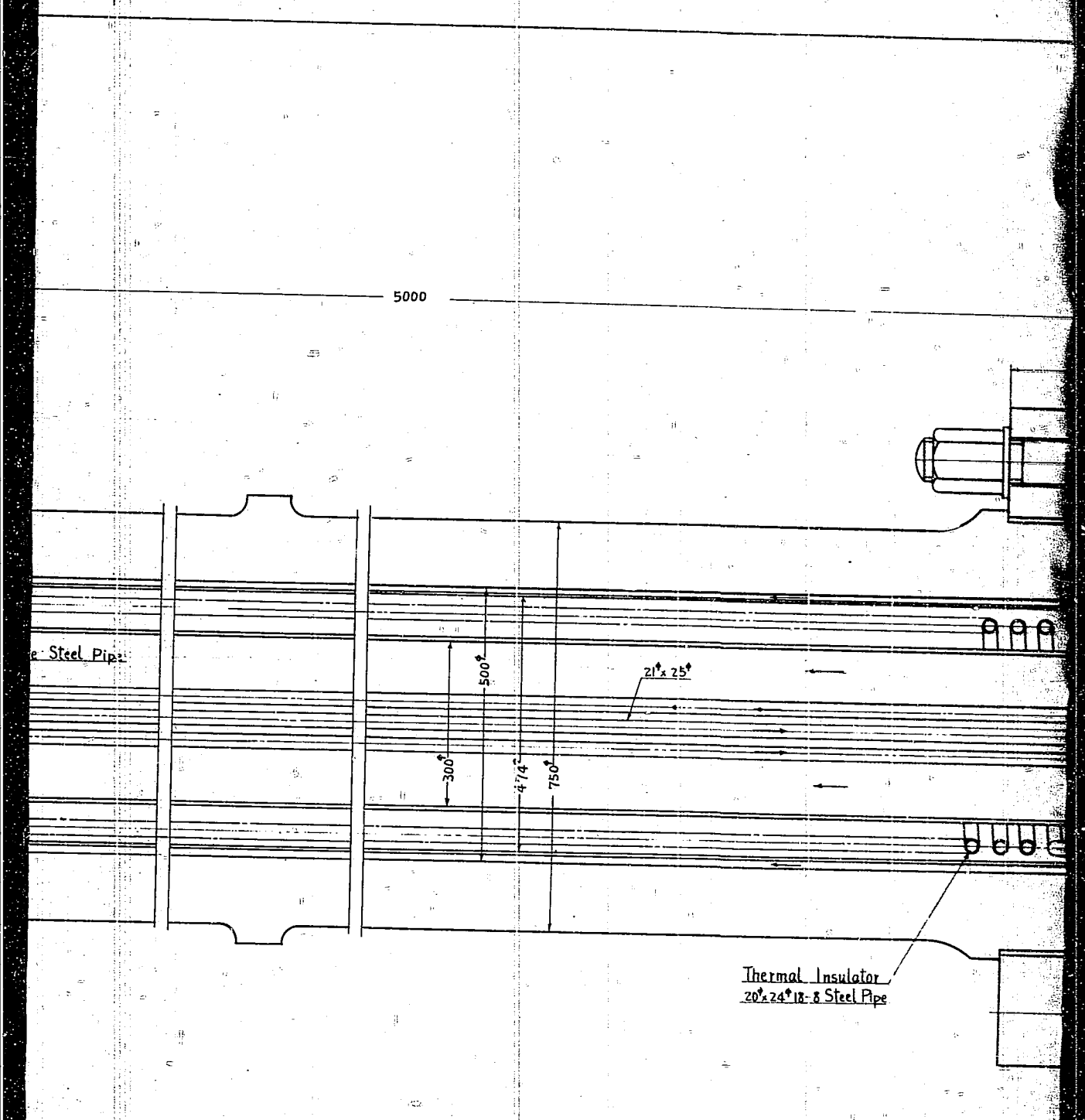
U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
FLOW CHART OF SEMI-COMMERCIAL HYDROGENATION PLANT		
	PLATE I (B) 16	X-38(N)-2

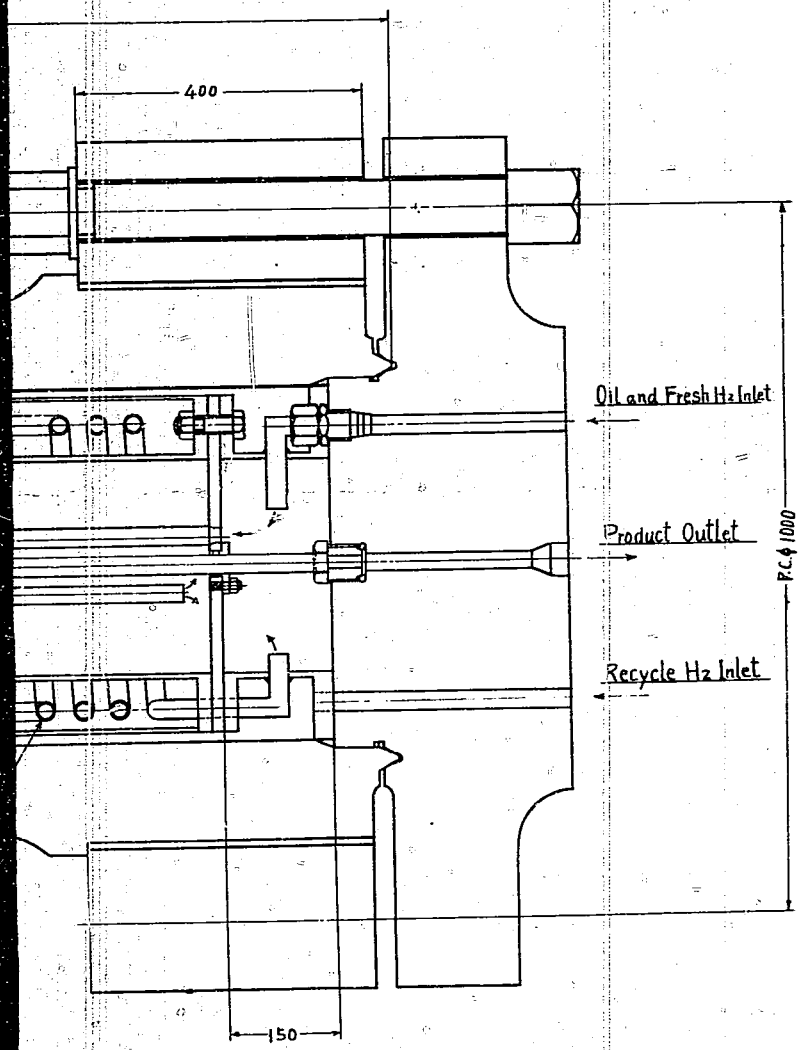

5000
400
400
P.C.φ 1000
21/4"x25° U Type Steel Pipe.
300°
500°
474°
750°
21/4"x25°
Oil and Fresh H2 Inlet
Product Outlet
P.C.φ 1000
Recycle H2 Inlet



U.S. NAVAL TECHNICAL MISSION TO JAPAN	RESTRICTED	
THE CONSTRUCTION OF REACTION CHAMBER		
27 DEC. 45	PLATE II (B) 16	X-38(N)-2


400
P.C.φ 1000
2½"x2½" U Type Steel Pipe


5000
e Steel Pipe
300
500
414
750
21" x 25"
Thermal Insulator
20" x 24" 18-8 Steel Pipe



U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
THE CONSTRUCTION OF REACTION CHAMBER		
27 DEC. 45	PLATE II (E) 16	X-38(N)-2

ENCLOSURE (B) 17

STUDIES ON THE MANUFACTURE OF AVIATION GASOLINE FROM SOYA-BEAN OIL

by

CHEM. ENG. LIEUT.
N. SAKOTA

Research Period: 1944-1945

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

Dec. 1945

ENCLOSURE (B)17

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Figure 1(B)17 Typical Autoclave Time - Temperature - Pressure Relationship (Run No. 68) ..... Page 287

Figure 2(B)17 Typical Material Balance ..... Page 288

ENCLOSURE (B)17

SUMMARY

Aviation gasoline was obtained from soya-bean oil by thermal cracking in an autoclave. Gasoline was produced in about 20% yield with an octane value of 88.9 with 0.15%-lead.

I. INTRODUCTION

A. History of Project

In Japan, research on the preparation of gasoline from soya-bean oil by heating with Japanese acid clay had been previously carried on but aviation gasoline was not successfully prepared. The present research was undertaken to investigate preparation of aviation gasoline by thermal cracking of soya-bean oil under high pressure. It was hoped that isomerization would occur during thermal cracking under these condition.

These studies began in October 1944 and were continued until the present time.

B. Key Research Personnel Working on Project

Chem. Eng. Commander H. FUJIMOTO.
Chem. Eng. Lieutenant N. SAKOTA.

II. DETAILED DESCRIPTION

A. Test Apparatus

The apparatus used in the experiment was a horizontal, 10 liter rotating autoclave.

B. Test Procedure

400 grams of the oil, with properties shown below, were heated in the autoclave at 470°C for 30 minutes. The pressure was indicated on a manometer attached to the apparatus. The chemical changes taking place during the reaction are indicated by Figure 1(B)17. The gasoline fraction boiling below 170°C was washed with 10% H_2SO_4, then 5% NaOH, rectified, dried with anhydrous Na_2SO_4, and the physical and chemical properties determined.

Properties of Charged Oil

D_{15}^{15}	0.925
N_D^{20}	1.4751
Acid Value	1.45
Saponification Value	188.5
Iodine Value	138.0

C. Experimental Results

Data on thermal, cracking runs in the autoclave are given in Table I(B)17. A material balance is given by Figure 2(B)17. The total gasoline from all runs has the chemical and physical properties shown in Table II(B)17.

ENCLOSURE (B)17

III. CONCLUSION

Soya-bean oil, heated to 450°C, was cracked to liquid and gaseous substances. A gasoline fraction was isolated in 20% yield. The octane number of this gasoline was 88.9 (leaded 0.15%) and about 40% of the fraction was composed of aromatic hydrocarbons. The cracking of soya-bean oil is a possible source of supply for aviation gasoline blending stock.

The high octane of the gasoline was due to the presence of 40% aromatics formed by the aromatization of paraffins during the reaction.

This process was not used on a commercial scale. Engine performance data on the gasoline were not obtained.

ENCLOSURE (B)17

Table I(B)17

DATA ON THERMAL CRACKING IN AUTOCLAVE

Test Number		62	63	64	65	66
Max. Press.	(kg/cm^2)	45	48	45	45	45
End. Press.	(kg/cm^2)	15	15	16	15	15
Yields (Wt%)	Oil	43.0	37.5	45.0	38.3	38.3
	Water	2.7	5.0	4.5		
	Carbon	7.5	5.4	6.3	4.5	4.0
Analysis of evolved gas (%)	CO_2	12.0	12.5	11.6	12.2	14.5
	O_2	0.2	0.1	0.3	0.6	0.5
	C_nH_{2n}	4.1	4.0	4.5	3.4	4.2
	CO	8.8	9.7	10.0	13.8	6.1
	H_2	23.4	22.5	19.5	17.5	21.4
	C_nH_{2n-2}	36.1	28.7	39.5	36.3	40.2

ENCLOSURE (B)17

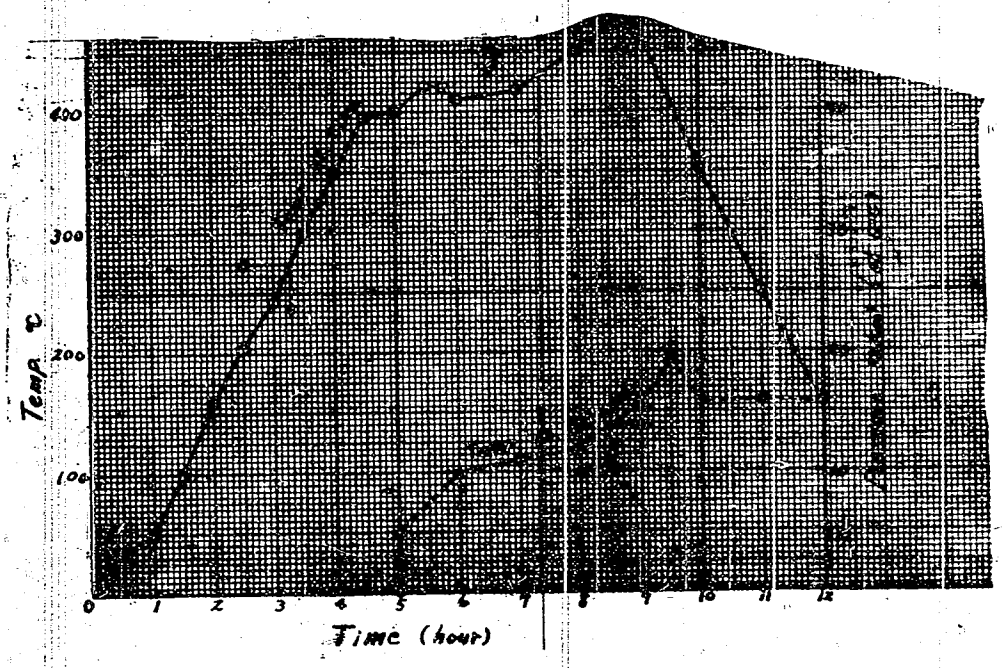

Figure 1(B)17

TYPICAL AUTOCLAVE TIME-TEMPERATURE-PRESSURE RELATIONSHIP (RUN NO. 68)

ENCLOSURE (B)17

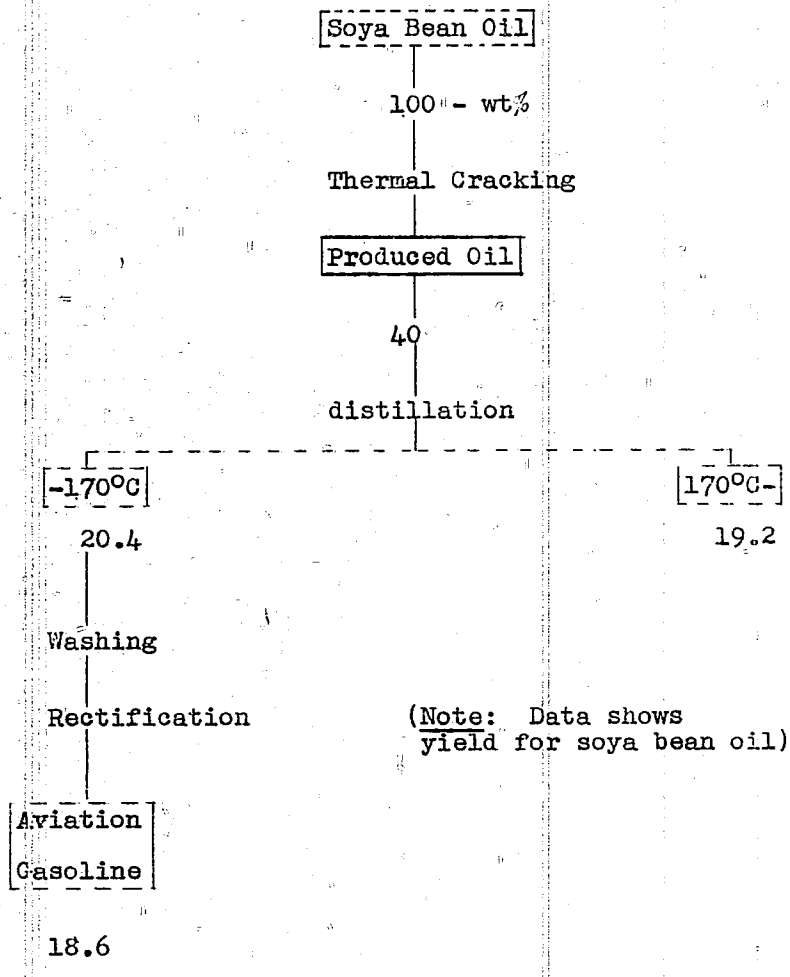

Figure 2(F)17
TYPICAL MATERIAL BALANCE

ENCLOSURE (B) 18

STUDIES ON THE MANUFACTURE OF AVIATION GASOLINE BY HIGH PRESSURE HYDROCRACKING OF SOYA BEAN OIL

by

CHEM. ENG. LT. COMDR. T. IJIMA
and
CHEM. ENG. LT. S. INABA

Research Period: Jan.-Aug. 1945

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

Dec. 1945

ENCLOSURE (B)18

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Figure 1(B)18 Autoclave (51) Used in the Cracking of Soya Bean Oil ..... Page 292

ENCLOSURE (B)18

SUMMARY

The object of this project was to determine the optimum operating conditions in the hydrocracking of soya bean oil for the manufacture of high octane aviation fuel. It was found that by hydrocracking soya bean oil over MoS_3 catalyst at 1.0 space velocity, 200 kg/cm^2 hydrogen pressure, and temperature of 420-450°C., an aviation gasoline was obtained in 40% yield, which had an octane number (with 0.15% lead) of 80-85.

I. INTRODUCTION

This project was started in January 1945 in order to obtain an additional source of high quality aviation fuel. No previous reports or data were available on this subject.

In order to find comparatively good conditions for hydrocracking soya bean oil, experiments were first made in small autoclaves of 2-5 liters capacity. Molybdenum sulphide, (MoS_3), was selected for use in the pilot plant after testing several catalysts, including molybdenum oxide (MoO_3), nickel oxide (NiO), tungsten oxide (WO_3) and copper oxide (CuO). The optimum reaction temperature and hydrogen pressure were determined to be in the range of 420-450°C and 200 kg/cm^2, respectively. Next, experiments were performed in the small scale, continuous type pilot plant. The pilot plant used was the same as that described in the authors report on the hydrocracking of pine root oil. Although many unsolved problems still remain, the results are given in the following paragraphs

II. EXPERIMENTAL RESULTS

Properties of the raw material are tabulated below:

Specific Gravity d_4^{15}	0.9204
Boiling Point °C	300-320
Iodine Value	109.45
Saponification Value	165.31
Fraction Distilled at 300°C%	14.5

Records of experimental data obtained on autoclave scale were destroyed in August 1945. Pilot plant data are summarized in Tables I(B)18 and II(B)18.

The main problem in this process was to discover the best catalyst capable of producing aviation gasoline with at least 91-95 octane number. Various additional catalysts were subsequently tested on autoclave scale, including Cr_2O_3, Fe_2O_3, FeS, VO_2, TiO_2, and their mixtures, but only with TiO_2 catalyst was it possible to produce a superior gasoline with an octane number of 87. Pilot plant tests were made on MoS_3, which was the best known prior to discovery of the TiO_2, but it had a short life and produced a lower octane gasoline.

ENCLOSURE (B)18

III. CONCLUSIONS

An aviation gasoline of sufficiently high octane number could not be obtained from soya bean oil by means of high pressure hydrocracking with MoS_3 catalyst. The most important problem for future study is the discovery of a more active catalyst for this type of hydrocracking. Because soya bean oil is composed of long paraffinic chains having many unsaturated double bonds, it is possible to convert it into iso-paraffinic or naphthenic hydrocarbons with high octane value. Therefore it is believed desirable to continue this study, putting stress on catalyst investigations. As a result of these experiments, it was shown that an aviation gasoline of 80-85 octane number (0.15% lead) could be obtained in yield of about 40% from raw soya bean oil under reaction conditions of 200 kg/cm^2 hydrogen pressure, temperature of 420-450°C and space velocity about 1.0 over MoS_3 catalyst.

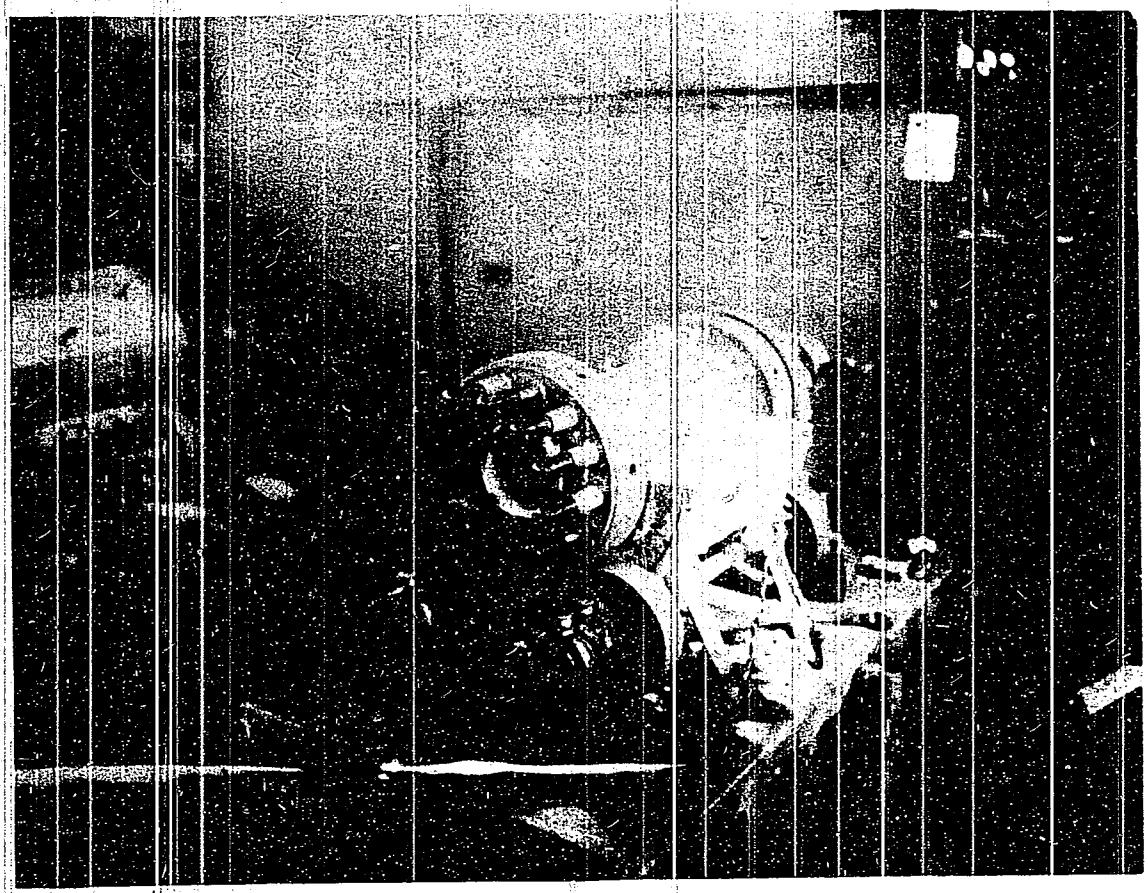

Figure 1(B)18

AUTOCLAVE (51) USED IN THE CRACKING OF SOYA BEAN OIL

ENCLOSURE (B)18

Table I(B)18

REACTION CONDITIONS & YIELDS
(Pilot Plant Test Data)

		Run No.			
		1	2	3	4
Reaction Conditions	Catalyst	MoS_3	MoS_3	MoS_3	MoS_3
	Reaction Temperature °C	420	430	450	470
	Preheaters Temperature °C	300	300	300	300
	Reaction Pressure kg/cm²	200	200	200	200
	Charged Oil lit/hr	2.89	2.88	2.93	3.05
	Total Charged Oil lit	23.17	5.77	17.59	24.40
	Charged Hydrogen Gas m^3/hr	3.25	3.12	3.44	3.11
	Total Charged Hydrogen Gas m^3	26.36	6.24	20.64	24.93
	Space Velocity (Liquid)	1.0	1.0	1.0	1.0
	Run Length hrs.	8	2	6	8
Products	Total Liquid Products lit.	22.27	5.82	14.80	17.32
	Liquid Products lit/hr	3.22	2.91	2.46	2.16
	Total Discharged Gas m^3	15.39	4.16	13.38	16.12
	Discharged Gas m^3/hr	1.94	2.08	2.26	2.01
	Water-wt% of Charged Oil	1.71	1.16	2.42	2.06
	Absorbed H_2-wt% of Charged Oil	5.68	4.56	5.42	4.81
Cracked Oil	Yield-wt% of Charged Oil	78.6	82.4	65.6	56.2
	Yield-vol% of Charged Oil	96.1	100.0	84.1	70.9
	Acidic Matter in Cracked Oil Vol%	2.0	0	0	0
	Iodine Value (I. V.)		12.17	6.97	19.16
	Saponification Value (S.V.)		0.536	1.369	0.699
	Specific Gravity (S.G.) d_4^{15}	0.7566	0.7512	0.7200	0.7326
	Initial Boiling Point (I.B.P.) °C	43.5	40.5	34.0	39.0
	10% Boiling Point °C	93.0	71.5	58.5	65.5
	20% Boiling Point °C	126.2	94.5	74.5	91.0
	30% Boiling Point °C	165.0	139.0	89.0	109.0
	40% Boiling Point °C	222.2	148.0	90.6	136.0
	50% Boiling Point °C	270.2	188.0	128.0	170.5
	60% Boiling Point °C	296.0	254.5	158.5	215.0
	70% Boiling Point °C	304.2	292.5	220.0	274.0
	80% Boiling Point °C	309.5	306.0	270.0	303.2
	90% Boiling Point °C	318.0	313.0	308.0	316.0
	Final Boiling Point (F.B.P.) °C	343.0	336.0	311.0	334.0
	Total Distillate Vol%	97.0	96.5	95.0	94.0
	Residue Vol%	0.5	1.5	1.35	0.8
	Loss Vol%	2.5	2.0	3.65	5.2
Residual Gas Composition	CO_2 Vol%	0.1	0.2	0.1	0.2
	O_2 Vol%	0	0.1	0.1	0.3
	C_nH_{2n} Vol%	3.9	5.6	5.0	4.8
	CO Vol%	0.2	0.2	0.3	0.2
	H_2 Vol%	81.2	12.0	78.9	78.8
	n. (Carbon Number)	0.6	0.7	0.6	0.5

ENCLOSURE (B)18

Table II(B)18

PROPERTIES OF AVIATION GASOLINE PRODUCED
(Pilot Plant Test Data)

		Run No.			
		1	2	3	4
Reaction Conditions	Reaction Temperature °C	420	430	450	470
	Specific Gravity (S.G.) d_4^{15}	0.7030	0.6916	0.6910	0.6901
	Acidic Matter in Aviation Gasoline Vol%	0	0	0	0
Fractional Distillation	Initial Boiling Point (I.B.P.) °C	39.0	45.0	39.0	40.0
	10% Boiling Point °C	67.0	65.0	59.0	59.0
	20% Boiling Point °C	77.0	75.0	72.5	66.5
	30% Boiling Point °C	88.5	85.5	81.5	74.2
	40% Boiling Point °C	98.4	94.0	90.0	78.0
	50% Boiling Point °C	107.6	102.0	98.0	89.0
	60% Boiling Point °C	119.0	111.0	109.0	99.0
	70% Boiling Point °C	129.0	120.0	120.0	107.0
	80% Boiling Point °C	139.9	131.0	133.0	121.0
	90% Boiling Point °C	156.8	145.5	155.5	132.2
	97% Boiling Point °C	185.0	170.0		
	Final Boiling Point °C	188.0	185.5	177.0	164.0
	Total Distillate Vol%	97.4	98.0	93.0	95.0
	Residue Vol%	0.12	0.6		1.0
	Loss Vol%	2.48	1.4		4.0
	Yield-Vol% of Cracked Oil	31.7	48.0	64.9	51.0
Composition	Unsaturated Hydrocarbon (U.) Vol%	0	4.0	0	0
	Aromatic Hydrocarbon (A.) Vol%	6.0	8.0	16.0	8.0
	Naphthenic Hydocarbon (N.) Vol%	6.0		7.8	14.4
	Paraffinic Hydrocarbon (P.) Vol%	88.0	88.0	76.2	77.6
	Aniline Point (A.P.) °C	68.1	71.1	67.2	65.3
Octane Number	Clear	59.1	58.0	60.3	62.3
	With 0.15% of Lead	83.0	83.4	85.3	85.4

ENCLOSURE (B) 19

STUDIES ON PREPARING FUELS FROM RUBBER

by

ENG. COMDR.
H. FUJIMOTO

Research Period 1943-1944

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

Dec. 1945

ENCLOSURE (B)19

LIST OF TABLES AND ILLUSTRATIONS

Table I(B)19 Results of Fractionating Mixture of Heavy Gasoline and Kerosene ..... Page 298

Figure 1(B)19 Apparatus for Continuous Rubber Cracking ..... Page 300

ENCLOSURE (B)19

SUMMARY

Rubber sheet is decomposed by dry distillation to give a high yield of terpene hydrocarbon mixtures as shown below (by volume):

Oil	95%
Residue	1%
Gas and loss	4%

A study was made of rubber decomposition in a continous cracking pipe-still, and a yield of about 90% of oil and 5% of gasoline was obtained. By hydrocracking the oil product, a 41.6% yield of aviation gasoline, with octane rating of 72.9 clear and 92.4 with 0.15% lead, was obtained.

I. INTRODUCTION

This research was done during the period, November 1943 to June 1944, but the process was not developed commercially because imports of rubber were limited due to transportation difficulties.

II. DETAILED DESCRIPTION

The catalytic cracking pilot plant was used for these tests with the catalyst chamber by-passed. The flow and operating conditions are shown in Figure 1(B)19.

Rubber was cut into blocks about 20x20x5 cm and charged to a direct-fired batch still, where it was heated to about 200°C and melted to fluid which could be pumped. The rubber was in a partially decomposed state which solidified if cooled. The melted rubber was charged to the pipe still and the products were fractionated in the usual way. Experimental results (for Run No.2) are given below:

Process Conditions

Temperature of furnace tube outlet	410°C
Pressure of furnace tube inlet	5 atm
Pressure of furnace tube outlet	2 atm
Total charge of rubber	16,850 kg
Charging rate	240 lit/hr
Recycle ratio	3
Heating time	5.5 min
Heating area of furnace tubes	27 m^2

Yields (% of charge)

Light gasoline	0.2% by wt
Heavy gasoline	35.7%
Kerosene fraction	41.7%
Residual	19.1%
Gas	1.9%
Water	1.3%

ENCLOSURE (B) 19

Properties of Blend of Light and Heavy Gasolines

Sp.gr (15/4)	0.822
Distillation	
up to 100°C by Vol	12.5%
100-200°C by Vol	66.7%
200-300°C by Vol	14.7%
above 300°C by Vol	3.1%

Properties of Kerosene

Sp.gr (15/4)	0.936
Distillation	
up to 100°C	0.9%
100-200°C	2.9%
200-300°C	44.4%
300-360°C	42.2%
residue	7.1%

Analysis of Cracked Gas

Hydrogen	16.2%
Methane	34.2%
Ethane	8.3%
Propane	13.0%
Butanes	4.5%
Ethylene	3.0%
Propylene	5.5%
Butylenes	3.7%
C5 or over	4.6%
others	7.3%

The heavy gasoline and kerosene were mixed together and fractionated in the laboratory into the following cuts:

Table I(B)19

RESULTS OF FRACTIONATING MIXTURE OF HEAVY GASOLINE AND KEROSENE

		up to 100°C	100 to 200°C	200 to 300°C	300 to 360°C	Residue	Gas	Water
Yields (wt%)		7.6	26.1	24.0	17.6	15.3	2.5	1.3
Sp.gr (15/4)		0.666	0.817	0.885	0.917	1.001		
Distillation	I.B.	27	86	168	130			
	10%	33	132	203	195			
	50%	37	169	256	319			
	90%	47	194	310	319			
	E.P.	83	241	339	319			
O.V.	plain	80.2	71.2					
	0.15% Pb	81.7	75.7					

The fraction boiling up to 100°C was hydrogenated. 500cc of charge, 20gm of powdered nickel oxide catalyst, and H_2 under 100 atm. pressure, in a 2400cc autoclave, were heated to 200°C for one hour. The consumption of hydrogen was 178 litres and the properties of the total liquid product were as follows:

Sp. gr (15/4)	0.622
Distillation	
I.D	22°C
10%	28°C
50%	31°C
90%	47°C
E.P	74°C
Octane Value	88
O.V.* with 0.15% Pb	111

*(calculated from 50:50 blend with n-heptane)

The mixed oil of heavy gasoline and kerosene from thermal decomposition of rubber, which had the following properties, was treated in the hydrocracking pilot plant (described in Enclosure (B)16) charging 10 litres per hour.

Sp. gr (15/4)	0.880
Distillation	
10%	140°C
50%	249°C
E.P	395°C

NiO-MoO_3-clay catalyst was used, and the reaction took place at 460°C, 200 atm. and S.V. of 0.5. The yield of reaction product was 103% by volume of charging stock, and the density of the reaction product was 0.796. The reaction product was distilled and the following aviation gasoline was obtained in yield of 41.6% to the charging stock.

Sp. gr (15/4)	0.755
Distillation	
I.D	46°C
10%	78°C
50%	119°C
90%	162°C
97%	171°C
Olefines	4.4%
Aromatics	8.4%
Naphtenes	41.2%
Paraffins	46.0%
Octane value, plain	72.9
Octane value, leaded 0.15%	92.4
Vapour pressure kg/cm^2	0.27

III. CONCLUSION

This gasoline was very clear and sweet, and appeared to be suitable as an aviation gasoline.

Engine tests were not made on this stock, however, and further work on this project was stopped because of limitations in the supply of crude rubber.

No difficulties were noted during the operation of the cracking unit. An examination of the Run 2 showed the furnace tubes to be clean, although some coke was deposited in the bottom of the evaporator and also at the pressure reducing valve. It is believed that the run could have been continued for about 10 days before shutting down due to coking. Difficulties were encountered in the rubber melting apparatus, and Run No. 1 was cut short due to

ENCLOSURE (B)19

coking and smoking resulting from decomposition due to too rapid heating.

To the author's knowledge, cracking of rubber on commercial scale was not done in Japan.

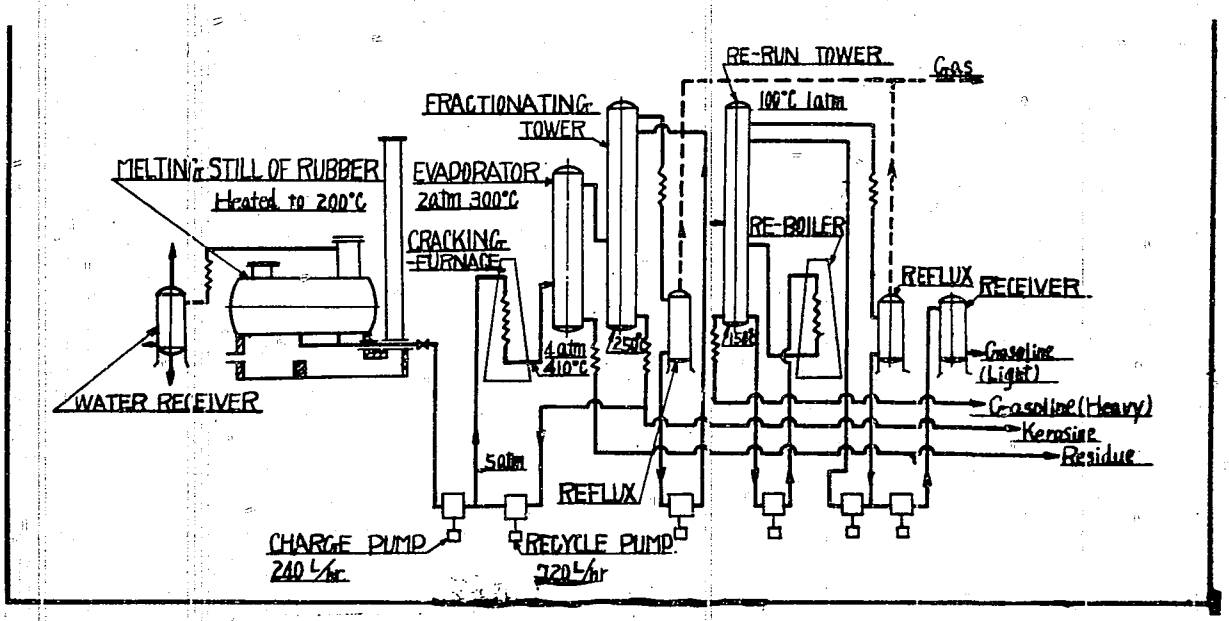

Figure 1(B)19
APPARATUS FOR CONTINUOUS RUBBER CRACKING

ENCLOSURE (B) 20

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

by

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Research Period: 1941-1944

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

Dec. 1945

ENCLOSURE (B)20

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Plate II(B)20 Flow Sheet of Pilot Plant for Preparation of Iso-Octane

ENCLOSURE (B)20

SUMMARY

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

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

I. INTRODUCTION

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

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

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

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

II. DETAILED DESCRIPTION

A. Preparation of n-Heptane

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

$$2\ C_3H_7\ COOH \xrightarrow[Cat.]{} C_3H_7COC_3H_7 + CO_2 + H_2O \qquad (1)$$

$$(C_3H_7)_2CO + 2H_2 \xrightarrow[Cat.]{} C_7H_{16} + H_2O \qquad (2)$$

1. Preparation of butyrone (Reaction 1)

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

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

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

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

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

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

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

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

The following catalysts were investigated:

(1) Powdered $CaCO_3$

(2) $CaCO_3$-Active clay (2:1)

(3) $CaCO_3$-$BaCO_3$-Active clay (1.1:0.5:1.0)

(4) $CaCO_3$-$MgCO_3$-Active clay (1.7:0.5:1.0)

(5) ThO on pumice: Prepared by dipping in thorium nitr solution, drying, and igniting at 500°C. Concentration ThO is 25.8% by weight.

(6) U_3O_8 on pumice: Prepared by same method as (5). C centration of U_3O_8 is 48.4% by weight.

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

It was found that U_3O_8 and ThO supported on pumice were excel lent catalysts. Using these catalysts, the reaction temperat could be decreased to 400-430°C compared to a reaction temper ture of about 500°C using other catalysts, and the feed rate could be increased.

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

Additional butyrone is present in the lower and higher boilin fractions of the distillate.

TABLE I(B)20

PREPARATION OF n-BUTYRONE FROM n-BUTYRIC ACID BY ACTION OF CATALYSTS

			Experiment No.									
			1	2	3	4	5	6	7	8	9	10
Catalyst:	Name		$CaCO_3$	$CaCO_3$ Clay	$CaCO_3$ $BaCO_3$ Clay	$CaCO_3$ $MgCO_3$ Clay	ThO on pumice			U_3O_8 on pumice		
	Mixing ration (by weight)			2:1	1.7:0.5:1.0	1.7:0.5:1.0	25%			48.4%		
	Weight used (gm)		50	90	74	60.5	45	45	52	64	64	64
Volume of feed used (ml/hr)			38	81	95	75	98	83	37	81.5	103	200
Reaction temperature (°C)			500	500	500	470	450	430	415	400	410	440
Yield of condensate: (% by vol.)			86.7	80.2	66.2	70.5	76.6	76.1	76.5	77.2	76.7	76.5
Properties of condensate	Sp. Gr. (d_4^{20})		0.9100	0.8920	0.8648	0.8433	0.8123	0.8235	0.8180	0.8170	0.8170	0.8153
	Distillation Test	I.B.P. (°C)	65	68	65	65	80	70	65	72	72	64
		~141°C (% by vol.)	27	25	21	17	60	4.0	5.0	5.0	5.0	5.0
		141~145°C (% by vol.)	18	31	45	52	87	84	90	88	88	90
		145~ (% by vol.)	55	44	34	31	7.0	12.0	5.0	7.0	7.0	5.0
Yield of Butyrone: (% by vol.)	To used feed (%)		15.6	24.9	29.8	36.6	66.6	64.0	68.8	68.0	67.0	69.0
	To the theoretical (%)		20.2	32.4	38.7	47.5	86.5	83.0	90.6	88.2	87.0	89.6
Volume of gas formed: (l/hr)			36.3	11.3	16.9	12.7	12.0	10.5		11.0	13.9	25.6
Gas analysis: (by vol.)	CO_2 (%)		67.4	61.9	56.3	72.6	98.6	99.2	99.0	98.8	100.0	99.5
	O_2 (%)		0.4	0.3	0.3	0.2						
	C_nH_{2n}	C'_2 (%)	4.4	4.6	5.6	2.4						
		C'_3 (%)	10.5	11.6	15.1	6.1						
		C'_4 (%)	4.7	6.8	4.7	8.0						
	CO (%)		2.9	5.5	7.6	3.4						
	H_2 (%)		1.3	1.2	1.7	0.8						
	C_nH_{2n-2} (%)		5.8	6.7	8.5	4.2						
	N_2 (%)		2.6	1.4	0.2	2.1						
	O_n (%)		1.5	1.6	1.6	1.4						
Volume of unreacted acid	In condensate (%)		52	41.8	23.7	13.7	trace	5.1	trace	0.7	1.1	trace
	To used feed (%)		45	33.5	15.7	9.2		3.9		0.6	0.8	

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

d_4^{20} 0.8156

n_D^{20} 1.4070

B.P. ..... 144°C

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

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

$$(C_3H_7)_2CO + H_2 = (C_3H_7)_2CHOH \text{ } (H_2 \text{ addition}) \quad (1)$$

$$(C_3H_7)_2CHOH = C_3H_7 \cdot CH:CHC_2H_5 + H_2O \text{ (dehydration)} \quad (2)$$

$$C_3H_7 \cdot CH:CHC_2H_5 + H_2 = C_7H_{16} \text{ } (H_2 \text{ addition}) \quad (3)$$

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

b. Catalyst.

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

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

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

c. Experimental procedure for hydrogenation of butyrone.

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

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

TABLE II(B)20

PREPARATION OF n-HEPTANE FROM BUTYRONE BY HYDROGENATION

		Experiment No.				
		1	2	3	4	5
Catalyst:	Name	Cu-Ni oxide mixed with active clay		Cu-Cr oxide	Cu-Cr oxide mixed with active clay	
	Mixing ratio	1:2	1:3		1:4	1:4
	Ratio to used feed (%)	15	20	10	20	20
Reaction temperature (°C)		250	250	350	290	250
Reaction time (hr)		1	1	1	1	1
Initial H_2 pressure (atm)		110	110	110	110	110
Maximum H_2 pressure (atm)		169	171	220	184	168
Final H_2 pressure (atm)		68	68.2	81.2	74.8	70.7
Pressure difference (atm)		42	41.8	28.8	35.2	39.3
Yield of product (% by vol.) to used Butyrone		95.3	96.0	100.5	96.0	93.3
Sp. Gr. (d_4^{20})		0.6857	0.6865	0.7420	0.6859	0.6853
Distillation Test.	I.B.P. (°C)	78.0	90.0	51.0	62.3	52.0
	~97° (%)	3.0	4.0	5.2	3.6	5.0
	97~98° (%)	91.2	89.9	44.8	90.4	90.0
	98~ (%)	5.8	6.1	48.9	4.8	5.0
Yield of pure n-heptane (97~98° fraction)	To use butyrone (% by vol.)	86.9	86.4	45.0	86.8	84.0
	To feed butyric acid (% by vol.)	59.8	59.4	31.0	59.9	58.0

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

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

B.P. (at 760mm Hg.) ..... 98.4°C

d_4^{20} 0.6836

n_D^{20} 1.38777

3. Pilot plant for n-heptane

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

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

a. Unit for producing n-butyrone.

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

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

b. Hydrogenation unit.

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

c. Purification unit

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

40 liters of the 2nd fraction was washed 3 times with 10 liters of 96% H_2SO_4 and then once with 10 liters of 5% NaOH and finally, 4 times in 10 liters of water.

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

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

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

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

$$i\text{-}C_4H_9OH \xrightarrow[Al_2O_3]{} i\text{-}C_4H_8 + H_2O \quad (1)$$

$$2i\text{-}C_4H_8 \xrightarrow[H_2SO_4]{} i\text{-}C_8H_{16} \quad (2)$$

$$i\text{-}C_8H_{16} + H_2 \xrightarrow[Ni]{} i\text{-}C_8H_{18} \quad (3)$$

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

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

b. Experimental apparatus:

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

c. Procedure

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

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

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

d. Results

The results obtained were as follows:

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

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

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

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

b. Experimental apparatus:

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

c. Procedure

Iso-butylene gas, dried by calcium chloride, is led into a 3 liter absorbing flask, charged with 1 liter of 63% H_2SO_4 and is agitated with a glass stirrer at 5-15°C. The unabsorbed gas is passed through a gas bottle and the volume is determined. The rate of absorption of iso-butylene is calculated from the volume of unabsorbed gas.

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

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

d. Results

The experimental results obtained were as follows:

Condition of polymerization

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

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

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

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

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

Absorption temperature	5°C
Volume of iso-butylene charged	8 liters/hr
Iso-butylene absorbed	approx. 98% by vol.
Polymerization temperature	90°C
Polymerization time (at 90°C)	one minute
Iso-butylene polymerized	approx. 90%
Iso-octene in product	approx. 65% by vol.
Yield of iso-octene to used iso-butylene	approx. 34% by wt.

The sulphuric acid can be used repeatedly.

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

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

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

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

B.P. (at 760mm Hg.)	99.3°C
d_4^{20}	0.6921
n_D^{20}	1.3916
Bromine value	below 0.01

Complete data relative to these experiments are not available.

4. Pilot plant for iso-octane.

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

Results obtained in the pilot plant were as follows:

ENCLOSURE (B)20

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

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

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

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

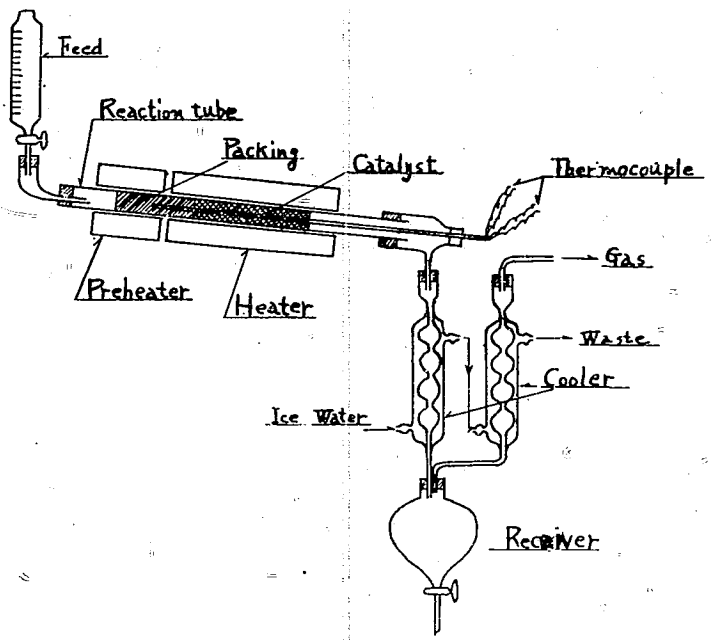
This product was hydrogenated in the presence of a nickel catalyst at 180-200°C and 10-30 atm. of hydrogen with a space velocity of 0.3-0.5. The completely hydrogenated product, having a bromine value below 0.01, was fractionated in 10% cuts, and the refractive index, specific gravity, and boiling point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

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

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

Figure 1(B)20

APPARATUS FOR PREPARATION OF BUTYRONE FROM BUTYRIC ACID



ENCLOSURE (B)20

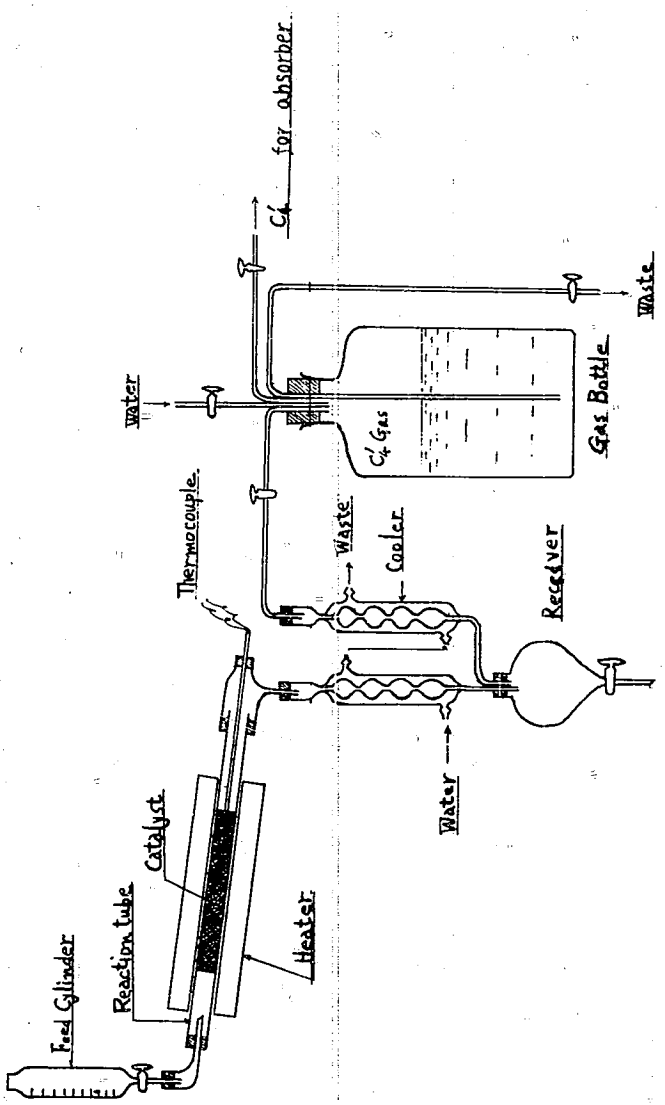


Figure 2(B)20

APPARATUS FOR PREPARATION OF i-C_4H_8 FROM i-C_4H_9OH

ENCLOSURE (B)20

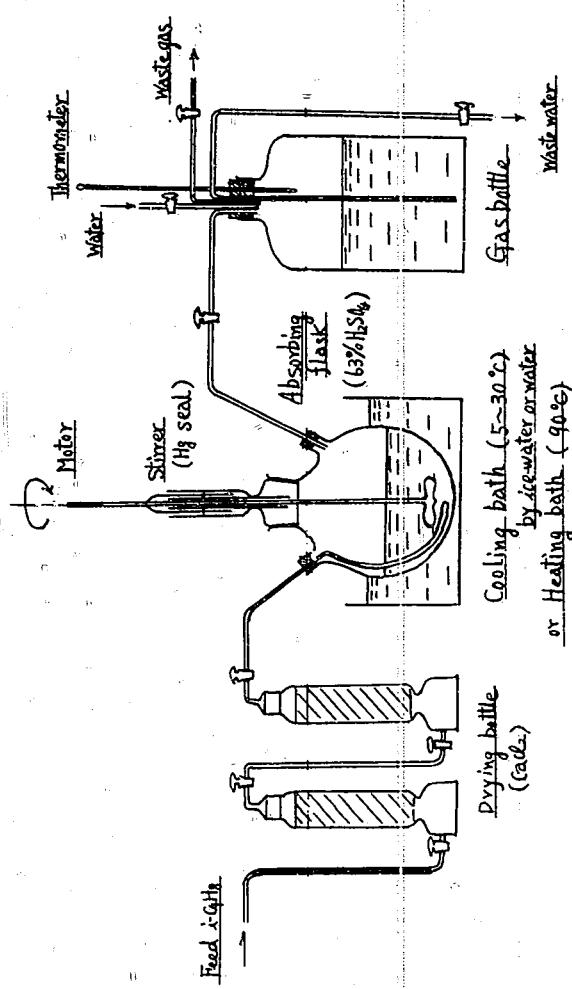
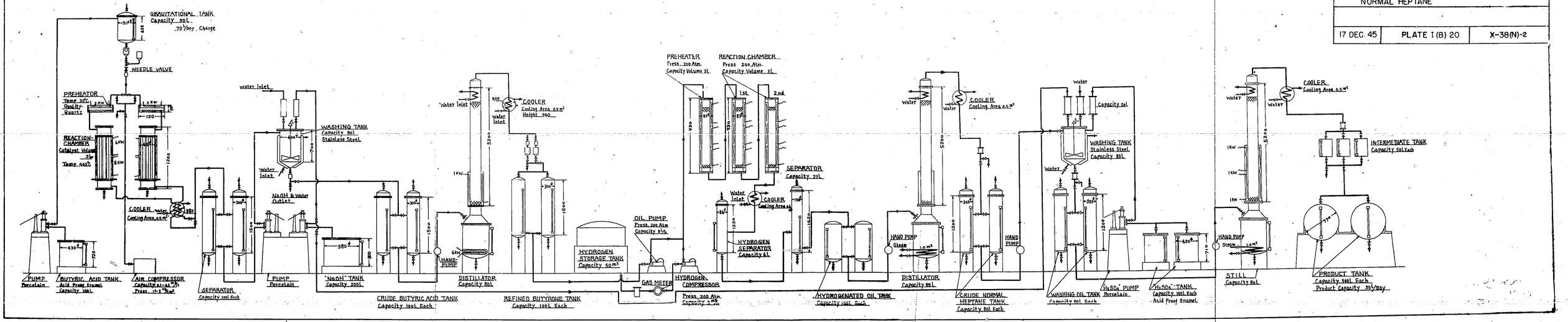
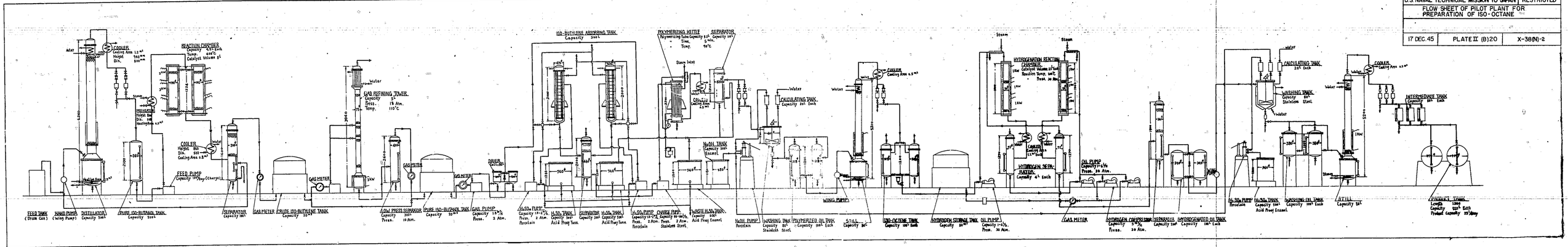


Figure 3(B)20
APPARATUS FOR PREPARATION OF i-C_8H_{16} FROM i-C_4H_8

U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
PILOT PLANT FOR PREARATION OF NORMAL HEPTANE		
17 DEC. 45	PLATE I (B) 20	X-38(N)-2



U.S. NAVAL TECHNICAL MISSION TO JAPAN	RESTRICTED	
FLOW SHEET OF PILOT PLANT FOR PREPARATION OF ISO-OCTANE		
17 DEC. 45	PLATE II (B)20	X-38(N)-2



ENCLOSURE (B) 21

STUDIES ON OIL-PROOF PAINTS

by

CHEM. ENG. LIEUT.
M. OKAZAKI

Research Period: 1944

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

Dec. 1945

ENCLOSURE (B)21

SUMMARY

Investigation of a suitable paint, lacquer, or varnish for the protection of rusting or corroding of the inside of drum-cans was undertaken. Synthetic resin lacquers having acrylic acid and cellulose acetate as chief components have the best qualities. They are easy to use, dry quickly, and are especially resistant to fuel oil such as aniline-containing gasoline. Other paints, having the usual synthetic resins or natural resins and vegetable resins as a base are not suitable for the above purpose. Although the acrylic resin lacquers dry quickly and are resistant to fuel oils, the supply is not plentiful in Japan, and this is the difficulty in the practical use of these paints.

I. INTRODUCTION

A. History of Project

The object of this investigation was to find a suitable paint or lacquer for the inside of drum-cans which would dry quickly, prevent corrosion of the can and contamination of contents when filled with such materials as aniline-containing gasoline.

B. Key Research Personnel Working on Project: Chem. Eng. Lt. M. OKAZAKI.

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

The apparatus, used in the test, was an air-bath which was used for drying the painted steel strips.

B. Test Procedure

1. Twelve paints, selected from the literature and considered to have suitable characteristics, were examined in the following manner.

   Steel strips (50mm x 20mm x 1.5mm) were coated with the paint or lacquer by dipping and were dried in glass bottles which were maintained at 120° - 160°C. in an air bath if necessary.

   After drying, the strips were immersed in methanol, butanol, analine, and aniline containing gasoline, for 50 days. At the end of this period, the condition of the painted surface was examined.

2. The four paints which were least affected by the various fuel oils were applied to the inner surface of steel drums, which had been used once. After drying at ordinary temperature, the cans were filled with gasoline containing 5% aniline and allowed to stand in the open air for two months. At the end of this period the condition of the paint and contamination of the fuel was observed.

C. Experimental Results

1. The four materials, selected as the best, were synthetic lacquers composed chiefly of cellulose acetate solvent and acrylic acid re resins. These lacquers had superior qualities in regard to drying and resistance to fuel oil. Although they have thin films. these

films are mechanically strong and are not objectionable.

2. It was found that white colored lacquers were best, since it was easier to observe the inside of the drum-cans.

3. Synthetic resins were less attacked by fuel oils than natural resins.

4. Cellulose acetate appeared to be a more satisfactory solvent than nitro-cellulose.

5. The lacquers examined had the advantage of drying much more rapidly than the paints and varnishes.

6. Water paints frequently cause rusting of the steel surface before drying, hence are not satisfactory.

III. CONCLUSIONS

A. Lacquers composed of cellulose acetate solvent and acrylic acid resins were found to be the most satisfactory materials for protecting the inside of drum-cans against attack by gasoline with 5% added aniline.

B. The supply of raw materials for these lacquers is scarce and will present a problem if they are to be used in industrial practice. Commercial use of these lacquers was no longer necessary, since the use of gasoline with added aniline was discontinued.

ENCLOSURE (B) 22

ENGINE TESTS OF AROMATIC HYDROCARBONS FOR AVIATION FUEL

by

CHEM. ENG. LT. COMDR.
Tatsuo NAKAYAMA

Research Period: 1942-1944

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

Dec. 1945

ENCLOSURE (B)22

LIST OF TABLES AND ILLUSTRATIONS

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ENCLOSURE (B)22

SUMMARY

To examine the performance of aromatic hydrocarbons as aviation fuel and to utilize the new source of fuel, aromatic hydrocarbons such as benzene (C_6H_6), toluene, xylene, solvent naphtha, Benzex (from SO_2 extraction of East India topped gasoline), and dry distilled oil of caoutchouc were subjected to the engine tests. It was necessary that the aviation fuel contain less than 20% of benzene, as the benzene readily caused detonation. Toluene had the best performance as an aviation fuel and equalled or surpassed iso-Octane. Xylene and higher aromatics also had good antiknock properties, but it was necessary to improve the fuel supply apparatus, as these aromatics had poor volatility. It should be possible to obtain a good antiknock aviation gasoline by blending over 70% of aromatics, excepting benzene, with natural gasoline.

I. INTRODUCTION

A. History of project

Research was carried on from December 1942 to March 1944.

B. Key research personnel working on project: Eng. Lt. Comdr. Tatsuo NAKAYAMA.

II. DETAILED DESCRIPTION

A. Description of test apparatus and test procedure

It was the same as that of Enc.(B)11 of Article 3 of this series, "Engine Test of Alcohol as Aviation Fuel."

B. Experimental results

The properties of the samples and their allowable maximum engine performances are given in Table I(B)22. The occurrence of detonation was detected by cylinder temperature and change in exhaust gas color. For each set of operating conditions, the engine was operated continuously for a period of three minutes.

Samples No. three, four, five (containing benzene) had higher octane numbers than samples No. six, seven, eight, nine, and ten (benzex contains higher aromatics), but the allowable maximum performances of the former are lower than those of the latter. Samples No. one and twelve (toluene and xylene) had much higher antiknock properties and allowable maximum performances than those of benzene.

III. CONCLUSIONS

Benzene is not satisfactory, even if blended with natural gasoline. The blends have higher octane numbers, but their engine performances are not good.

Toluene showed the best performances and its volatility was good enough to use in carburetor engines. Xylene and higher aromatics and their mixtures also have good antiknock properties, but their volatilities are very low, and hence in order to use them, it was necessary to attach an apparatus to the fuel supply or to mix these heavy aromatics with natural light gasoline.

ENCLOSURE (B)22

The aromatics actually used in aviation gasoline consisted of 20-30% of benzex (Sample No. 6) in natural gasoline manufactured in East Borneo (B.P.M. Oil Product Factory).

Table I(B)22

PROPERTIES OF SAMPLES AND ALLOWABLE MAXIMUM ENGINE PERFORMANCE

Sample No.	Name	Composition (by volume)	Octane Number	Test Engine	RPM	Max. HP	Max. Boost (mm/g)	Reference Fuel Data		
								Fuel	Max. HP	Max. Boost
1	Toluene	Industrial pure toluene 100%	More than 100	"Kinsei" 4 type mono-cylinder	2000	80	600	iso-Octane 0.2% Leaded	70	450
2	Mixture of toluene	Toluene 80% gasoline 20%	90	"Sakae" 4 type 14-cylinders	2700	1200	450	A 100 G	1100	350
3	Benzene	Pure benzene 100%		"Kinsei" 4 type mono-cylinder	2500	60	150	A 91 G	65	200
4	Mixture of benzene-1	Benzene 10% A 92 G 90%	93	"Kinsei" 4 type mono-cylinder	2500	60	150	A 91 G	65	200
5	Mixture of benzene-2	Benzene 20% A 92 G 80%	93	"Kinsei" 4 type mono-cylinder	2500	60	150	A 91 G	65	200
6	Benzex	Benzex 100%	90	"Kinsei" 4 type mono-cylinder	2400	85	350	A 91 G A 95 G	65 85	200 450
7	Mixture of Benzex-1	Benzex 90% gasoline 10%	85	"Kinsei" 4 type mono-cylinder	2400	85	350	A 91 G A 95 G	65 85	200 450
8	Mixture of Benzex-2	Benzex 80% gasoline 20%	85	"Kinsei" 4 type mono-cylinder	2400	80	300	A 91 G A 95 G	65 85	200 450
9	Mixture of Benzex-3	Benzex 60% gasoline 40%	80	"Kinsei" 4 type mono-cylinder	2400	70	250	A 91 G A 95 G	65 85	200 450
10	Mixture of Benzex-4	Benzex 50% gasoline 50%	80	"Kinsei" 4 type mono-cylinder	2400	65	200	A 91 G A 95 G	65 85	200 450
11	Solvent Naphtha	Solvent naphtha 100%	98	"Kinsei" 4 type mono-cylinder	2500	85	450	A 91 G	75	300
12	Xylene	Industrial pure xylene 100%	More than 100	"Kinsei" 4 type mono-cylinder	2000	80	600	iso-Octane 0.2% Leaded	70	450
13	Dry Distillate of casuthouou	Aromatics 75% Leaded 0.15%	95	"Kinsei" 4 type mono-cylinder	2200	75	500	A 95 G	75	500

A 100 G, A 95 G and etc. are aviation gasolines whose octane number are 100, 95 and etc.

ENCLOSURE (B) 23

UTILITY TEST OF AROMATIC FUELS
(AIRCRAFT ENGINE TESTS)

by

Eng. Captain T. KONDO and
Eng. Lt. Comdr. S. SOMA

Research Period: October 1943 - May 1944

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

Dec. 1945

ENCLOSURE (B)23

SUMMARY

Two kinds of aromatic fuel, "Benzex" and Solvent Naphtha produced in the First Naval Fuel Depot and sent to the First Naval Technical Depot for utility tests, contained a large amount of free carbon in the exhaust gas, contaminating the ignition plugs after few hours operation. Moreover, because of its heavy specific gravity, the fuel distribution to each cylinder of an aircooled radial engine was not satisfactory. The tests were suspended without detailed data.

I. INTRODUCTION

A. History of Project

In October, 1943, in order to obtain high octane number aviation gasoline, two samples of aromatic fuel were produced in the First Naval Fuel Depot and sent to the First Naval Technical Depot for utility tests which were discontinued in May 1944.

B. Key Research Personnel Working on Project

Eng. Captain T. KONDO; Eng. Lt. Comdr. S. SOMA.

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

Homare 20 type (aircooled radial 18 cylinders with carburetor)
Kasai 20 type (aircooled radial 14 cylinders with solid injection)
Atsuta 30 type (watercooled inverted Vee type 12 cylinders with solid injection)

B. Test Procedures and Experimental Results

The two kinds of aromatic fuel, "Benzex" and Solvent Naphtha, 15% gasoline 85% toluene and xylene etc., produced in the First Naval Fuel Depot and sent to the First Naval Technical Depot had the following properties:

	"Benzex"	Solvent Naphtha
First drop	70°C	70°C
10% pt.	90°C	90°C
50% pt.	120°C	140°C
90% pt.	150°C	155°C
97% pt.	170°C	180°C
Vapour press	0.15 kg/cm^2	0.15 kg/cm^2
Leaded	0.1% Octane number (91)	0.1% Octane number (91)
Specific gravity	0.80	0.82

An attempt was made, at first, to obtain performance curves of several engines with these fuels, on the performance test benches with Frond dynamometers. But operating conditions were very unsatisfactory, and investigations were discontinued. That is, fuel distribution to each cylinder in a radial engine, such as Homare 20 type, was not satisfactory because of heavy specific gravities and rather high 50% distillation temperatures of the fuels.

The tendency of irregular fuel distribution was great in high power operation because of the very rich mixture ratios, and before detailed data could be obtained, investigations were discontinued using Homare 20 type engine.

As the fuels had low volatility and were rather viscous, combustion conditions in the combustion chamber were unsatisfactory even when the fuels were applied to solid injection engines, such as Kasei 20 type and Atsuta 30 type. Moreover, as the exhaust gas of these fuels contained a large amount of free carbon, the ignition plugs of the solid injection engine were severely contaminated, and had to be renovated even after few hours operation.

Thus there was no prospect of using these fuels in solid injection engines and the investigation was discontinued. Flight tests were of course not attempted.

III. CONCLUSIONS

Investigations on these aromatic fuels showed unsatisfactory results and were discontinued.

ENCLOSURE (B) 24

STUDIES ON THE STANDARDIZATION OF AVIATION GASOLINE IN WAR TIME

(In Two Parts)

by

Chem. Eng. Lt. Comdr. H. HOSHIMIYA
and
Chem. Eng. Lieut. K. TSUNODA

Prepared for and reviewed with author by the
U. S. Naval Technical Mission to Japan

Dec. 1945

ENCLOSURE (B)24

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ENCLOSURE (B)24

PART I

STUDIES ON STANDARIZATION OF AVIATION GASOLINE IN WAR TIME

by

Chem. Eng. Lt. Comdr.
H. HOSHIMIYA

Research Period: 1943-1944

SUMMARY

To supply a large quantity of aviation gasoline the changing of the specifications of the gasoline was attempted. Various samples from Sumatra and Borneo crude oils with various distillation curves were tested in full size aircraft engines. The engine performance showed that the temperature of 50% and 90% distilled point could be raised to 115-125°C and 180-200°C from 105°C and 150°C respectively, and thus the production of aviation fuel greatly increased, but the octane number of the gasoline was lowered about 0.2-0.8 with every one percent increase of gasoline from the crude oil, due to the low octane number of the high boiling fractions.

To prevent the lowering of antiknock property it is necessary to use aniline, tetraethyl lead and oxy- and oxo-compounds.

I. INTRODUCTION

It is obvious that there was a great demand for aviation gasoline in war time. However, it was difficult with the transport capacity and materials available to increase the aviation fuel supply by increasing plant facilities.

Therefore the author tried to increase the production by means of changing fuel specifications.

A. Present specifications of volatility for navy aviation gasoline follow:

Vapour pressure ..... below 0.6 kg/cm^2

Distillation Characteristics

Initial Pt.	below 60°C
10%	below 80°C
50%	below 105°C
90%	below 150°C
97%	below 170°C
Sum of 10%, 50%, 90%	over 260°C

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B. Relation between vapour pressure and yield: When the vapour pressure is higher than a certain limit, the fuel pipe is choked due to vaporization in the fuel pump or carburator by influence of temperature and pressure. On the other hand, higher vapour pressure gasoline has higher antiknock and better starting quality. Therefore, it is necessary to attempt the cooling of fuel, pressurizing of fuel tank and the use of a submerged fuel pump, electrically driven. The relationship of vapour pressure, octane number and yield of gasoline is shown in Table I(B)24, for, as an example, isobutane and isopentane.

TABLE I(B)24

Blended Isobutane	Vap. Press. (kg/cm^2)	Octane No.	Blended Isopentane	Vap. Press. (kg/cm^2)	Octane No.
0.0%	0.26	83.5	0%	0.48	90.0
2.5%	0.39	86.0	5%	0.49	90.5
5.0%	0.53	88.0	10%	0.53	91.0
7.5%	0.75	90.5	20%	0.69	92.0
10.0%	0.87	91.0	30%	0.79	93.4

C. Relationship between distillation characteristics and yield of aviation fuel: Distillation characteristics of aviation gasoline affect engine starting, distribution of fuel, acceleration, etc. It is well known that the lower the distillation characteristics, the better, but this defeats the purpose of increasing the yield of aviation gasoline.

The possible increase of quantity of aviation gasoline from the four-point method and the proposed change in specifications of aviation gasoline were computed. The yields of aviation gasoline fractions calculated by the four-point computation method on 38 crude oils of Sumatra and Borneo are shown in Table II(B)24.

As shown in Table II(B)24, the yield of aviation gasoline is limited by the following percentages at the four control points:

10% Point 2.6%
50% Point 97.4%
90% Point 0
97% Point 0

Therefore, the 50% point, 105°C, was the controlling one. Since 1937, the following specifications had been used in summer as non-vapor lock fuel and no accidents occurred.

	Special 92 gasoline (1940 average value)	Specification (ordinary)
Initial point	70.6°C	60° max.
10%	101.6°C	80° max.
50%	115.5°C	105° max.
90%	137.1°C	150° max.
97%	148.8°C	170° max.
Vapour pressure	0.16 kg/cm^2	0.60 kg/cm^2

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TABLE II(3)24

Crude oil	Number	Yield of four point method				Yield of Aviation Gasoline	Octane number o.15 $Pb(C_2H_5)_4$ added
		10%	50%	90%	97%		
North Sumatra	1	153.8	52.26	55.42	58.91	52.26	(87.0)
	2	124.9	50.22	52.90	57.43	50.22	(87.5)
	3	132.0	51.50	54.41	57.71	51.50	(88.1)
	4	160.0	55.00	56.50	59.40	55.00	(89.0)
	5	92.8	44.60	50.70	57.60	44.60	
Aboeu	11	37.4	17.3	19.80	21.80	17.30	(86.5)
	12	52.8	20.66	22.81	25.22	20.66	(87.0)
	13	50.1	20.70	22.40	24.30	20.70	(87.5)
	14	42.7	17.80	20.50	23.00	17.80	(90.5)
	15	48.4	18.70	21.80	23.60	18.70	(89.5)
	16	44.8	18.50	23.20	26.50	18.50	(88.0)
	17	40.2	16.00	18.40	21.50	16.60	(88.0)
	18	53.5	23.40	25.00	27.00	23.40	(87.5)
	20	38.63	16.34	19.06	21.59	16.34	(87.5)
Telaga Said	21	21.5	11.00	14.50	16.50	11.00	(90.0)
	22	28.7	12.60	16.30	18.30	12.00	(90.0)
	23	17.9	8.60	12.04	14.54	8.60	(89.5)
	24	16.0	8.74	12.84	15.23	8.74	(88.5)
Jambi	25	79.7	32.90	42.00	32.90	32.90	(90.4)
Mangunjaya	26	5.5	2.70	4.50	2.70	2.70	(88.0)
	27	5.4	2.04	3.21	2.04	2.04	(91.1)
	28	5.9	3.00	4.40	3.00	3.00	(90.0)
Coria (heavy)	30	4.8	3.06	4.50	3.06	3.06	(90.6)
	31	5.5	3.60	5.98	3.60	3.60	(91.0)
	32	5.6	3.30	4.70	3.30	3.30	(92.0)
	33	3.5	3.00	4.60	3.00	3.00	(90.0)
	34	4.5	2.70	4.60	2.70	2.70	(91.5)
	35	4.0	3.00	4.20	3.00	3.00	92.6
	36	4.8	3.22	4.52	3.22	3.22	92.0
	37	2.9	2.20	3.97	2.20	2.20	89.8
Coria (light)	38	32.8	21.02	26.24	21.02	21.02	
	45	27.2	19.10	25.90	19.10	19.10	92.4
	39	24.0	17.60	24.50	26.80	17.60	92.4
Mill	40	5.3	8.46	15.53	17.50	5.30	91.3
	41	4.66	3.54	7.09	8.59	3.54	91.5
Sangasanga	42	13.07	10.47	19.16	23.39	10.47	91.9
	43	9.50	9.14	19.35	21.71	9.14	92.8

Therefore, when the 50% point was elevated to 115°C the author expected such a fuel would be used only for specially built engines, particularly for solid injection type engines. So the author tried to calculate the increase of yield when specifications were modified as shown in Table II (B)24.

The specifications are given in Table III(B)24.

TABLE III(B)24

	I	II	III (Present specifications)
Initial Pt.	60°C max.	60°C max.	60°C max.
10%	80°C max.	90°C max.	80°C max.
50%	115°C max.	125°C max.	105°C max.
90%	150°C max.	180°C max.	150°C max.
97%	170°C max.	200°C max.	170°C max.

Limiting Distillation Factor:

10%	30.5%		0
50%	27.8%		94.5%
90%	41.7%		0
97%	0		5.5%

Average yield of aviation gasoline from each oil field is shown in Table IV(B)24.

By the above proposed modification of specifications, the yield of aviation gasoline increased 25% by the first modification and 80% by the second modified specification. This represented increased production of gasoline of ca. 300,000 kl and 1,000,000 kl per year from the East Indies oil (8,450,000 kl/y), regarding total crude oil.

D. Degradation of antiknock properties by proposed modifications of specifications is shown in Table V(B)24. Octane numbers would be lowered by 1.5-7.4.

E. Method of regaining loss of octane number:

1. Increasing the amout of tetraethyl lead.
2. Blending of isooctane.
3. Blending of aniline.
4. Blending of ethanol, acetone, butyrone, diisopropyl ether etc.

ENCLOSURE (B)24

TABLE IV(B)24

Crude Oil	Number of Samples	% Present Yield	First % Yield	% Increase	Second % Yield	% Increase
North Sumatra	5	50.71	54.00	6.5	69.1	36.5
Talangimar	4	10.15	13.92	27.3	16.75	65.0
Ababu	9	18.88	21.31	12.9	28.1	48.0
Mangunjya	3	2.58	3.57	38.1	4.7	82.0
Jambi	1	32.40	42.00	27.6	52.0	58.0
Mili	2	4.40	4.98	13.1	12.4	72.0
Ceria (light)	3	19.24	25.80	34.5	31.3	63.5
Ceria (heavy)	8	3.01	4.15	38.0	5.49	83.0
Sangasanga	2	10.40	13.07	25.6	20.9	101.0
TOTAL	37	16.92		24.65		78.66

TABLE V(B)24

Crude Oil	Present Yield (%)	Octane No.	First Modification		Second Modification	
			Increased Yield (%)	Octane No.	Increased Yield (%)	Octane No.
North Sumatra	50.71	87.5	54.0	85.5	69.1	81.5
Talangimar	10.15	89.0	13.92	87.0	16.75	85.5
Ababu	18.88	88.2	21.31	86.5	28.1	84.0
Mangunjya	2.58	91.1	3.57	90.0	4.7	89.5
Jambi	32.90	90.4	42.0	86.0	52.0	83.0
Mili	4.40	91.5	4.98	91.0	12.4	87.0
Ceria (light)	19.24	91.1	25.80	88.5	31.3	86.5
Ceria (heavy)	3.01	91.5	4.15	90.5	5.49	90.0
Sangasanga	10.40	94.0	13.07	93.0	20.9	89.5

ENCLOSURE (B)24

II. CONCLUSIONS

First modified specification is good for combat planes even in winter.

Second modification is satisfactory for use in summer for combat planes by practical aeroplane test. Therefore Japanese naval specifications of aviation gasoline were changed by the first and second modifications (Table VI(B)24.

The two heavier aviation fuels, modifications 1 and 2, were successfully used during the war.

TABLE VI(B)24

A 87 G and A 91 G			
Properties	1939 - 3	1944 - 7	1945 - 5
Fractional Distillation		Modification 1	Modification 2
Initial Pt.	60°C max.	60°C max.	70°C max.
10% Pt.	80°C max.	90°C max.	90°C max.
50% Pt.	105°C max.	115°C max.	125°C max.
90% Pt.	150°C max.	160°C max.	180°C max.
97% Pt.	170°C max.	170°C max.	200°C max.
Sum of 10%, 50%, 90%	260°C min.	260°C min.	260°C min.
Leaded	0.1% max.	0.15% max.	0.15% max.
Vapour Pressure	0.53 kg/cm^2	0.6 kg/cm^2	0.6 kg/cm^2

ENCLOSURE (B) 24

PART II

ENGINE TESTS OF AVIATION GASOLINE WITH INCREASED TETRAETHYL LEAD CONTENT

by

Chem. Eng. Lieut.
K. TSUNODA

Research Period: 1944

SUMMARY

Objectives of Project: The objective of this engine test is to find the influence of the increased tetraethyl lead content in aviation gasoline upon the engine performance and ignition plugs, and to decide the utility of such gasoline as high octane aviation fuel.

Significant Results: The author tested the aviation fuels with the contents of:

tetraethyl lead ..... 0.3 vol%
ethylene dibromide ... 1.0, 1.3 and 1.5 equivalent

The significant results were as follows:

1. The aviation gasoline containing 0.3 vol.% tetraethyl lead did not show the same engine performance compared with the gasoline of same octane number of ordinary tetraethyl lead content (i.e. 0.15%).

2. Ethylene dibromide acted as an inhibitor of the contamination of the spark plugs with lead deposits, but an excess of ethylene dibromide caused the plugs to burn.

INTRODUCTION

A. History of Project: In order to obtain more aviation fuel from a definite quantity of the base oil, we have no other way than to degrade the specification, that is, to enlarge the distillation range. As the result of the elevation of the final cutting temperature its octane number inevitably decreases. Then it is necessary to increase the tetraethyl lead content of the gasoline to maintain the same octane number, but this is supposed to give more contamination upon the spark plug. The author, therefore, increased the ethylene dibromide content as an inhibitor of the contamination due to lead and examined the influence of both additives by long running engine tests. These engine tests were done from May to November 1944, in relation to the revision of the specification of aviation fuel during the war time.

ENCLOSURE (B)24

B. Key research personnel working on project:

Chem. Eng. Lieut. K. TSUNODA.

II. DETAILED DESCRIPTION

A. Description of the test apparatus:

Engine: Kinsei 4 type single cylinder testing machine made by Ishikawajima Aircraft Company, Ltd.
Cylinder: diameter 140mm
stroke 150mm
Compression ratio 6.6
(Other details: presented blue prints)

B. Test procedures and conditions: The author chose the long-running (30 hours) engine tests to find various influences of the new fuel upon the engine performance and the spark plug. Details of the condition are shown in Table VIII(B)24.

C. Experimental results

1. Physical and chemical properties of fuel samples

TABLE VII(B)24

Sample	Content of tetraethyl lead	Content of ethylene dibromide	Octane No.	Distillation Character				
				F. drop	10%	50%	90%	95%
A	0.3 vol.%	1.0 equiv.	Ca. 92	50	80	115	160	180
B	0.3 vol.%	1.3 equiv.	Ca. 91	50	90	130	170	190
C	0.3 vol.%	1.3 equiv.	Ca. 97	35	70	115	150	160
D	0.3 vol.%	1.5 equiv.	Ca. 96	50	80	115	155	170

2. Performance test

a. At first the author tested the fuel sample "A" at lower and higher power to decide which condition gives the worst influence upon the ignition plug.

ENCLOSURE (B)24

TABLE VIII(B)24

Experiment No.	Sample No.	Brake Horsepower	Revolution (RPM)	Boost (mmHg)	Situation of test	
					Front plug	Rear plug
1	A	10	1500	250	Began to misfire after 10 hours and then changed to new plug.	In good condition throughout the test.
2	A	50	2500	150	Began to misfire after 15 hours but did not change plug during the test.	Misfired after 10 hours.
3	B	50	2500	150	Power began to fall after 6 hours and it was necessary to stop the test after 13 hours.	
4	C	50	2500	150	In good condition throughout the test.	
5	D	50	2500	150	Same as Experment No. 4.	

As shown in Table VIII(B)24, in the case of lower power (Experiment No. 1: 250mm boost and 1500 RPM) the front plug which was supposed to be kept at lower temperature than the rear one began to misfire after 10 hours by the contamination with lead deposits but the rear plug which was supposed to be in moderate temperature was in good conditions during the test.

In the case of higher power (Experiment No. 2: 150mm boost and 2500 RPM) both front and rear plug began to misfire after 10-15 hours. From these facts the author supposed that in the former condition the misfiring was not due to the increased contents of tetraethyl lead but perhaps to the lubricating oil as the cylinder was kept at relatively lower temperature, and if the cylinder temperature were kept moderately high it should be free from any contamination throughout the test. Therefore the author decided to examine following fuel samples under conditions of higher power output.

b. The author tested sample "B" in which the content of ethylene dibromide was 1.3 equivalent in order to prevent misfiring of the plug. In this case the engine power began to fall after 6 hours and the test was stopped after 13 hours due to low horsepower. As shown in Table 7, Enclosure B-24, this fuel sample had lower octane number compared with another sample. This was perhaps due to the character of the base gasoline, so that the author used samples "C" and "D" which were prepared to have nearly same octane number.

c. In the test of the sample "C" which contained 1.3 equivalent ethylene dibromide both plugs were in good conditions throughout the test that is, the contamination was small and the center pole of the spark plug was only a little burnt.

d. Then we increased the content of ethylene dibromide to 1.5 equivalent. In sample "D" both plugs were in good condition. that is, there was no perceptible contamination, but the center pole of the plug was considerably burned.

III. CONCLUSION

Although only a few experiments were made and definite conclusions could not be drawn, it could be said at least as follows:

A. Aviation gasoline which contains 0.3% tetraethyl lead does not show the correspondent engine performance with its octane number. For example sample "B" has 91 octane number but it cannot pass the engine endurance test. Our original purpose was to gain such fuels that have 91 octane number and corresponding engine performance with their octane number. Therefore the effort to get new specification by means of enlarging the distillation range of gasoline was negative from the standpoint of the engine performance.

B. Then the first purpose of the test program was changed and only the indluence of ethylene dibromide as an inhibitor was examined by using high octane number fuels which were endurable for long-running engine tests, and having regular specification boiling points, for example, sample "C" and "D". From these results of test, it could be concluded as follows, when tetraethyl lead content was increased from 0.15 vol.% to 0.30%, the suitable equivalent of ethylene dibromide was 1.3.

ENCLOSURE (B) 25

UTILITY TESTS OF AVIATION GASOLINE OUTSIDE SPECIFICATIONS

by

MECH. ENG. CAPT. T. KONDO

MECH. ENG. LIEUT. COMDR. S. SOMA

Research Period: 1943-1944

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

Dec. 1945

ENCLOSURE (B)25

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ENCLOSURE (B)25

SUMMARY

Aviation gasoline No. 1 and No. 2 prepared by the First Naval Fuel Depot as wartime gasoline standards were acknowledged useful as well as the standard gasoline of the same octane number from the results of the bench and flight tests on various engines made in the First Naval Technical Depot.

In connection with engine starting, No. 1 gasoline was somewhat unsatisfactory at atmospheric temperatures below 10°C and No. 2 gasoline was entirely unsatisfactory at atmospheric temperatures below 20°C. Especially in winter, at atmospheric temperatures near 0°C, engines could not be started. It was, therefore, necessary to use the normal standard gasoline for starting. The sufficient amount for each engine was 5 liters. In connection with distribution of fuel to each cylinder, No. 1 gasoline was somewhat unsatisfactory in comparison with ordinary standard gasoline, and No. 2 gasoline was also unsatisfactory, but were sufficient for practical use.

Acceleration with these fuels was satisfactory for all engines. In connection with dilution of lubricant oil, No. 1 gasoline showed more dilution than ordinary gasoline, i.e., 0.8 - 1.0% of oil weight, and No. 2 gasoline showed a very large degree of dilution reaching to 1.2 - 1.4%. Careful attention, therefore, was required to use the gasoline without trouble.

I. INTRODUCTION

(A) History of Project

In the middle of 1943, the quantity of aviation gasoline in Japan became short, and an attempt was made to modify the ordinary aviation gasoline specification by the First Naval Fuel Depot. Bench and flight tests on various engines, using two types of samples, were carried out by the First Naval Technical Depot.

Satisfactory results were obtained in the middle of 1944, and immediate steps were taken to establish a specification for a standard wartime aviation gasoline.

(B) Key Research Personnel Working on Project

Mech. Eng. Capt. T. KONDO the First Naval Technical Depot

Mech. Eng. Lieut. Comdr. S. SOMA the First Naval Technical Depot

II. DETAILED DESCRIPTION

(A) Description of Test Apparatus

Engines: Homare 20 type, Kasei 20 type, Sakae 30 type, Atsuta 30 type

Airplanes: Shiden (fighter with Homare 20 type engine)
Raiden (fighter with Kasei 20 type engine)
Zero type fighter (with Sakae 30 type engine)
Suisei (diving bomber with Atsuta 30 type engine)

ENCLOSURE (B)25

(B) Test Procedures and Experimental Results

Two types of modified aviation fuel prepared by the First Naval Fuel Depot and sent to the First Naval Technical Depot had the following properties.

Table I (B)25

PROPERTIES OF MODIFIED AVIATION FUELS

	Wartime	Modification	
	No. 1 Gasoline	No. 2 Gasoline	Ordinary Standard
First drop	60 °C max	70 °C max	60 °C max
10 % pt	90 °C max	90 °C max	80 °C max
50 % pt	115 °C max	125 °C max	105 °C max
90 % pt	160 °C max	180 °C max	150 °C max
97 % pt	170 °C max	200 °C max	170 °C max
Sum of 10, 50 & 90%	260 °C min	260 °C min	260 °C min
Leaded	0.15% max	0.15% max	0.1% max
Vapour Pressure	0.6kg/cm^2	0.6kg/cm^2	0.53kg/cm^2
Octane No.	91	87	91 & 87
Specific gravity	0.73 - 0.74	0.74 - 0.76	0.725

These fuels were examined in several engines connected to Froud dynamometers. Investigations were made with maximum allowable boost pressures and minimum economical consumptions.

The following data were obtained using maximum boost pressure. See Table II (B)25.

Table II (B)25

AV - GAS ENGINE TESTS USING MAXIMUM BOOST PRESSURE

Engines Type	By Modification* No. 1 (oct. No. 91) (mm/Hg)	By Modification** No. 2 (oct. No. 87) (mm/Hg)	Remarks
Homare 20	(1st speed) + 500 (2nd speed) + 350	(1st speed) + 150 (2nd speed) + 50	Over +125mm/Hg with supplementary fuel
Kasei 20	(1st speed) + 450 (1st speed) + 300	(1st speed) + 450 (2nd speed) + 300	Over + 160mm/Hg with supplementary fuel
Sakae 30	(1st speed) + 300 (2nd speed) + 200	(1st speed) + 150 (2nd speed) + 50	
Atsuta 30	(1st speed) + 325 (2nd speed) + 250	(1st speed) + 150 (2nd speed) + 100	

*Ordinary standard (oct. No. 91) same as modification No. 1 (oct. No. 91)
**Ordinary standard (oct. No. 87) same as modification No. 2 (oct. No. 87)

It was shown by these data that the two types of modified gasoline gave the same results as the ordinary standard gasoline. Following data were obtained on minimum economical consumption.

ENCLOSURE (B)25

Table III (B)25

MINIMUM ECONOMICAL CONSUMPTIONS
AT 2000 RPM BOOST PRESSURE
(200 mm/Hg)

	gr/hp-hr		
Engine Type	By modification No. 1 (oct. No. 91)	By modification No. 2 (oct No. 87)	Ordinary Standard (oct. No.91&87)
Homare 20	210	220	205
Kasei 20	215	225	210
Sakae 30	210	220	205
Atsuta 30	220	225	215

It was evident from these data that with minimum economical consumption, the No. 1 and No. 2 gasoline showed a somewhat larger amount of consumption in gm/hp-hr than when ordinary standard fuel was used. The specific gravities, however, of these modified fuels were somewhat higher that the ordinary standard fuel as shown in the previous table; these had the same economical consumptions in liter/hp-hr. These performances were confirmed by flight tests of various airplanes, that is, Shiden, Raiden, Zero type fighter, and Suisei.

Starting and acceleration with these fuels were investigated during these flight tests. No particular test method was utilized in connection with the investigation; the flight tests began in October 1944 and were continued until May, 1945. Starting and acceleration at atmospheric temperature was examined. From these results, acceleration with No. 1 and No. 2 gasoline was satisfactory with the ordinary acceleration mechanisms in all atmospheric temperatures, but starting ability with No. 1 gasoline was unsatisfactory at atmospheric temperatures below 10°C, that is, winter daytime or very cold autumn mornings. Under these conditions engines could not be started easily.

The starting ability of No. 2 gasoline was not satisfactory at atmospheric temperatures below 20°C, that is , autumn daytime; and, in winter, when the temperature was below about 10°C, engines could not be started easily.

To avoid this, ordinary standard gasoline was used to help starting, and it was found afterwards that 5 liters for one airplane was enough. Engines with solid fuel injection systems, such as Kasei 20 type and Atsuta 30 type had no such starting troubles.

Lubricating oil dilutions by these fuels were also examined during these flight tests, and the 40 liters Zero-fighter lubricating oil tanks after 30 hours operation were investigated. Two or three liters of new oil was added after every few hours flight, and the entire oil was exchanged with new oil after 30 - 40 hours operation. Properties of the oil samples are as follows (from memory): (See Table IV (B)25)

ENCLOSURE (B)25

Table IV (B)25

PROPERTIES OF OIL SAMPLES

	No. 1 Gasoline	No. 2 Gasoline	Ordinary Standard Gasoline
Viscosity	118(S") Saybolt	110(S") Saybolt	Over 120(S") Saybolt
Ignition pt	95 °C	85 °C	over 80 °C
Dilution degree (weight)	0.8 - 1.0 %	1.2 - 1.4 %	0.4 - 0.6 %

From these data, the degree of oil dilution with gasoline No. 1 was somewhat larger that that of ordinary standard gasoline, and with gasoline No. 2 the dilution was very large and careful attention was required to use these gasolines without causing bearing trouble.

III. CONCLUSIONS

These flight tests were started in October 1943 and satisfactory results were obtained at the end of May 1944, at which time the naval specification of aviation gasoline was changed to the wartime specification.

ENCLOSURE (B) 26

UTILITY TESTS OF AVIATION GASOLINE WITH INCREASED TETRAETHYL LEAD CONTENT

by

Nav. Mech. Eng. Captain T. KONDO

Lt. Comdr. S. SOMA

Research Period: 1944-1945

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

December 1945

ENCLOSURE (B)26

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ENCLOSURE (B)26

SUMMARY

Practical engine tests were made, using aviation gasoline with 0.3(vol.)% of tetraethyl lead and 1.3 equivalents of ethylene dibromide added. This gasoline was sent from the First Naval Fuel Depot and tested on typical engines (i.e. SAKAE 20 type and HOMARE 20 type). It was found that aviation gasoline with 0.3 (vol.)% tetraethyl lead was not satisfactory for practical use, because the spark plugs in the engines were fouled and misfire was caused by this fuel after about 10-15 hours operation time. Otherwise, in the case of the usual tetraethyl lead content (i.e. 0.15%) misfire did not occur until after about 30 hours.

I. INTRODUCTION

A. History of Project

In order to obtain a larger amount of aviation fuel from a fixed quantity of base oil, the following investigations were made at the First Naval Fuel Depot.

(1) Extension of distillation range.
(2) Increase of final cut temperature, and
(3) Increase of tetraethyl lead content in gasoline to increase the octane number.

A trial sample with 0.3 vol.% tetraethyl lead and 1.3% equivalent ethylene dibromide added, was sent to the First Naval Technical Depot from the First Naval Fuel Depot, to determine whether this fuel was satisfactory for practical use or not.

Endurance tests with this sample were made on typical engines, but detailed and conclusive experimental data are not available, due to the lack of the above-mentioned aviation gasoline, and to the contamination of spark plugs by lubricating oil entering the combustion chamber.

B. Key Research Personnel Working on Project

Nav. Mech. Eng. Captain T. KONDO
Nav. Mech. Eng. Lt. Comdr. S. SOMA

From December 2, 1944 to February 2, 1945

II. DETAILED DESCRIPTIONS

A. Description of Test Apparatus and Sample

1. Engines: Sakae 20 type
Homare 20 type

2. The physical properties of fuel samples which were sent from the First Fuel Depot were as follows:

Density d_4^{20} 0.75-0.77
Distillation test
Initial drop ..... 60°C
10% pt. ..... 90°C
50% pt. ..... 115°C
90% pt. ..... 170°C
97% pt. ..... 180°C
Octane No.* 91

B. Test Procedures and Conditions

Outline of endurance test is as follows:

1. Sakae 20 Type (Spark plug Y_1R porcelain insulators)
(Spark plug Y_1H mica insulators)

Table I(B)26
TEST DATA

Terms of Test	Boost	Operating Time	hp	RPM
Rated hp test	+200mm/Hg (1st speed) +200mm/Hg (2nd speed)	5 minutes alt. 90 times	1100 950	2700 2700
Cruising test	−300mm/Hg (1st speed)	30 hours	400	2000
Take off test	+350mm/Hg (take off) −350mm/Hg (slow)	5 minutes alt. 60 times	1120	2700 600

2. Homare 21 type (spark plug Y_1H)

Boost Pressure ..... 350mm/Hg (1st speed)
Operating Time ..... 17 hrs.
Rated horse power 1900
RPM 3000

C. Experimental Results

Each spark plug was exchanged with new ones after 10-15 hours in the endurance test of both engines, because of contamination and misfire. The spark plugs were clogged with lead oxide adhering to the surface of the insulator surrounding the center pole. Aviation gasoline containing 0.3 vol.% tetraethyl lead showed the same engine performance compared with the same gasoline with the usual tetraethyl lead content. (i.e. 0.15%) Although in the case of the usual tetraethyl lead content gasoline contamination of lead upon the spark plugs was avoided by increasing the horse-power or the cylinder temperatures, it was very difficult to prevent contamination using the above-mentioned gasoline.

III. CONCLUSIONS

It was found that the fuel samples sent from the First Naval Fuel Depot were not satisfactory for practical use, because it was necessray to exchange the spark plugs at very short intervals, compared with the usual leaded gasoline (i.e. ½ hour). Experiments using aviation gasoline with 0.2 vol.% tetraethyl lead were also planned but were discontinued owing to the shortage of aviation gasoline in Japan.

*Content of tetraethyl lead 0.3 vol.%, content of ethylene dibromide 1.3 equivalent.

ENCLOSURE (B) 27

RESEARCH ON SUBSTITUTES FOR ETHYLENE DIBROMIDE

by

Chem. Eng. Lt. Comdr.,
H. HOSHIMIYA

Research Period: 1941 - 1942

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

December 1945

ENCLOSURE (B)27

SUMMARY

Butylene chloride is the most suitable substitute for ethylene dibromide, but when this substance is used, the plugs must be changed every 25 hours of engine operation.

I. INTRODUCTION

In 1941, it was one of the most urgent problems to seek substitutes for ethylene dibromide for the following reasons:

A. Dimunition of imported stock of ethyl fluid.
B. Decrease in production of bromine from salt brine liquor due to rainy weather in 1940 - 1941.
C. Delay in construction of bromine production plant from sea water.

The author selected chlorine compounds as substitutes for ethylene dibromide, because the resources of iodine and fluorine were also very meagre in Japan. Also, the patents of Ethyl Gasoline Corp. disclosed the use of chlorine compounds.

II. DETAILED DESCRIPTION

A. Laboratory Test

Mixtures of ten compounds were selected from the standpoint of mass production out of liquid chloride compounds. These ten chlorine compounds were substituted in the ethyl fluid on the basis of an equivalent amount of ethylene dibromide. Then each of these fluids in the concentration of 0.15% tetra ethyl lead was added to the regular gasoline. After burning these gasolines in the laboratory, the deposits of the burnt gas on a glass plate were examined by a microscope. The author selected for further study the compounds showing the most amorphous deposits, for example, butylene chloride or benzyl chloride.

B. Single Cylinder Engine Tests

By single cylinder engine test, the effects on the plug and lubricating oil were examined (in co-operation with Mech. Eng. Comm. N. SAITO) and the results were compared with ethylene bromide and ethylene chloride (the latter is one of the patented compounds of the Ethyl Gasoline Corp.). Butylene chloride was more desirable than benzyl chloride or ethylene chloride, both in regard to corrosion or sludge formation in the engine.

C. Full Scale Engine Test

Using a full scale engine ("Sakae" engine for combat planes) the following test data were obtained.

Ethylene Dibromide	more than 40 hrs	)
Butylene Dichloride	25 hrs$^{\phi}$	) until misfiring of
Ethylene Dichloride	17 hrs$^{\phi}$	) plug

$^{\phi}$Based on memory

ENCLOSURE (B)27

III. CONCLUSIONS

Butylene chloride is the most suitable substitute for ethylene dibromide, but when this substance is used the plugs must be changed every 25 hours (ca) of engine operation.

ENCLOSURE (B) 28

STUDIES ON A METHOD OF TESTING THE STABILITY OF ETHYL FLUID

By

CHEM. ENG. LT. COMDR.
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NAV. ENG.
G. ISHIDA

Research Period: 1941-1943

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

December 1945

ENCLOSURE (B)28

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ENCLOSURE (B)28

SUMMARY

Ethyl fluid is liable to decompose during storage, and form an amorphous deposit which not only lowers the antidetonating effect but also impairs the engine operation. Therefore, a method for testing the stability of ethyl fluid was tried. It was based on the determination of the turbidity nephelometrically (using a pair of the selenium photogalvanic cells) after exposing the sample to ultra violet rays having a constant intensity for a definite time. The stability tester was designed and constructed by the Tokyo Electric Co. on the basis of the above principle.

I. INTRODUCTION

Hitherto, many attempts were made to measure the stability of ethyl fluid by gravimetric or volumetric measurement of the precipitate or the gas formed by heat or sunlight. Accurate results were not obtained and the technique was troublesome. In 1941, Chem Eng. Capt., Dr. S. YAMAGUCHI and Nav. Eng. G. ISHIDA devised the above-mentioned method and the tester was constructed in 1943. It was then decided to adopt it as the authorized stability tester for ethyl fluid.

II. DETAILED DESCRIPTION

A. Apparatus and Procedure

The diagrammatic figure of the tester is shown in Figure 1(B)28. At first the intensity of the ultraviolet rays from the mercury lamp was adjusted by a chromium photocell through an iris, a shutter, a sample vessel, a shutter and a filter. The photocurrent of the chromium photocell was amplified and indicated by a microammeter. The sample vessel was made of silica. The filter served to match the characteristics of the mercury lamp and the chromium photocell. The intensity of the mercury lamp was checked by adjusting the rheostat of the electric source, and when the amplified photocurrent indicated 150 microamperes, the ultra violet rays were shut off, and 150cc of 0.1% tetraethyl lead solution in standard gasoline were placed in the silica vessel and exposed for exactly 15 minutes to the ultra violet rays. The turbidity formed in the sample caused by exposure to the ultra violet rays was determined by the absorption of visible rays from the chedked standard lamp. A pair of the selenium photogalvanic cells having the same characteristics were used, one of which was directly illuminated and the other was illuminated through the sample. The difference of the two photoelectromotive forces was determined potentiometrically using a galvanometer. The calibration of both selenium cells was carried out using a filter having a 10% absorption of rays, which was inserted in place of the sample vessel. The regulating dial of the potentiometer was set so that the galvanometer indicated 0 when the reading dial was at 10%. The stabilities of the samples were compared by the numbers on the reading dial of the potentiometer.

B. The Various Effects on Determination

1. Relation between the amount of the precipitate and the absorption of visible ray The amount of precipitate formed by exposure to ultra violet rays was measured gravimetrically after measuring the absorption of the visible rays. The result is shown in Figure 2(B)28. The absorption of rays is proportional to the amount of the precipitate within the limit of 10% absorption.

2. Effect of the temperature of the sample Figure 3(B)28 shows the effect of temperature on the formation of the turbidity. Though the effect of the temperature of the sample was small, it could not be neglected. The data indicates that for the temperature interval between 10°C and 30°C the error caused by the temperature difference was 10% of the determined absorption value.

3. Effect of time of exposure The absorption of rays through the sample was limited to 10%, since this represents the maximum absorption which can be measured. Fifteen minutes exposure of the sample to the ultra violet rays was found to be sufficient, since the final absorption was below 10% even in the case of the most unstable samples. As shown in Figure 4(B)28, 15 minutes exposure was suitable for the formation of the turbidity.

4. Effect of the constitution of the base gasoline A gasoline which is high in aromatics absorbs ultra violet rays more than a paraffine gasoline. A specially prepared standard gasoline "N - 1", was used as the base gasoline for these tests. The properties of "N - 1" gasoline are as follows:

Sp. gr. 15/4 ..... 0.7377

A.S.T.M. Distillation Characteristics

I.b.p. °C	38.5
10% p. °C	76.0
50% p. °C	106.0
90% p. °C	135.0
d.p. °C	158.0
t.d. %	98.0

Composition of Hydrocarbons (%)

Olefin	0.32
Aromatic	3.68
Naphthene	42.24
Paraffine	79.68

5. Effect of the change of absorption due to additives in ethyl fluid Ethylene dibromide, the stabilizers and the dyestuffs in ethyl fluid also absorb ultra violet rays and the absorption of visible rays changes on exposure. Though the change was small, the greatest error of this method is caused by this reason.

ENCLOSURE (B)28

Figure 1(B)28

DIAGRAMMATIC VIEW OF STABILITY TESTER

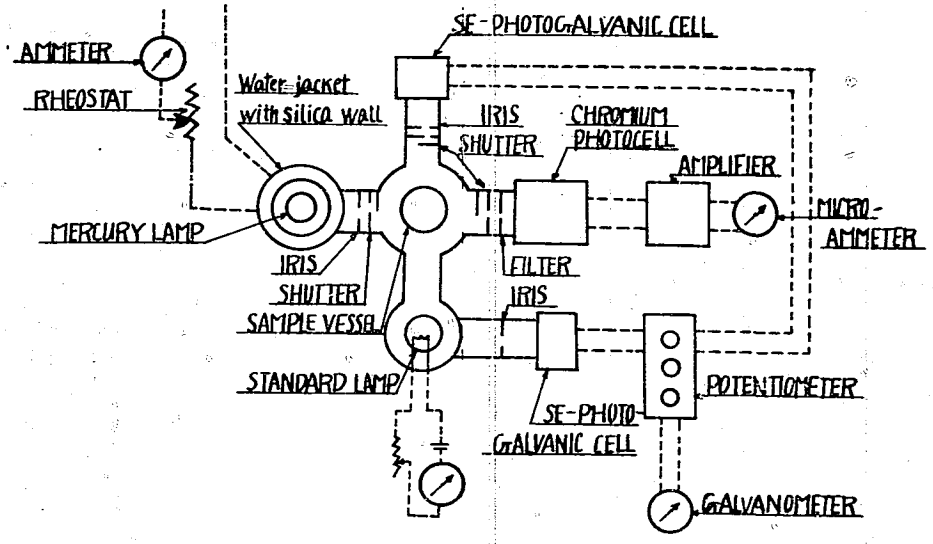
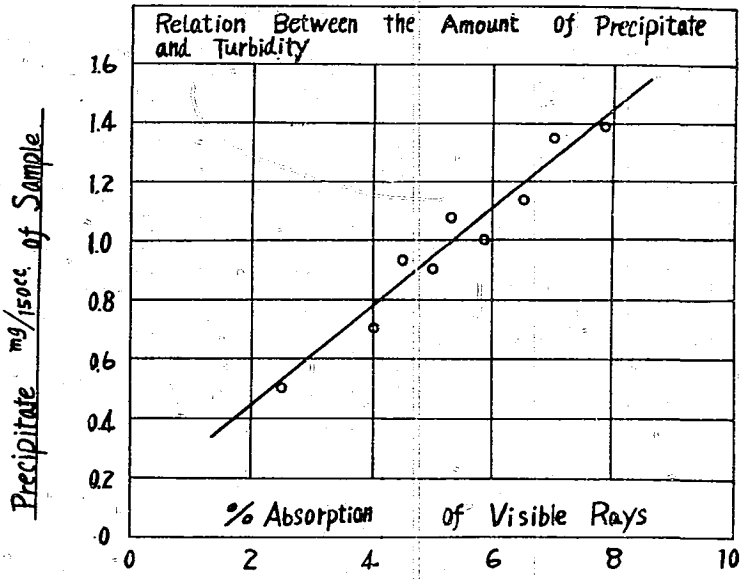


Figure 2(B)28

RELATION BETWEEN THE AMOUNT OF PRECIPITATE AND TURBIDITY



ENCLOSURE (B)28

Figure 3(B)28

RELATION BETWEEN THE FORMATION OF TURBIDITY AND THE TIME OF EXPOSURE

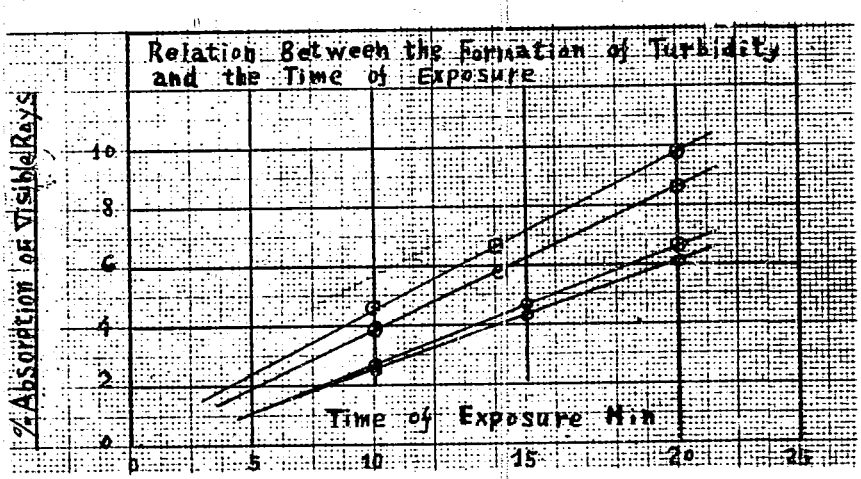
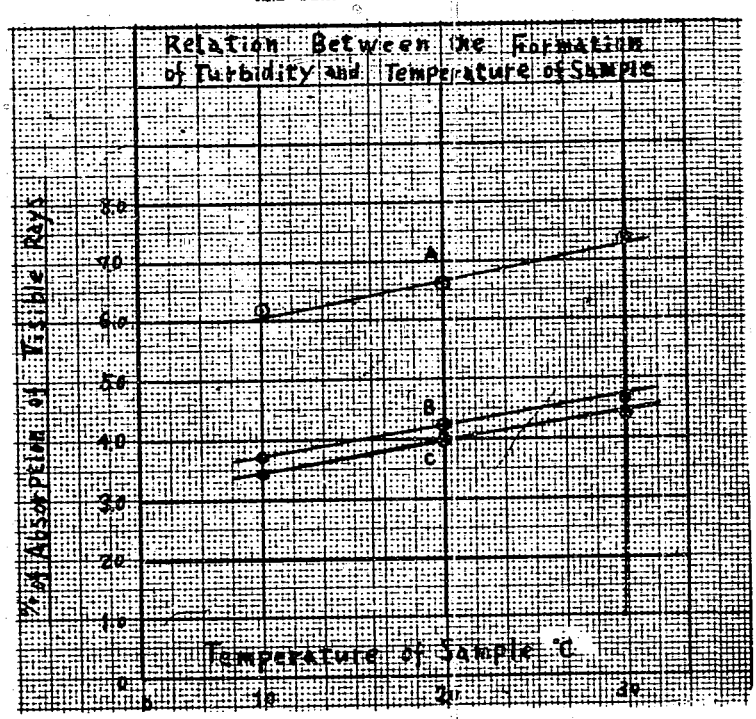


Figure 4(B)28

RELATION BETWEEN THE FORMATION OF TURBIDITY AND TEMPERATURE OF SAMPLE



ENCLOSURE (B) 29

RESEARCH ON ANTIDETONANTS OF THE ANILINE SERIES

By

CHEM. ENG. LT. COMDR.
H. HOSHIMIYA

Research Period: 1941-1942

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

December 1945

ENCLOSURE (B)29

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ENCLOSURE (B)29

SUMMARY

To obtain 91 octane rating gasoline from Sumatra crude oil, blending of aniline series antiknock agents was attempted. The most desirable agent was aniline itself, and each one percent of aniline-blended elevated the octane rating from 0.9-2.0. Nine defects of aniline could be avoided by the use of dopes.

I. INTRODUCTION

The octane rating of gasoline produced from Sumatra crude oil cannot reach 91 by adding only 0.15% of tetraethyl lead, the maximum amount of lead for practical use. Attempts were made to obtain 91 octane number aviation gasoline from Sumatra crude oil by the use of some aromatic-amines together with 0.15% of tetraethyl lead. Among all aromatic-amines tested, aniline was the most practical because of the abundance of the resources and the ease of production. Although a gasoline having 91 octane number was obtained by adding one to three percent of aniline and 0.15% of lead from Sumatra crude oil, the aniline-blended gasoline had many faults such as the deposits of residue on the walls of the supercharger and the piston head, the corrosive action on copper and iron, dissolving action on the paint of the oil-tight seams, and the cork float of the carburetor, the swelling action on rubber, and the fact that it was poisonous. Although most of these faults could be prevented by additives, some required the reconstruction of the fuel system of the aircraft. Therefore, the aniline-blended gasoline was not used practically in view of the difficulty of concession of the aircraft engines already in service.

II. DETAILED DESCRIPTION

A. On the Antiknocking Effect:

According to the extensive literature, aromatic-amines, in general, have a remarkable antiknocking effect. Among these aniline is the most practical because it is common. The characteristics of aromatic-amines as antidetonants are as follows.

1. They are effective when added in a concentration of several percent to gasoline.

2. They have an additive effect on gasolines containing tetraethyl lead.

3. They have some defects, among which are low solubility in gasoline and tendency to oxidize.

Many kinds of amines of aromatics and aliphatics were tested and the results are summarized below.

The comparison of the antiknock effect was done by the elevation of the octane number of gasoline to which was added one percent of amines. As shown below methyl aniline, xylidine, mesidine, diphenyl amine and n-methyl p-toluidine are more effective than aniline. However, aniline is the most practical.

Mines	Antiknocking Effect*
Aniline	2.65
p-Toluidine	3.88
1, 3-Xylidine	2.85

ENCLOSURE (B)29

Mines	Antiknocking Effect*
n-Methyl Aniline	3.2
n-Ethyl Aniline	1.6
p-Isopropyl Aniline	2.45
p-Tert. Butyl Aniline	2.20
n-Methyl α-Naphthyl Aniline	1.65
Benzal-p-Toluidine	0.2
Phenyl Hydrazine	-1.6
o-Anisidine	1.14
Phenyl Azide	-3.03
Mesidine	2.85
n-Diethyl Aniline	0.64
Diphenyl Amine	3.9
Methyl Anthranilate	1.15
n-Methyl Formanilide	2.65
n-Nitroso-i-Propyl Aniline	-0.25
2-Methyl Formanilide	-4.0
n-Propyl Amine	0.9
i-Propyl Amine	1.5
Triethyl Amine	0
n-Butyl Amine	0.3
t-Butyl Amine	0.8
Ethyl Amine	0.53
Diethyl Amine	1.30
Triethyl Amine	0.38
Triphenyl Amine	0.23
Diphenyl Ethyl Amine	1.53

*Octane Number Change-CFR (Motor Method)

Therefore, the antiknock effects of aniline on the various base fuels and pure hydrocarbons were measured. Generally, the antidetonant varies its effect with the constituents of the base fuels. (See Tables I(B)29 to IV(B)29.)

The variation of the antiknocking effect of aniline was measured by using several kinds of fuels. (Aniline was blended with the base fuels with 1.5 times by volume of n-butanol.) The properties of the fuels used are shown in Table I(B)29, and the antiknock effects of adding one, two, three, and five percent of aniline are shown in Table II(B)29. It seemed that the effect of aniline on hydrocarbons decreased with the order: normal paraffine, olefine, iso-paraffine and aromatic. Table III(B)29 and IV(B)29 show the increase of octane number of various fuels due to the addition of aniline together with tetraethyl lead.

B. Prevention of Separation of the Aniline Fuels:

The solubility of aniline in ordinary gasoline is about five percent at room temperature, and at low temperatures aniline separates in crystal form which may choke the fuel filter of the engine. The separation of in aniline-blended gasoline is prevented by the use of solvents of which normal butanol is the most effective.

C. Prevention of oxidation of aniline:

The effects of air, sun light, and its own impurities may cause the aniline to change colour. This colour change is due to the presence of aniline black.

One of the impurities which rapidly accelerates the discoloration of aniline is phenylene diamine. As the inhibitors of the oxidation of aniline, organic bases, phenol derivatives, ketones, aldehydes, azodyes, and their intermidiates, which have a reducing character, were tested. The results obtained were as follows:

No effect

Enantho-aldehyde	p-Dimethyl aminobenzaldehyde
Dephenyl amine	Dimethyl hydroquinone
Acetone	Tetraline
Pyridine	Diphenyl thiourea

Negative effect (Accelerators)

o-Nitrobenzaldehyde	α-Naphthylamine
Naphthol	Acetophenone
Diphenylmethane	Calcone

Positive effect

Salicylaldehyde	Quinoline
Paraldehyde	Amylsalicylate
Hydroquinone	

In general, aromatic aldehydes were effective, and benzal aniline was especially excellent in that when 0.1-2% for aniline was added, no discoloration occurred for a long period.

D. Problems in the Practical Use of Aniline:

1. After a performance of long duration in the engine using the three percent of aniline-blended gasoline, considerable black resinous matter was deposited on the parts of the supercharger, inlet pipe, piston ring and piston head.

But when the sludge content was less than 10 mg per 100cc in aniline-blended gasoline, it could be used for more than 50 hrs., especially when benzal aniline was added.

2. Corrosion and deposits of copper metal were both avoided by addition of dipiperidyl or thiourea, 0.1% or 0.01% respectively.

3. Oiltight paints of riveted fuel tank were dissolved especially acryl resin series, but this trouble was also avoided by replacing with acrylnitryl resin type paint.

4. Nitrocellulose paint on the coak float in the carburettor of the engine was also dissolved, but this was prevented by the use of acetyl cellulose paint.

5. Natural rubber was swelled by the aniline-blended gasoline, but synthetic rubber (Buna N) was not.

6. Poisonous effect of aniline vapor. In the aeroplane neither the vapour nor the exhaust gas of the blended gasoline were poisonous and only those engaged in blending aniline with gasoline had to take precautions.

Inspection for aniline vapour was accomplished by use of the indophenol reaction.

III. CONCLUSIONS

A. The most desirable antiknock agent of the aniline series is aniline itself.

B. For every one percent of aniline added, the octane rating of Sumatra gasolines was improved 0.9-2.0 numbers.

C. Several defects of aniline-blended gasoline were avoided, and it was suitable for practical use even in combat planes. However, its solvent action for paints made its storage in riveted tanks on aircraft carriers difficult. Also, the fumes from aniline would be objectionable aboard ship.

Figure 1(B)29

CLOSE UP VIEW OF THE EXPERIMENTAL APPARATUS FOR TETRA-ETHYL-LEAD

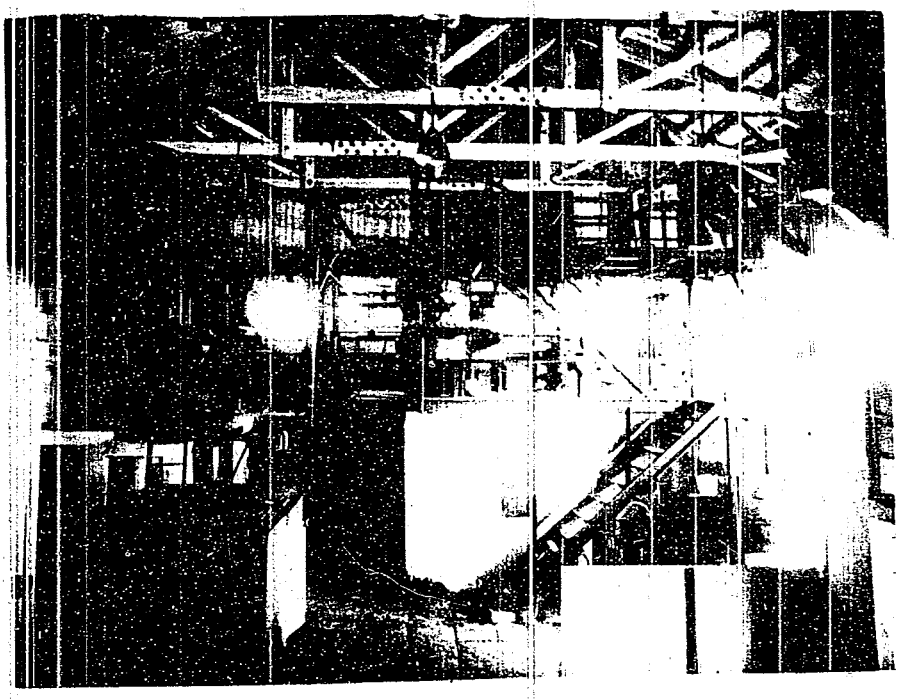

TABLE I(B)29

PROPERTIES OF THE BASE FUELS AND THE SAMPLES USED

		Sub-Standard		Soesoe		Talangimar*	Pendopo*	Mangunjya*	Sanga-Sanga (Borneo)	California	Midway Crude		
		I	II	I*	II						Catalytic Cracking	Thermal Cracking	Hydro-Cracking
Oct. No. (Plain		74.6	61.3	67.1	64.1	66.3	69.6	64.5	71.7	73.8		63.4	60.3
Oct. No. 0.1% Leaded		91	83.8	86.7	85.0	87.1 (0.125 Pb)	89.2	86.4 (0.125 Pb)	91.2	87.2	91	75.8	82.4
Sp. Gr. (15/4)		0.7368		0.7220	0.7402	0.7458	0.7233	0.7448	0.7588	0.7418	0.7448	0.7470	0.7647
Vapour Pressure		0.43	0.36	0.33	0.27	0.48	0.55		0.33			0.32	
Distillation Characteristics	10%	79	76	73	80	67	61	75	80	70	67	78	80
	50%	105	98	95	111	108	91	103	103	106	102	128	154
	90%	134	141	116	139	145	116	141	125	136	126	163	216
	97%	153	169	130	149	159	129		135	152		183	
Constituents of Hydrocarbons	Unsat.	1.2	0.1	0.8	2.0	1.1	0.6	0.5	0.5	0.4	10.3	5.8	1.0
	Arom.	4.7	5.9	10.4	14.1	12.9	13.3	13.7	27.4	9.5	14.3	26.3	9.1
	Napht.	45.2	34.4	30.2	21.7	26.8	36.2	34.3	31.0	40.0	34.3	2.0	26.1
	Paraf.	48.9	59.6	58.6	62.2	59.2	49.9	51.5	41.1	50.1	38.1	65.9	63.8

		Aniline	Butanol	n-Heptane	i-Octane	Methyl Pentane	Toluene	
	Sp. Gr. (15/4)	1.0250	0.8140	0.6838 (20/4)	0.6918 (20/4)	0.8802	0.8740	
	B. P. (°C)	118~119/100mm	1115.5~117	98.5	99.9	54~56	105~109	
	R. I. n_D^{20}	1.5863	1.3972	1.3879	1.3916			

*Sumatra Gasoline

ENCLOSURE (B)29

TABLE II(B)29

EFFECT OF ANILINE ON THE VARIOUS HYDROCARBONS PLUS 0.1% T.E.L.

Blended Hydrocarbon					
Aniline Added (% Br Vol.)	Octane No. (CFR Motor Method)	30% of n-Heptane	30% of i-Octane	30% of 2-Methyl Pentane	30% of Toluene
0	83.8	79.4	93.5	88.2	92.1
1	85.9	82.6	94.8	90.1	93.3
2	87.8	85.4	95.5	90.6	93.6
3	89.8	86.7	96.0	91.4	93.8
5	92.2	89.7	96.8	92.5	94.0
Mean effect of 1% Aniline	1.95	2.62	0.80	1.71	0.70
	Sub Reference Fuel Only	70%	70%	70%	70%

TABLE III(B)29

EFFECT OF ANILINE ON LEADED SOESOE GASOLINE (SUMATRA)

	% of Lead					
	I			II		
% of Aniline	0.10%	0.15%	0.20%	0.10%	0.15%	0.20%
0	85.0	86.7	87.8	86.7	89.1	90.8
1	86.3	88.9	89.5	88.5	91.1	93.3
2	87.7	89.8	90.6	90.4	92.8	94.5
3	88.5	90.9	91.3	91.4	93.3	95.3
5		92.0				
Mean Effect by 1%	1.27	1.72	1.42	1.85	1.75	1.95

TABLE IV(B)29

MEAN EFFECT PER ONE PERCENT OF ANILINE BY VOLUME ON LEADED GASOLINE

	Base Gas				
	Soesoe				
Leaded (% Br Vol.)	I	II	Talangimar	Pendopo	Mangunjya
0.10%	1.27	1.85	1.40	0.91	2.05
0.15%	1.42	1.95		0.78	1.90

	Base Gas				
			Cracked Gasoline		
Leaded	Sanga-sanga	Cali-fornia	Catalytic	Thermal	Hydrogen-ated Gas
0.10%	0.97	1.00	0.93	2.24	
0.15%	0.88			2.40	1.57

ENCLOSURE (B) 30

RESEARCH ON ANTIDETONANTS OF THE SELENIUM SERIES

(APPENDIX TO RESEARCH ON THE ANTIDETONANTS OF ANILINE SERIES)

by

Chem. Eng. Lt. Comdr. H. HOSHIMIYA

Research Period: 1937 - 1939

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

December 1945

ENCLOSURE (B)30

LIST OF TABLES AND ILLUSTRATIONS

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Table II(B)30 Mean Effects of Se-Compounds ..... Page 370

Table III(B)30 Results of Single Cylinder Engine Test ..... Page 371

Plate I(B)30 Flow Sheet of Di-Ethyl Selenide Pilot Plant

ENCLOSURE (B)30

SUMMARY

To obtain ultra high octane fuel (higher than 100 Octane), the research on the antidetonating compounds of selenium series was attempted. The most desirable agent was diethyl selenide, and, adding it to Stanavo 100 octane fuel (0.8% by volume), 112 Octane rating gasoline was obtained and the horse power was increased about 15%. But it was not used, except perhaps as a take-off fuel, because the availability of Selenium in Japan was meagre.

I. INTRODUCTION

This work was begun in 1937 and finished in 1939. By the use of ultrahigh octane fuel to obtain the maximum horse power with the engines already in service several antiknocking agents were blended in 100 octane fuel. (for example selenium, aniline, or oxo-compounds.) Of these compounds, the selenium series were better than any other compounds because these compounds were effective even in leaded gasoline. The synthesis of several compounds of selenium series were undertaken. When added to leaded gasoline, very high octane fuels were obtained. One of these compounds, diethyl selenide, was blended 0.8% by volume in 100 Octane rating gasoline and tested in a single cylinder and a full scale engine.

II. DETAILED DESCRIPTION

A. Synthesis of Selenium Alkyl Compounds

Five selenium compounds were prepared by the following methods.

1. Dimethyl selenide

Yield obtained was 59% of theoretical in a 3 liter flask. Optimum Conditions: reaction temp. 50-56°, reaction time 2 hrs by following chemical equation:

$$10CH_3KSO_4 + P_2Se_5 + 16NaOH = 5(CH_3)_2Se + 10KNaSO_4 + 2Na_3PO_4 + 8H_3O$$

2. Diethyl selenide

Yield obtained was at max. 87% of theoretical in a lead-lined 50 liter vessel. Flow diagram is shown in Plate I(B)30. Optimum conditions: Reaction temp. 75-80°C, reaction time 6.5 hrs.

$$10C_2H_5NaSO_4 + P_2Se_5 + 16NaOH = 5(C_2H_5)_2Se + 10Na_2SO_4 + 2Na_3PO_4 + 8H_2O$$

3. Diisopropyl selenide

Yield obtained was 48% of theoretical in a 3 liter glass flask. Optimum conditions: reaction temp., 70 - 75°C; reaction time, 3 hrs.

4. Dinormal-propyl selenide

Almost the same as diisopropyl selenide.

5. Diethyl diselenide

It was prepared from the residue of diethyl selenide.

ENCLOSURE (B)30

B. Properties of Selenium Alkyl Compounds

Table I(B)30

PROPERTIES OF SELENIUM ALKYL COMPOUNDS

	B.P.(°C)	n_D^{15}	Sp.gr $\frac{15^\circ}{4^\circ}$	Poisonous	odor
Dimethyl Selenide	58.5-59.0°	1.4915	1.4041	No, if in pure state	good
Diethyl Selenide	109.5	1.4833	1.2304		
Dinormal propyl Selenide	154-155	1.4795	1.1481		
Diisopropyl Selenide	150-151	1.4801	1.1570		
Diethyl diselenide	160-188	1.5725	1.6252	Very*	bad

*(4 times as poisnous as tetra ethyl lead)

Purification Method: Diethyl selenide was purified by repeated rectification, usually about 3 times. Length of the rectification tower was about 100cm and filled with active carbon and Raschig rings of glass.

C. Antiknock Properties

Antiknock effect of these Se-compounds in relation to hydrocarbon types was in the following order:

Leaded Case: Aromatics (Best) > Olefines > Paraffins > Napththenes (Poorest)

Unleaded Case: Paraffins (Best) > Aromatics > Naphthenes > Olefines (Poorest)

Mean effects of these Se-Compounds were as shown in table II(B)30.

Table II(B)30

MEAN EFFECTS OF Se-COMPOUNDS
(Data shows the increase in octane number)

	Blended Volume				
	0.05mol/L		0.08mol/L		
	Unleaded	Leaded	Unleaded	Leaded	Mean Value
Dimethyl Selenide	6.6	-1.3	9.3	3.5	4.525
Diethyl Selenide	8.1	-0.2	10.8	2.5	5.300
Diisopropyl Selenide	10.3	+3.5	10.6	4.7	7.275
Dinormal-propyl Selenide	7.5	-0.5	8.0	0.5	3.875
Diethyl diselenide	12.2	+4.1	15.8	8.0	10.250

D. Reaction Mechanism of The Decomposition of Diethyl Selenide

Diethyl selenide decomposes at high temperature. It begins to decompose at 250°C and gradually the decomposition becomes more severe. The stages of decomposition are shown by the following chemical formulae:

$$300^{\circ}\text{-}350^{\circ}\ (C_2H_5)_2Se = H_2Se + 2C_2H_4^{*}$$

$$400 - 450^{\circ}\ \text{and then}\ (C_2H_5)_2Se \longrightarrow 2C_2H_5 + Se$$

$$\longrightarrow Se + C_2H_4 + C_2H_6$$

*350-450°, also occurs-$H_2Se \longrightarrow H_2 + Se$

E. Engine Performance Tests

Engine Performance tests were conducted with these compounds blended with gasoline. Example: Stanavo 100 O.N. aviation gasoline, with 0.8% by vol. Diethyl selenide added, was tested in a single cylinder engine (Kinsei Engine). The results were as shown in Table III(B)30.

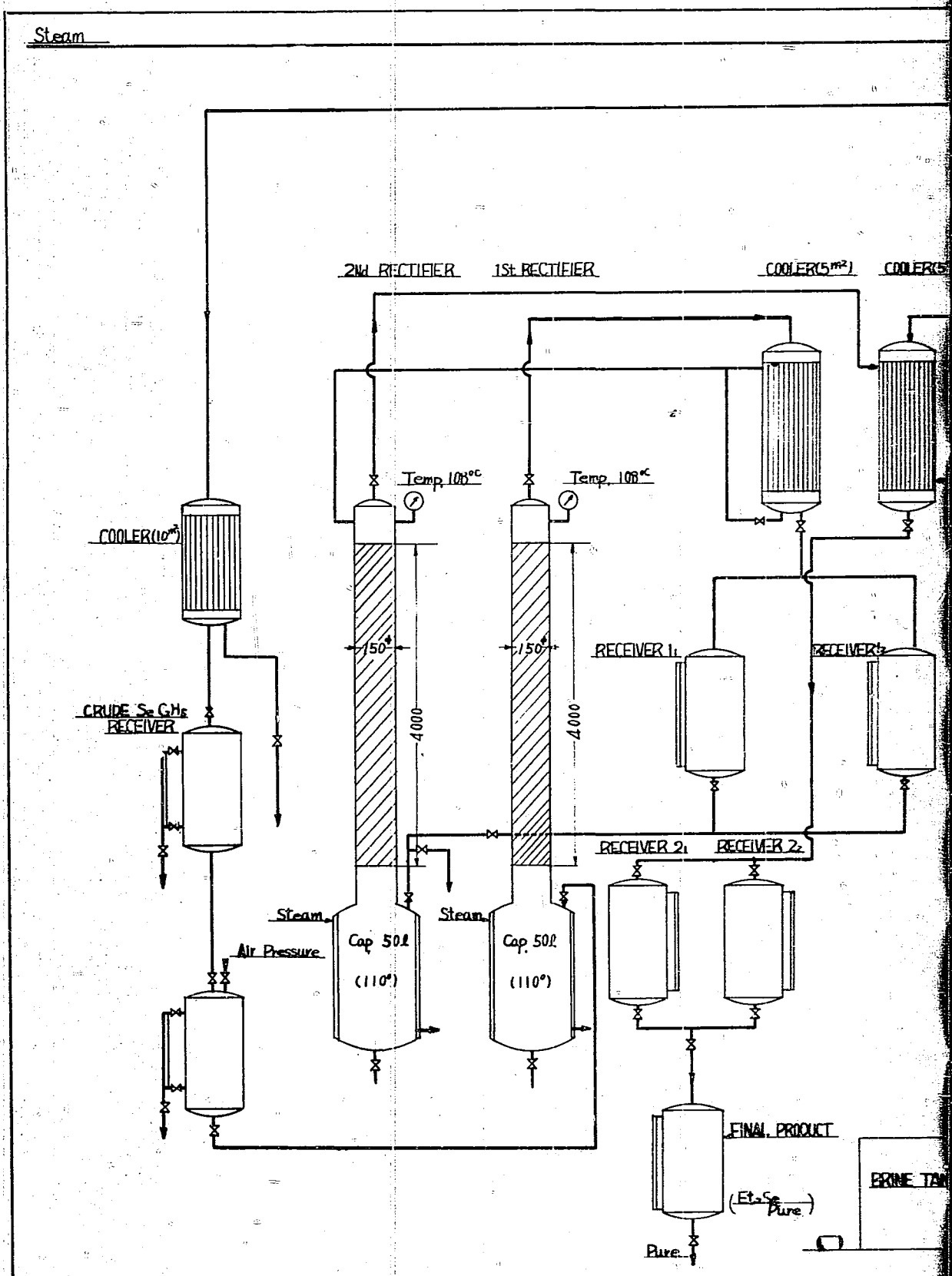
RESULTS OF SINGLE CYLINDER ENGINE TEST

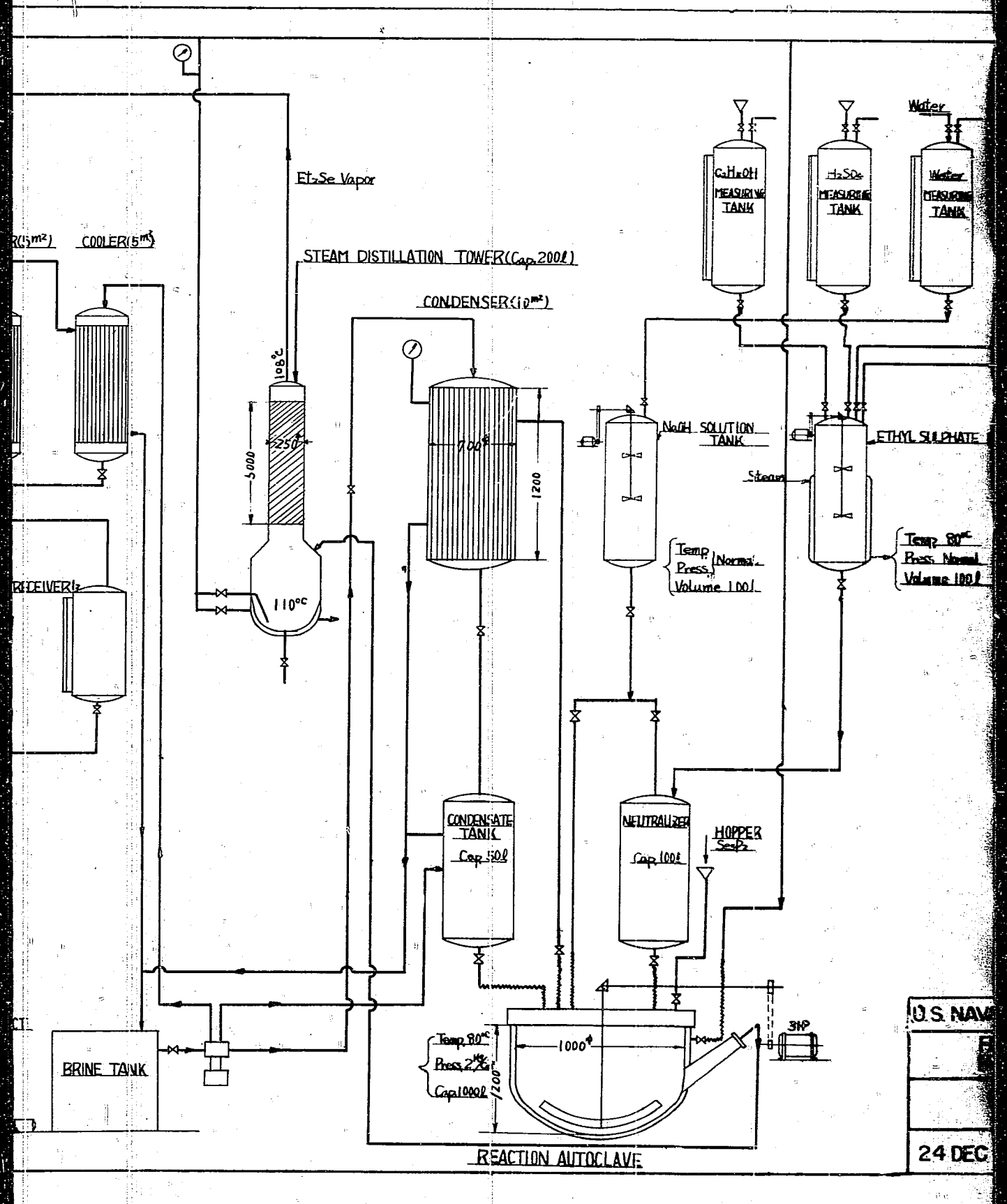
Table III(B)30

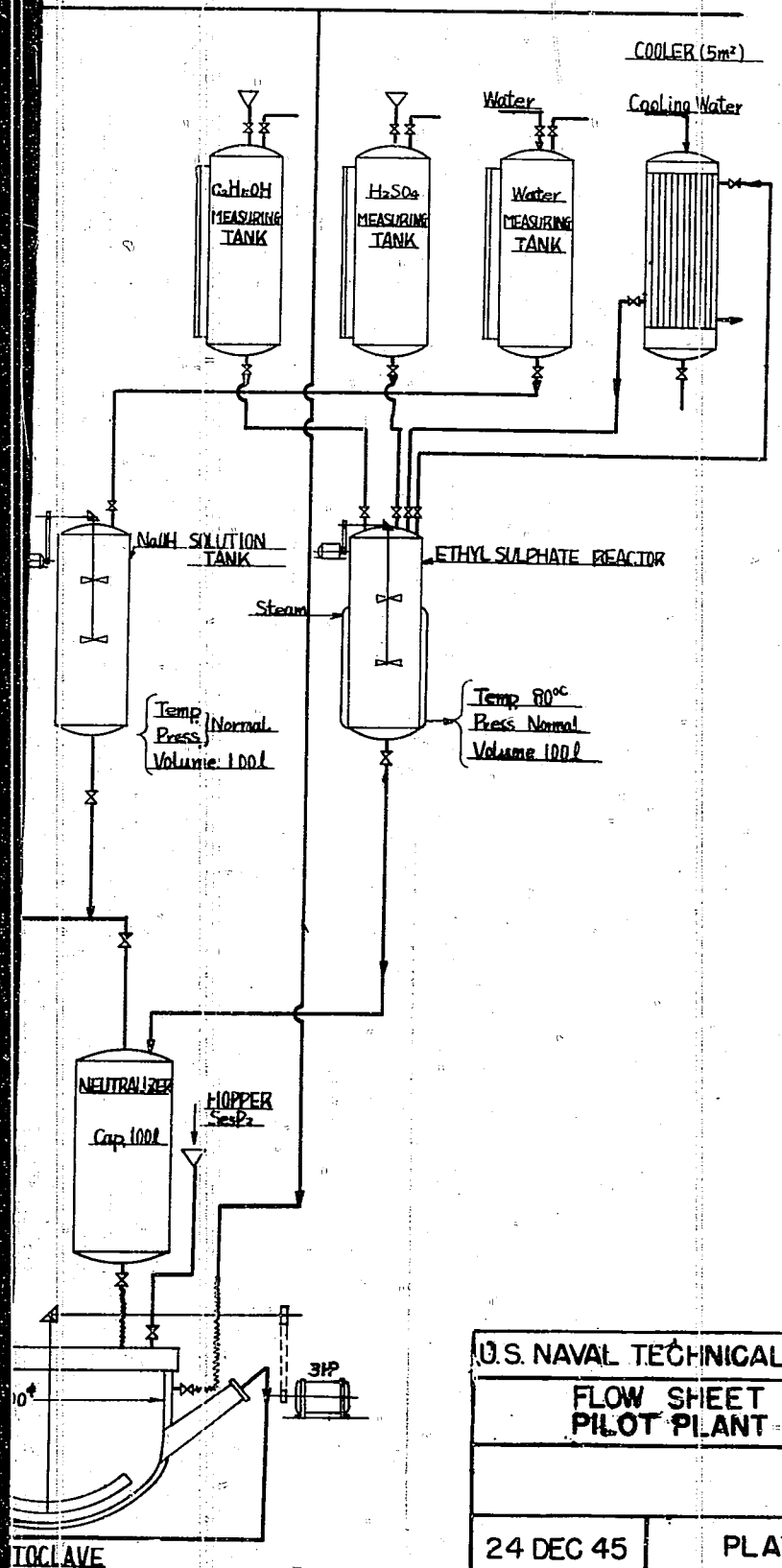
	RPM	Boost press. (mm hg)	hp	Fuel Consumption (lit/hr)	Temp. of Exhaust gas (°C)	Temp. of Cylinder wall (°C)
Stanavo Aviation Gasoline. (O.N. 100.8) only	2000	0	44.6	15.89	829	235
	2010	100	33.8	17.60	835	250
	2000	200	58.2	18.70	835	276
	2000	300 (limit)	61.4	19.88	879	289
Same gasoline with 0.8% by vol. $(C_2H_5)_2Se$ added (O.N. 112)	2000	0	45.2	15.51	830	245
	1980	100	52.9	17.12	840	260
	2010	200	59.0	18.70	850	275
	2000	300	65.0	20.68	851	289
	1980	370	67.6	21.95	850	305
	2000	430	72.0	22.50	850	310

III. CONCLUSIONS

The effect of antiknock compounds of the selenium series was additive to Tetraethyl lead and suitable as a blending agent to provide fuel having octane ratings above 100. But the use of this compound was limited to take-off purposes only by the low selenium resources in Japan.


Steam
2Nd RECTIFIER
1St RECTIFIER
COOLER(5m²)
COOLER(5
Temp. 105°C
Temp. 108°C
COOLER(10m²)
150φ
150φ
4000
4000
RECEIVER 1₁
RECEIVER 1₂
CRUDE Se C₂H₅
RECEIVER
RECEIVER 2₁
RECEIVER 2₂
Steam
Steam
Air Pressure
Cap. 50ℓ
(110°)
Cap. 50ℓ
(110°)
FINAL PRODUCT
(Et₂Se Pure)
Pure
BRINE TAN


Et₂Se Vapor
STEAM DISTILLATION TOWER(Cap.200ℓ)
CONDENSER(10m²)
COOLER(5m²)
108°C
250φ
3000
110°C
700φ
1200
C₂H₅OH MEASURING TANK
H₂SO₄ MEASURING TANK
Water
Water MEASURING TANK
NaOH SOLUTION TANK
ETHYL SULPHATE
Steam
Temp.
Press.
Volume 100ℓ
Normal
Temp. 80°C
Press. Normal
Volume 100ℓ
CONDENSATE TANK
Cap. 50ℓ
NEUTRALIZER
Cap. 100ℓ
HOPPER
Se₂P₂
BRINE TANK
Temp. 80°C
Press. 2 Kg/cm²
Cap. 1000ℓ
1200
1000φ
3HP
REACTION AUTOCLAVE
U.S. NAV
24 DEC



U.S. NAVAL TECHNICAL MISSION TO JAPAN	RESTRICTED
FLOW SHEET OF DI-ETHYL SELENIDE PILOT PLANT	
24 DEC 45	PLATE I (B) 30	X-38(N)-2

ENCLOSURE (B) 31

RESEARCH ON OXYGEN COMPOUNDS AS ANTIDETONANTS

by

CHEM. ENG. LIEUT. COMDR. D. HOSHIMIYA

Research Period: 1937-1938

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

Dec. 1945

ENCLOSURE (B)31

LIST OF TABLES AND ILLUSTRATIONS

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Table II(B)31 Effect of Blending ..... Page 376

ENCLOSURE (B)31

SUMMARY

To obtain a substitute for isooctane the use of oxygen compounds was investigated.

Ketones and ethers were better than several other oxygen compounds. By the C.F.R. test engine 100 octane rating fuel was obtained from 91 octane number gasoline as follows:

Pynacoline (vol.%) 17.5

Isopropyl Ether (vol.%) 20

2-Methyl Pentanone (vol.%) 26

Isooctane (vol.%) 45

But by the full scale engine test it was discovered that the antiknock properties of the oxygen compounds were depreciated under full power conditions of operation.

I. INTRODUCTION

Isooctane as the blending fuel for 100 octane rating gasoline was very searce in Japan. Therefore the author selected the oxygen compounds as the substitute of isooctane, and tested them by the use of C.F.R. engine only. The relation of the combination of oxygen to another group and the antiknock properties was tested. Among them ketone and ether groups were preferable, but by full scale engine tests it was discovered that these compounds were deficient in anti-knock quality.

II. DETAILED DESCRIPTION

All data are given in Table I (B)31. From that table it was concluded that;

$$R_2CO > R_2O > ROH$$

$$RCHO > ROH$$

(Among the corresponding compounds)

These compounds were blended in 91 octane gasoline and 100 O.N. gasoline was obtained as shown in Table II (B)31.

III. CONCLUSION

Ketones and ethers were better than the other several oxygen compounds. These substances were necessary for producing 100 octane rating gasoline from 91 octane number fuel as follows:

Pynacoline (Vol.%) 17.5

Isopropyl Ether (Vol.%) 20

2-Methyl Pentanone (Vol.%) 26

of Isooctane (Vol.%) 45

But by the full scale engine test it was discovered that the oxygen compounds were depreciated in antiknock properties at full power performance. Full scale engine test detailed data are not available.

ENCLOSURE (B)31

Table I(B)31
BASE FUEL: TALANGIMAR GASOLINE
(Pb 0.1% 86.7, 0.15% 89.9)

Compounds	Physical Properties			Antiknock Properties*			
	Sp. Gr. 150/4°	B.P. °C	N_D^{20}	Pb. 0.1% 20% Added (Vol.)	Pb. 0.15% 10% Added (Vol.)	Sum of Difference	Compare
Acetone	0.7940	55-58	-	91.2	91.0	2.6	V
Iso-Propyl Alcohol	0.7964	81-90	-	89.8	89.8		
Methyl Ethyl Ketone	0.8080	76-91	1.3800	93.5	91.9	8.2	V
Sec. Butyl Alcohol	0.8095	96-103	1.3968	88.5	88.7		
Pynacoline	0.8104	99.1-115	1.3980	93.9	91.8	6.4	V
Pynacolyl Alcohol	0.8205	111.5-122	1.4148	89.3	90.0		
2-Methyl Pentanone	0.8032	104-117	-	97.2	91.5	11.3	V
2-Methyl Pentanol	-	127-130	-	88.5	88.9		
n-Heptanone	-	138-143	-	90.7	93.2	7.1	V
n-Heptanol	0.8260	145-155	-	87.1	89.7		
n-Butyl Aldehyde	0.8210	115-116	-	-	90.6	1.8	V
n-Buthanol	0.8140	115-116.5	-	-	88.8		
Isopropyl Alcohol	0.7962	81-82.2	1.3778	-	90.9	3.6	^
Isopropyl Ether	0.6312	63-73.4	1.3718	-	94.5		

Table II(B)31
EFFECT OF BLENDING

	100 O.N. from 91 O.N.		100 O.N. from 87 O.N.	
	Aniline Not Used (Vol. %)	Aniline 3% Also Added (Vol. %)	Aniline Not Used (Vol. %)	Aniline 3% Also Added (Vol. %)
Pynacoline	17.5	13	29	17
Isopropyl Ether	20	0	28	18.5
2-Methyl Pentanone	26	8	39	19.5
of Isooctane	45	4	over 50	40

ENCLOSURE (B) 32

STUDIES ON THE INFLUENCE OF MOISTURE ON OCTANE VALUES

by

Chem. Eng. Lieut.
Masuo UEHARA

Research Period: 1942-1943

Translated for and Reviewed with Author by the
U.S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)32

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Figure 2(B)32 Hygrometer ..... Page 381

Figure 3(B)32 Absolute Humidity g m^3 ..... Page 386

ENCLOSURE (B)32

SUMMARY

Studying the influence of atmospheric moisture on octane value of gasoline with tetra ethyl lead, we derived the correcting formula as follows:

$$\triangle N = M^a - b$$

Where $\triangle N$ is Increase of octane value from that of gasoline in the air containing 5gm water in cubic meter dry air.

M is Humidity of air represented by gm water per cubic meter dry air.

a,b are Constants, and when the percentage of tetra ethyl lead added is between 0.07% and 0.1% to gasoline, a is 0.4505 and b is 2.065.

I. INTRODUCTION

A. History of Project.

The octane value of the same gasoline was noticed to be different in summer and winter , and this was considered to be effected by the atmospheric moisture.

Previously, J.R. MacGregor had discussed the same subject in S.A.E. Journal Vol. 40, No. 6 and the writer came to the conclusion that the moisture of air has an influence on the octane value of leaded gasoline, and, therefore, the present study has been carried out to get the correcting formula.

Date of the beginning: June 1942
Date of conclusion: June 1943

II. DETAILED DESCRIPTION

A. Description of Test Apparatus.

1. Humidity controller: The apparatus shown in Fig. 1(B)32 was used in the experiment, (1) and (3) are 0.16 m^3 cylindrical tanks which are enclosed in wood casings, the space between being filled with wool.

Cylinder (1) is filled with cracked ice and cylinder (3) serves as surge chamber.

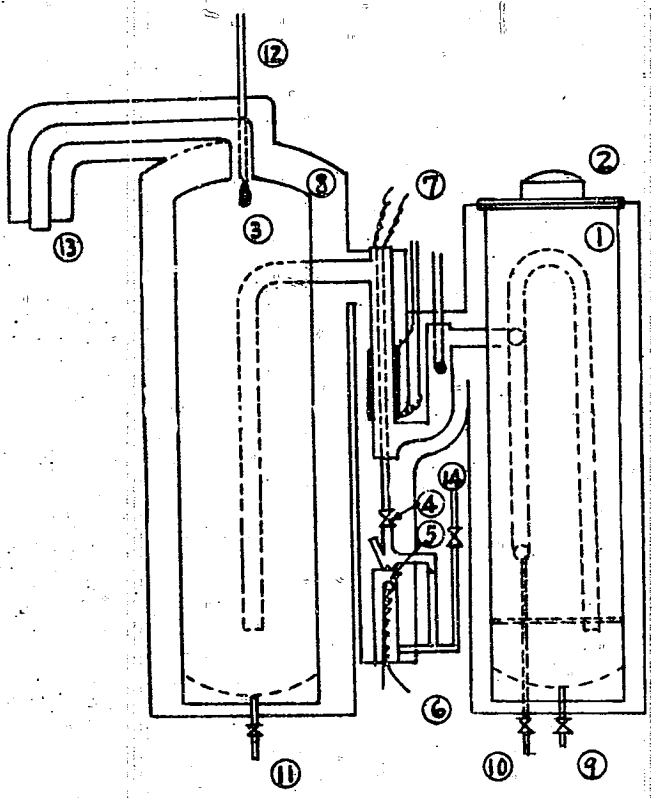
Intake air heater, (8) and steam generater, (6) are installed in the pipe between the cylinders (1) and (3).

2. Engine hygrometer: The units shown in Fig. 2(B)32 was used and was recognized as satisfactory in the reports of MacGregor.

Also, it was found that the hygrometer, Fig. 2(B)32, was practically perfect from our preliminary examinations. The wick surrounding the

ENCLOSURE (B)32

Humidity Controller
FIG. A



(1) Ice chamber
(2) Air inlet
(3) Surge chamber
(4) Valve (Steam controller)
(5) Steam generator
(6) Electric heater for steam generator
(7) Intake air heater
(8) Insulater
(9), (10), (11) Drain cock
(12) Thermometer
(13) Air outlet to engine
(14) Water bottle

Figure 1(B)32
HUMIDITY CONTROLLER

ENCLOSURE (B)32

Hygrometer

FIG. B

① Silencer
② Water bottle
③ Handle for Water feeding
④ Wet bulb thermometer
⑤ Dry bulb thermometer

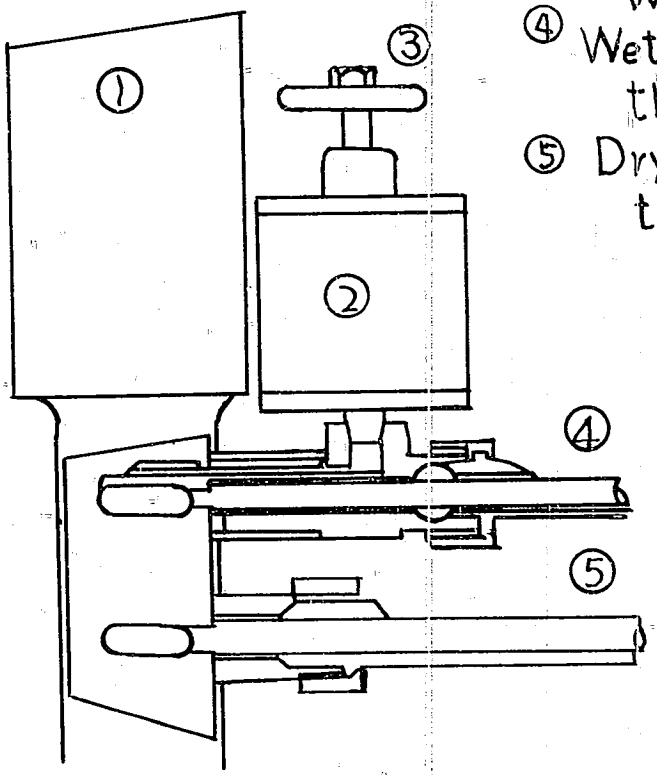


Figure 2(B)32
HYGROMETER

wet bulb is moistened continuously by water supplied from water bottle (2). The water is conducted from the bottle through a small tube projecting into the air stream, and displaced slightly by the thermometer bulb. The projecting portion of this tube has several small holes drilled radically through it to permit the escape of water at various points.

3. Determination of knocking: The engine we used was C.F.R. engine, made in U.S.A.

B. Description of Test Procedure.

1. Samples: The samples which were used for the experiment are in table A.

Table I(B)32
TEST SAMPLES

Sample	Source	Paraffinic H.C.	Aromatic H.C.	Unsaturated H.C.	Naphthenic H.C.
K - I	Straight run (Bahrein)	79.68	6.62	1.16	12.54
S - I	K-I 80 I.O 20	84.40	5.72	0.92	9.00
S - II	K-I 60 I.O 40	88.55	5.82	0.65	4.98
S - III	K-I 25 I.O 75	92.16	4.23	0.48	3.12
Commercial Iso-octane		95.50	3.98	0.52	0
S - IV	K-I 80 Benz 20	63.74	25.29	0.92	10.03
S - V	K-I 52 Benz 48	41.43	51.44	0.60	6.52
S - VI	K-I 30 Benz 70	23.90	71.98	0.34	3.76
Benzol	Chemical pure	0	100	0	0
N - I	Straight run (Oha)	53.76	3.68	0.32	42.24
Catalytic Cracked Fuel		41.16	12.33	3.68	42.80

Standard fuel was Normal Heptane and commercial Iso-octane, Octane No. 99.3 which, it was found, could be used the same as Iso-octane.

ENCLOSURE (B)32

2. Experimental procedure: The octane value of the samples were determined by the C.F.R. Motor method under that condition in which the moisture of engine intake air was controlled by the apparatus shown Fig. 1(B)32.

C. Experimental Results.

Table II(B)32
OCTANE VALUE OF PARAFFINIC FUEL
(T.E.L. : Tetra Ethyl Lead, added)

Sample	T.E.L. (%)	Absolute Humidity (g/m^3)	Octane No.
K - I	0.00	7.0	42.6
		12.0	42.6
		25.0	42.6
	0.01	5.6	46.6
		18.2	46.8
		29.0	46.9
	0.03	5.6	54.0
		18.6	55.1
		19.8	55.5
		29.2	56.4
	0.05	5.4	60.0
		14.1	61.5
		22.4	61.8
		31.8	63.0
	0.07	5.9	64.7
		13.1	66.2
		18.2	66.8
		32.5	67.1
	0.10	6.0	69.0
		12.5	70.0
		24.0	71.5
	0.20	6.5	72.0
		11.7	73.5
		16.8	73.8
		25.1	75.2
		33.3	75.7
S - I	0.00	5.3	56.5
		17.5	56.8
		29.3	56.7
	0.05	8.5	75.7
		19.1	76.7
		29.3	77.8
	0.10	6.0	79.4
		7.5	79.8
		17.0	80.8
		21.4	81.5
		32.2	81.4
		33.0	82.6
	0.20	6.0	83.4
		11.3	84.6
		17.6	85.3
		28.5	86.6
S - II	0	6.0	73.5
		20.8	73.4
		32.5	73.7
		34.5	73.5
	0.05	7.5	86.0
		19.5	87.2
		29.0	88.0
	0.10	5.5	91.5
		14.0	93.0
		21.0	93.2
		27.5	93.7
		30.5	93.8
	0.20	6.0	96.4
		25.0	99.0
		40.0	100.7
S - III	0	5.5	86.8
		12.8	87.0
		14.1	87.0
		25.9	87.0
	0.01	6.9	91.0
		9.0	91.2
		19.8	91.8
		28.7	92.4
	0.02	5.5	95.5
		18.8	96.9
		32.0	97.5
	0.05	5.8	99.8
		19.6	101.7
		29.7	102.2

ENCLOSURE (B)32

Table III(B)32
OCTANE VALUE OF AROMATIC FUEL

Sample	T.E.L. (%)	Absolute Humidity (g m^3)	Octane No.
S - IV	0	5.6 6.4 16.2 18.1 27.4	49.8 49.7 49.6 50.0 50.0
	0.02	7.4 17.8 24.3	61.0 61.3 61.9
	0.05	5.4 20.1 23.3	67.2 67.7 68.0
	0.10	5.6 18.1 28.9	72.4 74.0 75.0
	0.20	5.6 18.3 22.8	74.0 75.2 75.8
S - V	0	6.0 20.0 29.0 30.0	71.4 72.0 72.0 72.0
	0.05	6.0 10.0 12.0 19.5 30.5 33.0	80.5 81.3 81.4 82.0 83.1 83.2
	0.07	6.0 20.0 35.5	81.9 83.0 84.5
	0.10	5.5 17.5 24.0 29.0 30.5	83.8 84.8 85.4 85.6 85.9
S - VI	0.20	5.5 17.0 30.0	85.5 87.1 88.8
	0	5.7 19.4 27.1	80.3 80.9 81.3
	0.02	9.2 16.3 25.1	83.0 83.3 84.0
	0.04	5.8 14.4 18.9 30.2	85.4 85.5 86.5 86.9
	0.07	5.8 17.3 25.6	86.0 87.5 88.0
	0.10	6.0 17.5 24.6	87.0 88.6 89.2
	0.20	5.4 19.2 25.6	89.3 90.7 91.4

ENCLOSURE (B)32

Table IV(B)32
OCTANE VALUE OF OTHER FUEL

Sample	T.E.L. (%)	Absolute Humidity (g m^3)	Octane No.
N - I	0	5.4	73.7
		10.4	74.0
		13.6	74.2
		21.4	74.5
	0.05	5.5	85.1
		18.0	86.4
		20.0	86.6
		34.0	87.3
	0.10	5.3	88.9
		9.7	89.5
		10.2	89.8
		14.5	90.0
		23.4	91.0
	0.20	6.0	93.5
		14.0	95.4
		32.5	96.2
Catalytic cracked gasoline	0	5.4	76.0
		19.8	76.2
		22.6	76.3
	0.05	6.1	84.2
		19.8	85.3
		27.1	86.0
	0.10	5.5	87.8
		16.4	88.7
		25.3	89.2
	0.20	5.5	91.7
		17.7	92.5
		27.7	94.4

III. CONCLUSION

From the experiment, we found the following results:-

A. The influence of moisture on the difference of octane values of unleaded gasolines was within 1 octane number.

B. The influence of moisture on the octane value of leaded gasoline was remarkable.

The difference amounted to 3 octane when it was leaded 0.2% in the case of increasing moisture from 5 gm per cubic meter dry air to 25 g m^3.

C. The correcting formula, when the percentage of lead was from 0.07% to 0.1%, could be shown as follows:

ENCLOSURE (B)32

$$\Delta N = M^{0.4505} ___ 2.085$$

When ΔN, increase of octane value from that of the gasoline at the moisture of 5 gm/m^3 dry air.

M. Moisture of atmospheric air in gm per cubic meter dry air.

The curve calculated from this formula and plot of experimental results is shown in Figure 3(B)32.

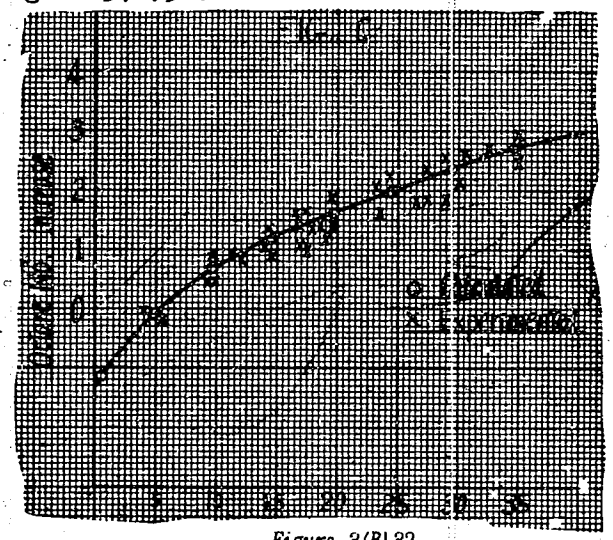


Figure 3(B)32

ABSOLUTE HUMIDITY g/m³

Add: Humidity control not used except experimentally.

ENCLOSURE (B) 33

ENGINE TEST METHODS FOR AVIATION FUELS AT OFUNA

by

CHEM. ENG. LT. COMDR. T. NAKAYAMA

Research Period: 1942-1945

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

December 1945

ENCLOSURE (B)33

LIST OF TABLES AND ILLUSTRATIONS

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Figure 4(B)33 Close-up View of Testing Shop for Full Scale Engine ..... Page 394

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Plate I(B)33 Experimental Laboratory for Mono-Cylinder Engines

Plate II(B)33 Experimental Laboratory for Mono-Cylinder Engines

Plate III(B)33 Flow Sheet of Mono-Cylinder Testing Apparatus

Plate IV(B)33 Single Cylinder Testing Engine

Plate V(B)33 First Experimental Laboratory for Aeroengines

Plate VI(B)33 Second Experimental Laboratory for Aeroengines

ENCLOSURE (B)33

I. INTRODUCTION

An engine test plant was installed at the First Naval Fuel Depot in 1942 in order to examine the performance properties of fuels and lubricants.

The three sections concerning aviation fuel and lubricants are as follows: The First section includes the single cylinder engine testing plant and aircraft engine bench testing plant to test aviation fuels and lubricants. The Third section is equipped with physical and analytical laboratories for lubricants. The Fourth section includes the C.F.R. testing engine to determine the octane number and the chemical analytical fuel laboratory.

The engine testing plant had two main objectives, one to discover new and better fuels and lubricants, and the other to assist this institute in their production.

The engine testing plants were built during 1942. The first work undertaken was in relation to high octane aviation fuel, and particularly engine tests of aromatic hydrocarbons, (Enc. (B)21). As the aviation fuel supply in Japan became more critical, efforts were directed to improve the production and supply of aviation fuel, we increased lead content, (Enc. (B)24, Part II).

Extensive research programs on substitutes for gasoline were then undertaken, and on the use of alcohol as aviation fuel, (Article 3 of this series, Enc. (B)17) and "Engine Test of Pine Root Oil as the Aviation Fuel" (Article 4 of this series, Enc. (B)10).

II. DETAILED DESCRIPTION OF APPARATUS

A. Single Cylinder Engine Test

Engine structure and flow sheet apparatus are shown by the attached blue prints, Plate I(B)33-Plate IV(B)33.

1. Dimensions of engine:

Cylinder bore	140mm
Stroke	150mm
Compression ratio	7.0(variable)
Maximum RPM	3000
Maximum hp	100
Maximum boost	+700mm Hg

2. Methods of operation

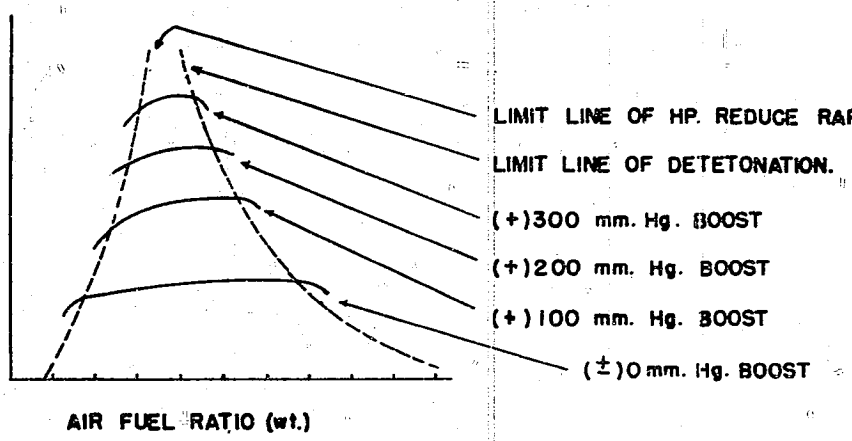
An electric dynamometer motors the engine during the starting period and when warming up of the engine is finished the fuel supply and ignition switch are turned on. Intake air is supplied by "Enke" type blower (two blowers are connected in series) and its mass of air flow is measured by nozzle attached at the intake pipe. The fuel is injected into the intake manifold. The temperature of the inlet lubricant oil is kept 70-75°C constantly.

One operator controls both air and fuel supply and the other operator controls load by means of the electric dynamometer. Test measuring process is as follows.

At a constant speed, the intake air pressure (boost) is increased step by step (±)0, (+)100, (+)200,-----mm Hg and at each boost, fuel consumption varied, and at each fuel consumption engine operation is

maintained for three minutes continuously to establish a steady operating condition for the engine.

The useful range of the air fuel ratio at each boost is tested and the maximum allowable boost and smooth running range of air fuel ratio (See Plate I(B)33.



3. Method of measuring

Detonation is judged by the cyliner temperature and the state of exhaust gas flame. During running, the engine is maintained continuously for three minutes at the same set of conditions. A constant cylinder temperature is reached after about 1-1.5 minutes if detonation does not occur.

If detonation occurs, the cylinder temperature climbs continuously, and finally increases very rapidly, accompanied by a change in the colour of the exhaust gas flame and occasional puffs of black smoke. The auto-ignition is judged by switching off the ignition spark and if the engine continues to run, it is considered that auto-ignition has occurred.

The cylinder temperature is measured by an electric thermocouple using chromel and aromel wires.

The couple wires are welded to the copper washer of the spark plug. Exhaust gas temperature is measured by the same electric thermocouple protected by stainless steel tube, the position of which is about 35mm from the cylinder exhaust port. The power output of the engine is measured by the electric dynamometer which loads the engine and controls the engine speed. The mass of the intake air is measured by a flow nozzle which is attached at the suction side of the blower. Fuel consumption is measured by a stop watch and 200cc measuring glass bottle which is connected between the fuel tank and the fuel pump. Air-fuel ratio is calculated by the above mentioned measuring data and also roughly indicated by the Cambridge Type gas analyser for exhaust gas.

B. Full-Scale Engine Test

The layout of the apparatus is shown by the attached blue prints, Plate V(B)33 and Plate VI(B)33. There are two means of absorbing the power in full-scale engine tests: one is air screw attached (Plate V(B)33), the other a water brake dynamometer (Froude Type)(Plate VI(B)33).

Both apparatuses can be used for a maximum of 3000 hp. The building is a sound-proof structure with a material made from hemp rags. The engine test installation attached to the air screw is mainly used for endurance test of the lubricant, while the engine attached to the dynamometer is mainly used for fuel performance tests.

The former test was not put into practice because of the shortage of supply of the aviation fuel and strict orders for saving fuel.

The operating method for the full-scale engine attached to the water brake was similar to that described for the single cylinder engine.

III. PROGRESS OF RESEARCH WORK

Performance tests with aromatic fuel were first made in December 1942 to investigate a new and high octane aviation fuel.

It was found that aviation fuel should contain less than 20% benzene (C_6H_6), otherwise detonation occurred.

Toluene showed the best performance results as aviation fuel and equaled or exceeded iso-octane. Xylene or higher aromatics i.e. solvent naphtha etc. (dry distilled oil from coal) also showed good anti-knock properties, but it was necessary to improve the fuel supply apparatus as these aromatics had poor volatility (Enc. (B)21). But the production of such aromatics was very small and they had other important uses in addition to their use as fuel. Therefore, alcohol was investigated as a substitute for gasoline.

For training plane engines (below 500 hp), alcohol blends were used. The alcohol content in aviation gasoline was increased step by step, i.e. 20%, 50%, and finally absolute alcohol was used.

The use of alcohol for training engines presented no insurmountable difficulties, but did require some shanges in carburettors and the starting and acceralation techniques.

Next, specifications of aviation fuel in order to obtain a larger amount of aviation fuel from a fixed quantity of base oil, and there was no other way to do this than to lower the specifications, that is, to enlarge the distillation range.

As a result of using low octane gasoline for training plane engines and elevation of temperature of the end point, the octane number decreased. Steps were taken to investigate the increase of tetraethyl lead content in gasoline to increase the octane number, but it was considered that this caused more contamination upon the spark plugs. The influence of increased tetraethyl lead content in aviation gasoline upon engine performance and ignition plugs, and inhibiting effects of $C_2H_4Br_2$ on the contamination due to the increased tetraethyl lead were also investigated (Enc. (B) 24).

The results showed that aviation gasoline with 0.3% (Vol.) tetraethyl lead could not be used, and that $C_2H_4Br_2$ acted as an inhibitor preventing contamination of lead upon spark plugs, but an excess burned the plugs. Moreover, the

supply of aviation fuel reached a critical stage, and there arose an urgent desire to use alcohol for the second class engines (below 1300 hp) in order to save gasoline.

The difficulties of using alcohol were its poor volatility and its low heat of combustion. The problem of low heat of combustion was solved by improvements in the fuel flow control of the carburettors.

In order to improve volatility, blends of fuel, ethyl ether acetone and gasoline were examined (Article 3 of this series, Enc. (B)17).

The effect of acetone and gasoline was good, but ethyl ether was unsatisfactory because of its preknock properties. Researches on using alcohol for high class engine was not completed. Finally, the use of pine root oil for aviation fuel was planned.

Aviation gasoline prepared by catalytic or hydrocracking of pine root oil fraction below 300°C was found to give the same engine performance as the standard aviation gasoline --91 O. N. (Article 4 of this series, Enc. (B)10).

Crude pine root oil boiling below 185°C could not be used alone, as aviation fuel, because of its poor volatility, low octane value and high tendency toward gum formation on the spark plugs, when engines were operated for long periods at low temperatures. However, when a small amount of crude pine root oil was added (20% by volume) to ethyl alcohol, the blend could be used with the same results as obtained with ethyl alcohol alone.

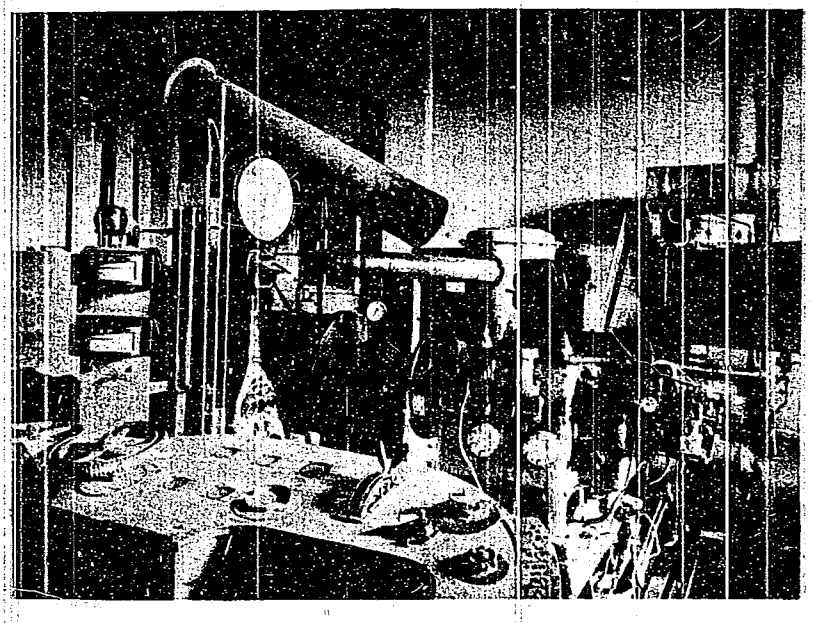


Figure 1(B)33
MONO-CYLINDER TESTING ENGINE

ENCLOSURE (B)33

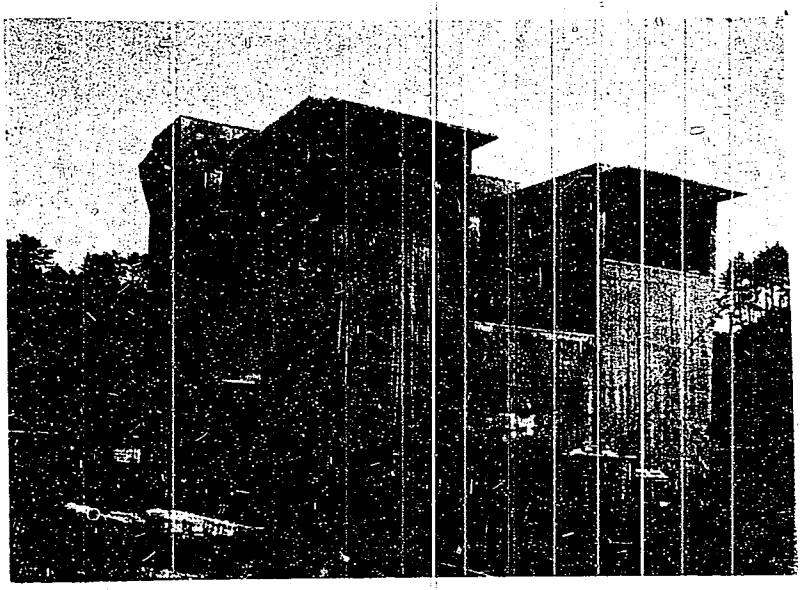


Figure 2(B)33
GENERAL VIEW OF THE
FIRST EXPERIMENTAL LABORATORY
FOR FULL SCALE ENGINE

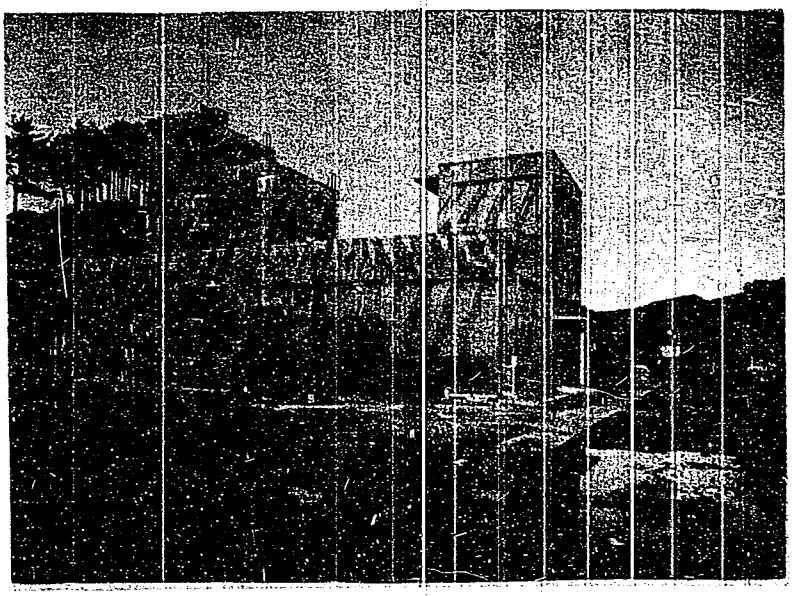


Figure 3(B)33
GENERAL VIEW OF THE
SECOND EXPERIMENTAL LABORATORY
FOR FULL SCALE ENGINE

ENCLOSURE (B)33

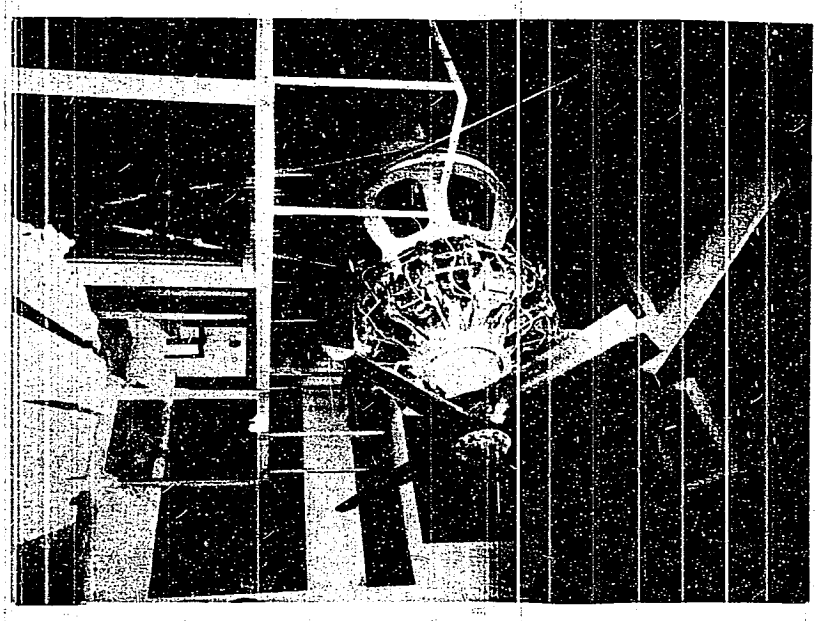


Figure 4(B)33
CLOSE UP VIEW OF TESTING SHOP
FOR FULL SCALE ENGINE

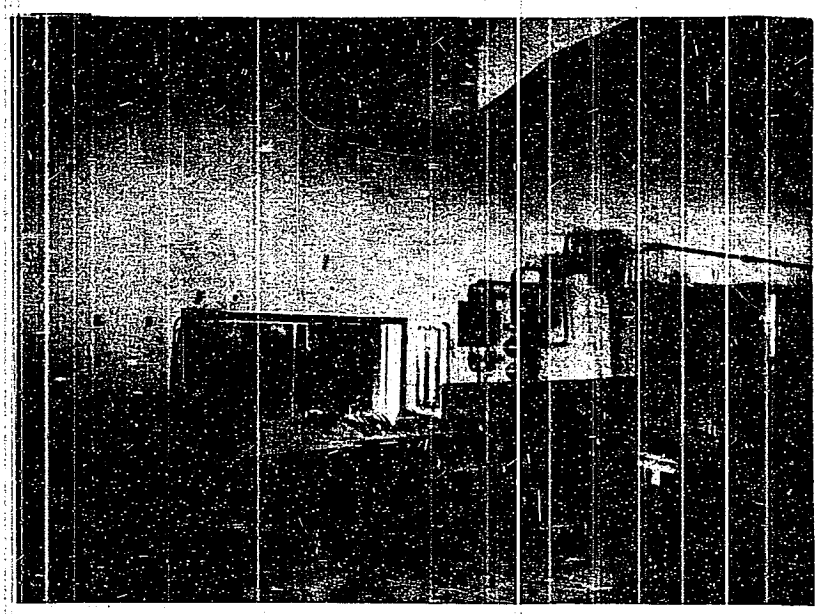
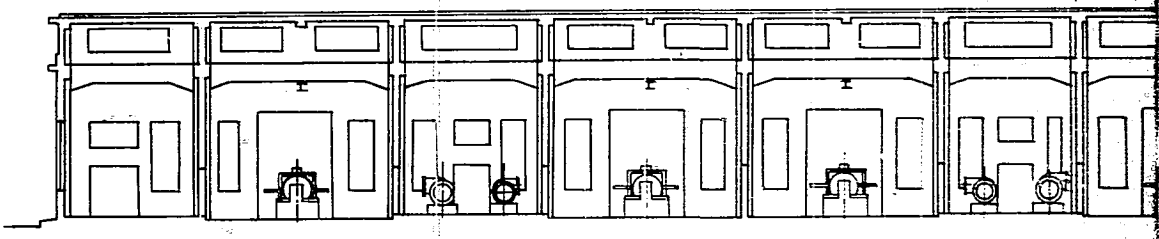
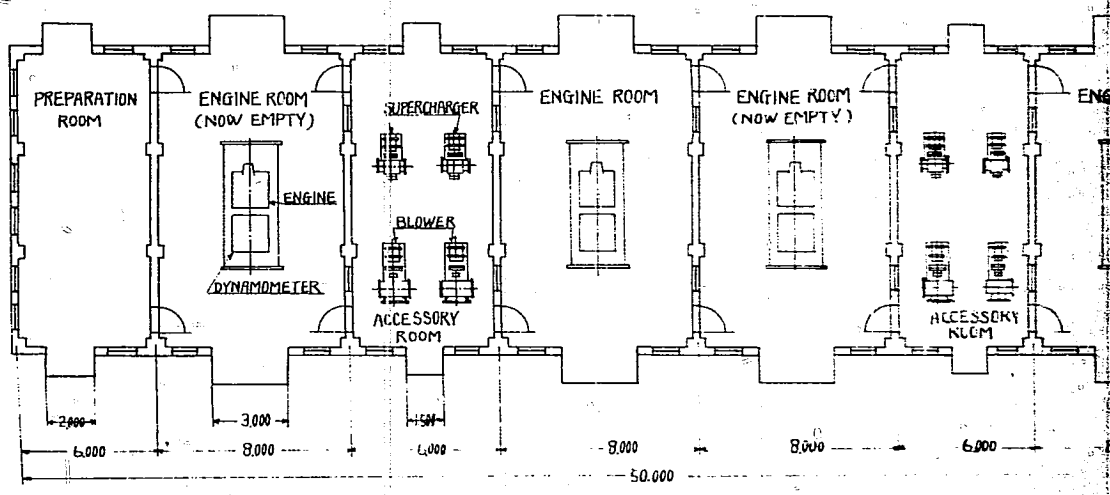
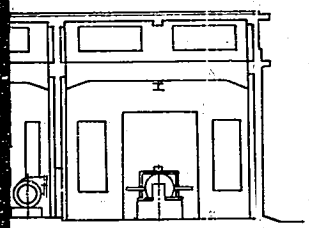
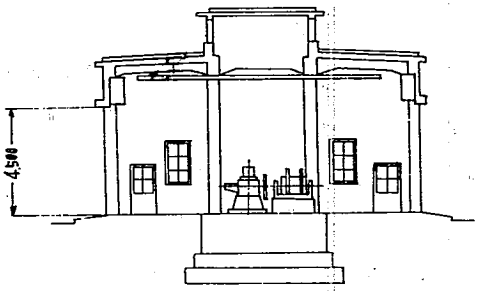


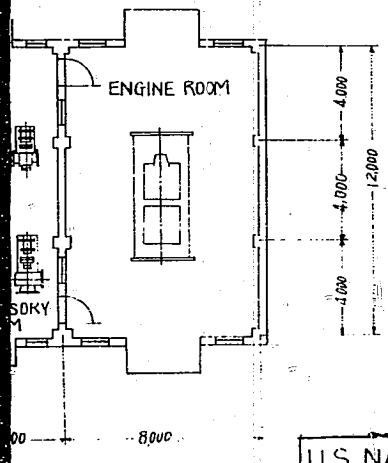
Figure 5(B)33
CLOSE UP VIEW OF THE
CONTROLLING PLATFORM




PREPARATION ROOM
ENGINE ROOM (NOW EMPTY)
ENGINE
DYNAMOMETER
SUPERCHARGER
BLOWER
ACCESSORY ROOM
ENGINE ROOM
ENGINE ROOM (NOW EMPTY)
ACCESSORY ROOM
2,000
3,000
6,000
8,000
8,000
8,000
6,000
50.000

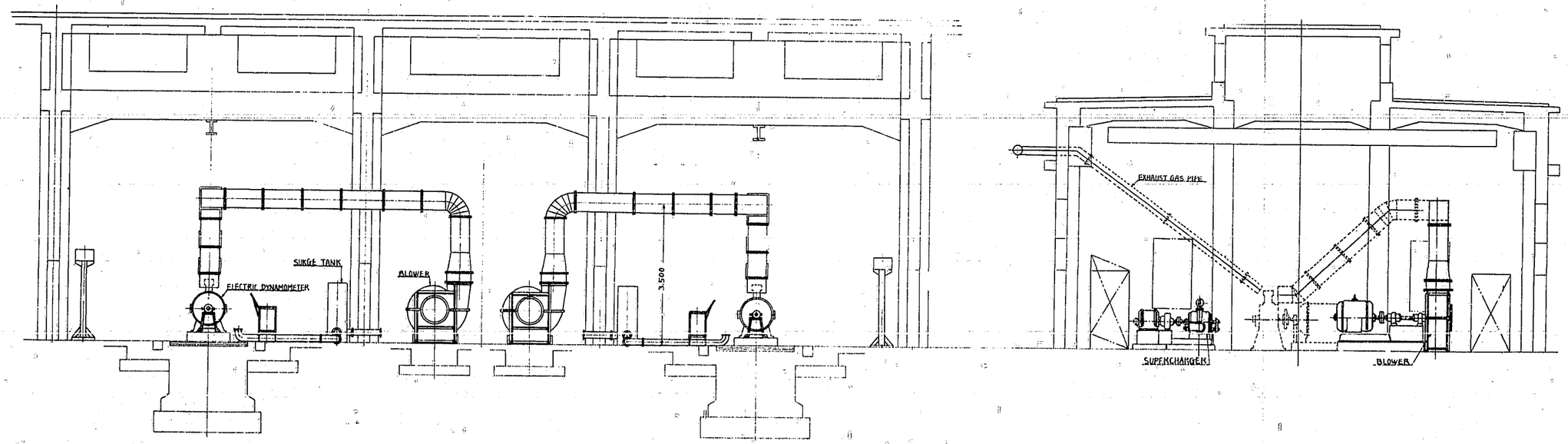


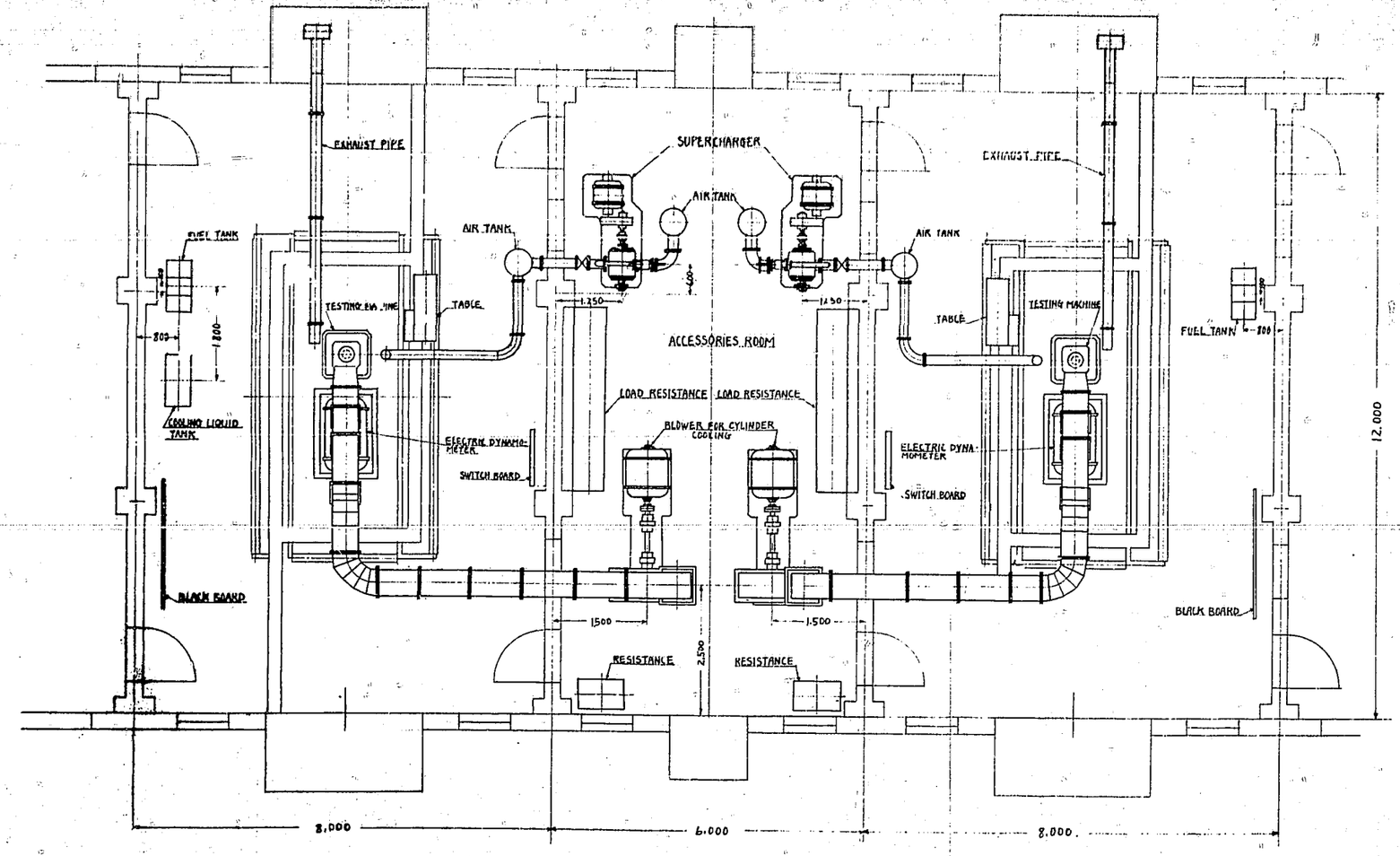




U S NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
EXPERIMENTAL LABORATORY FOR MONO-CYLINDER ENGINES		
3 DEC 45	PLATE I (B) 33	X-38(N)-2

(Ser. No. 074. Enc B-33)


SURGE TANK
ELECTRIC DYNAMOMETER
BLOWER
3,500
EXHAUST GAS PIPE
SUPERCHARGER
BLOWER



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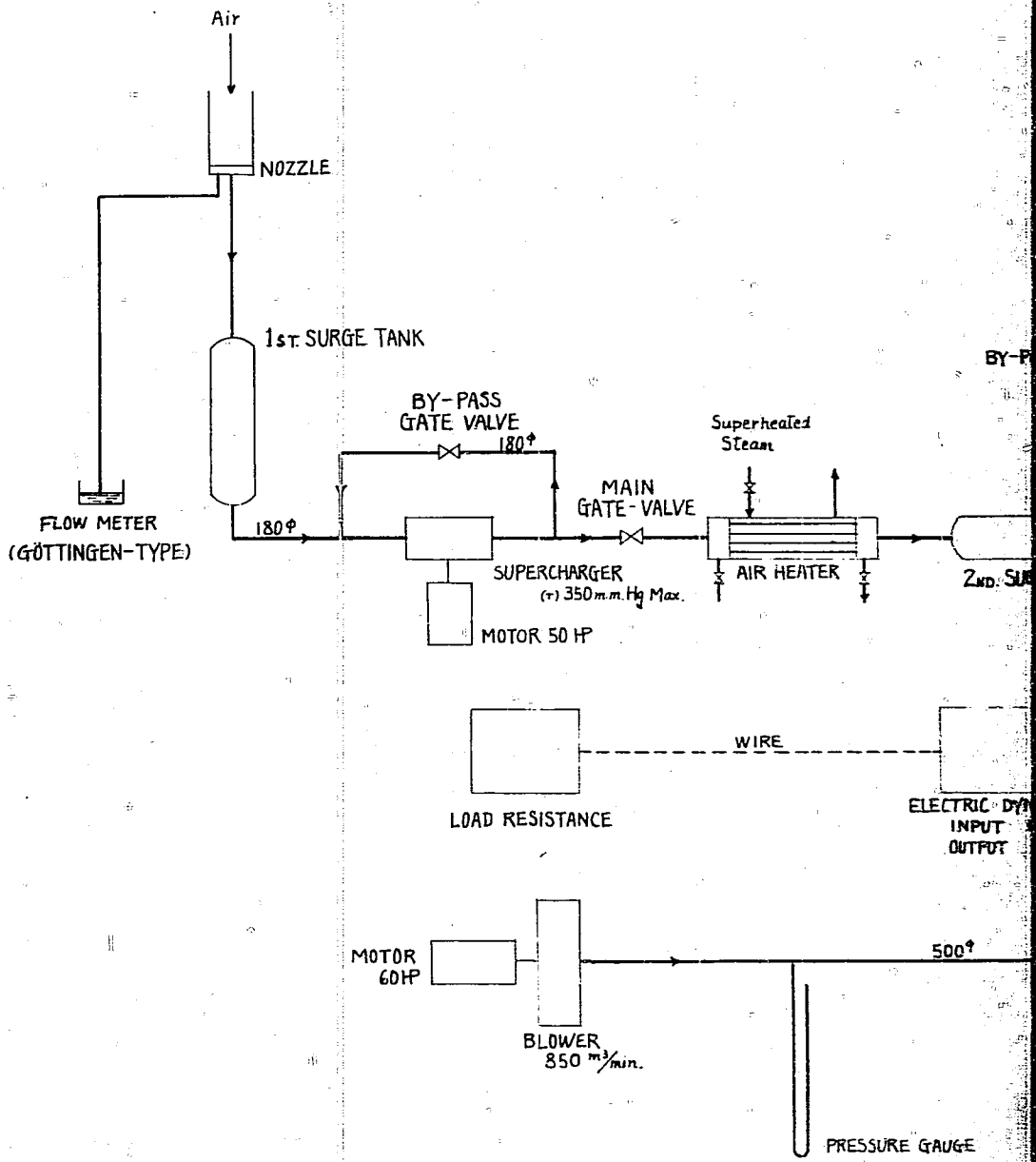
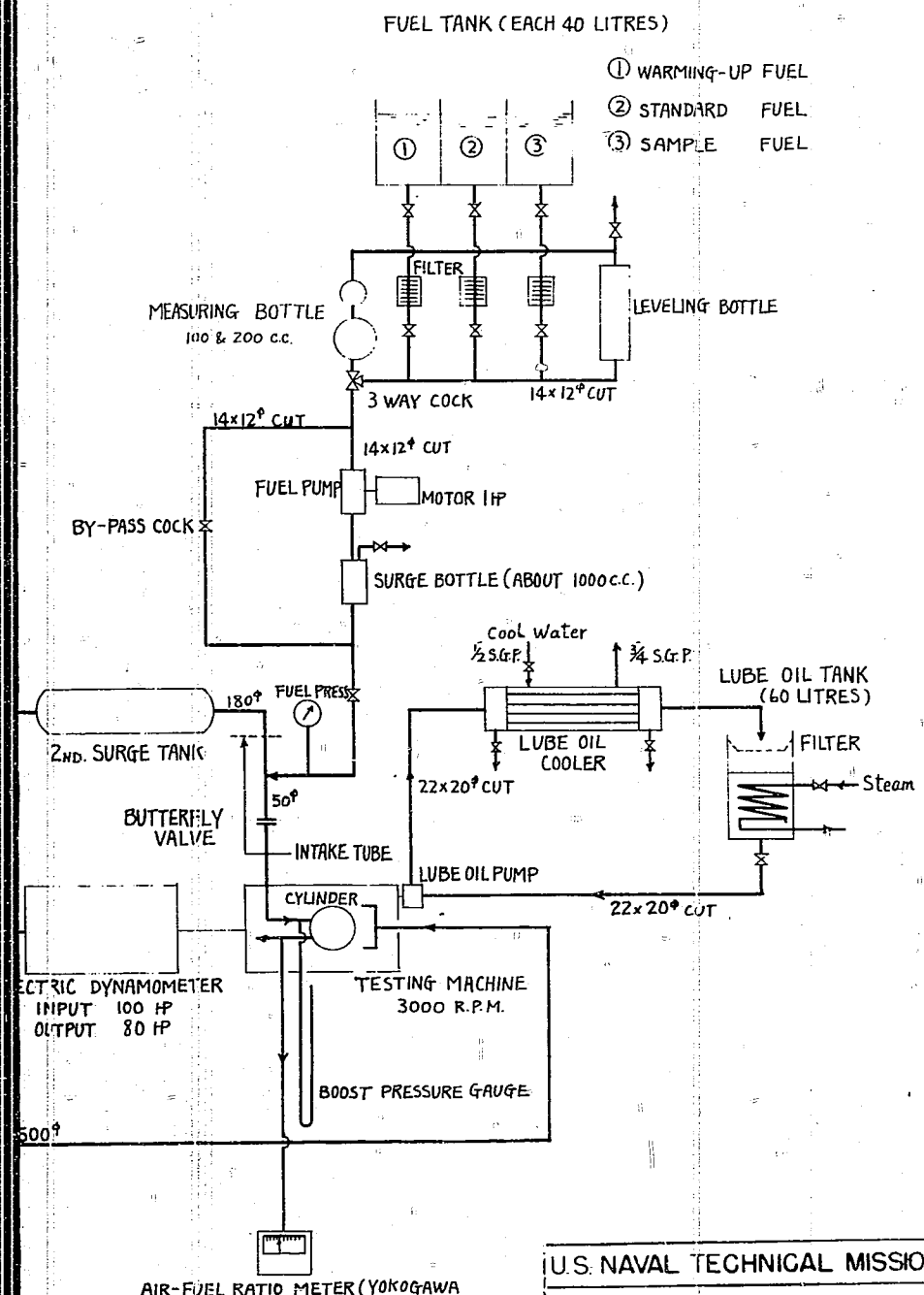
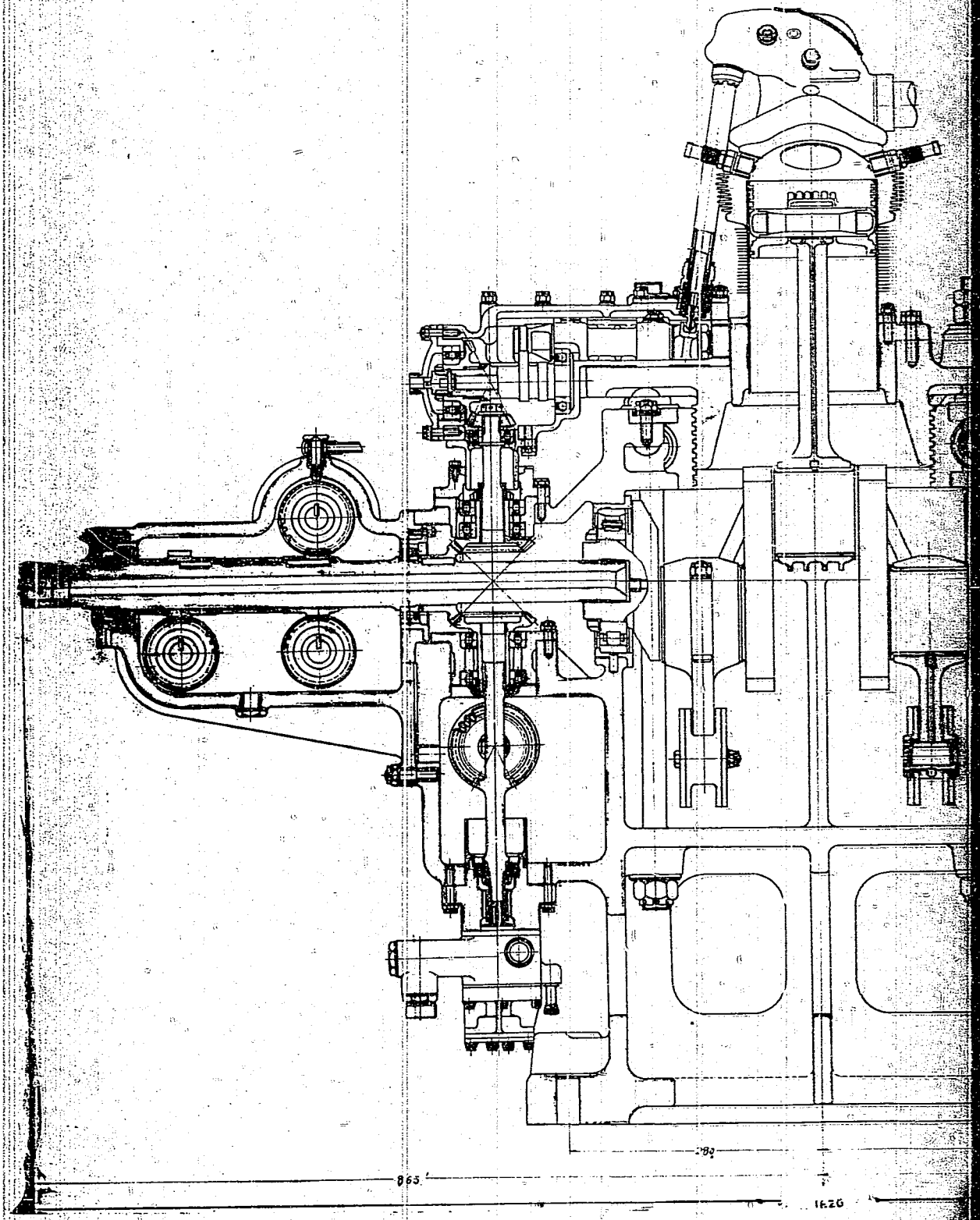
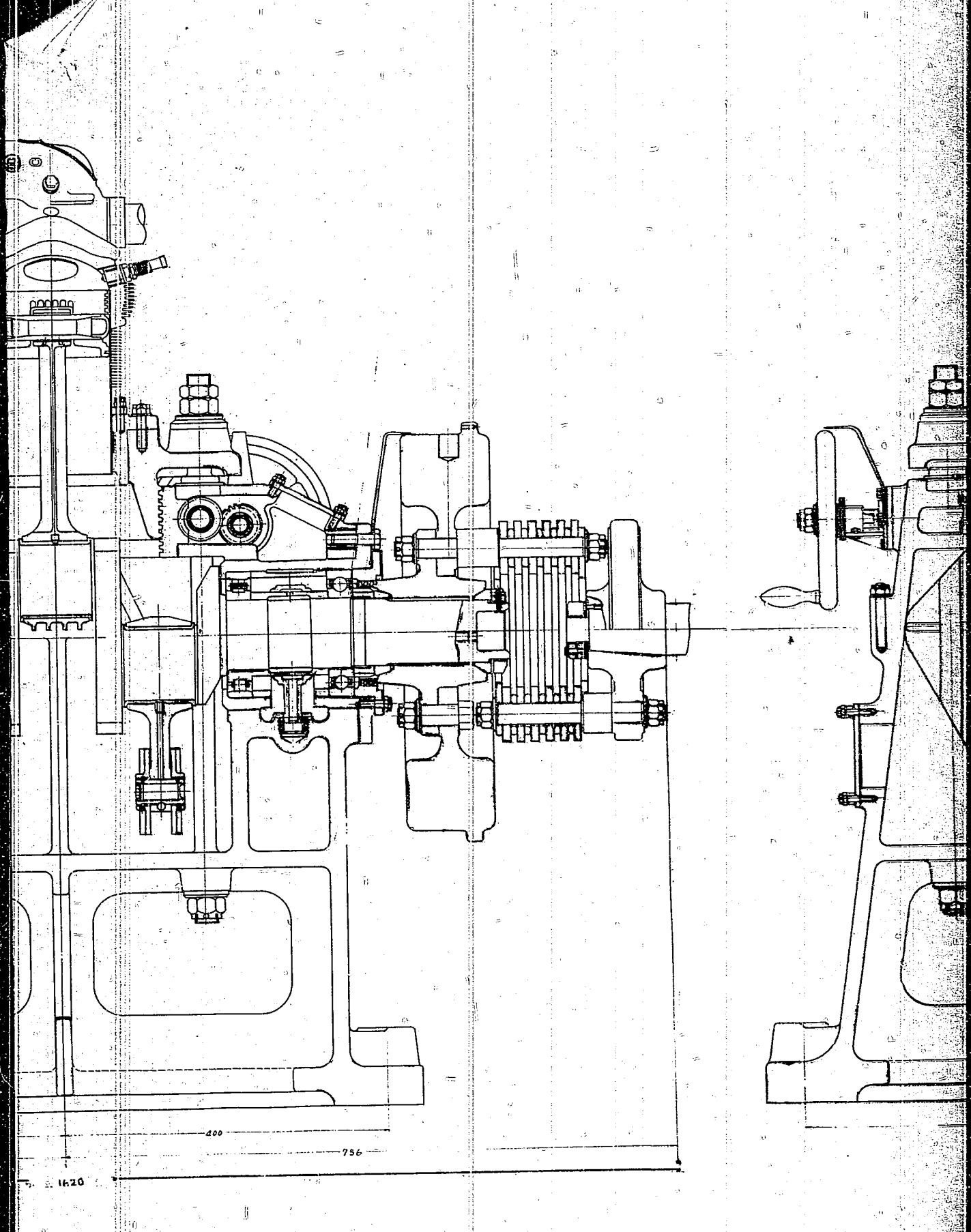
EXPERIMENTAL LABORATORY FOR MONO-CYLINDER ENGINES		
8 DEC. 45	PLATE II(B)33	38(1)-2

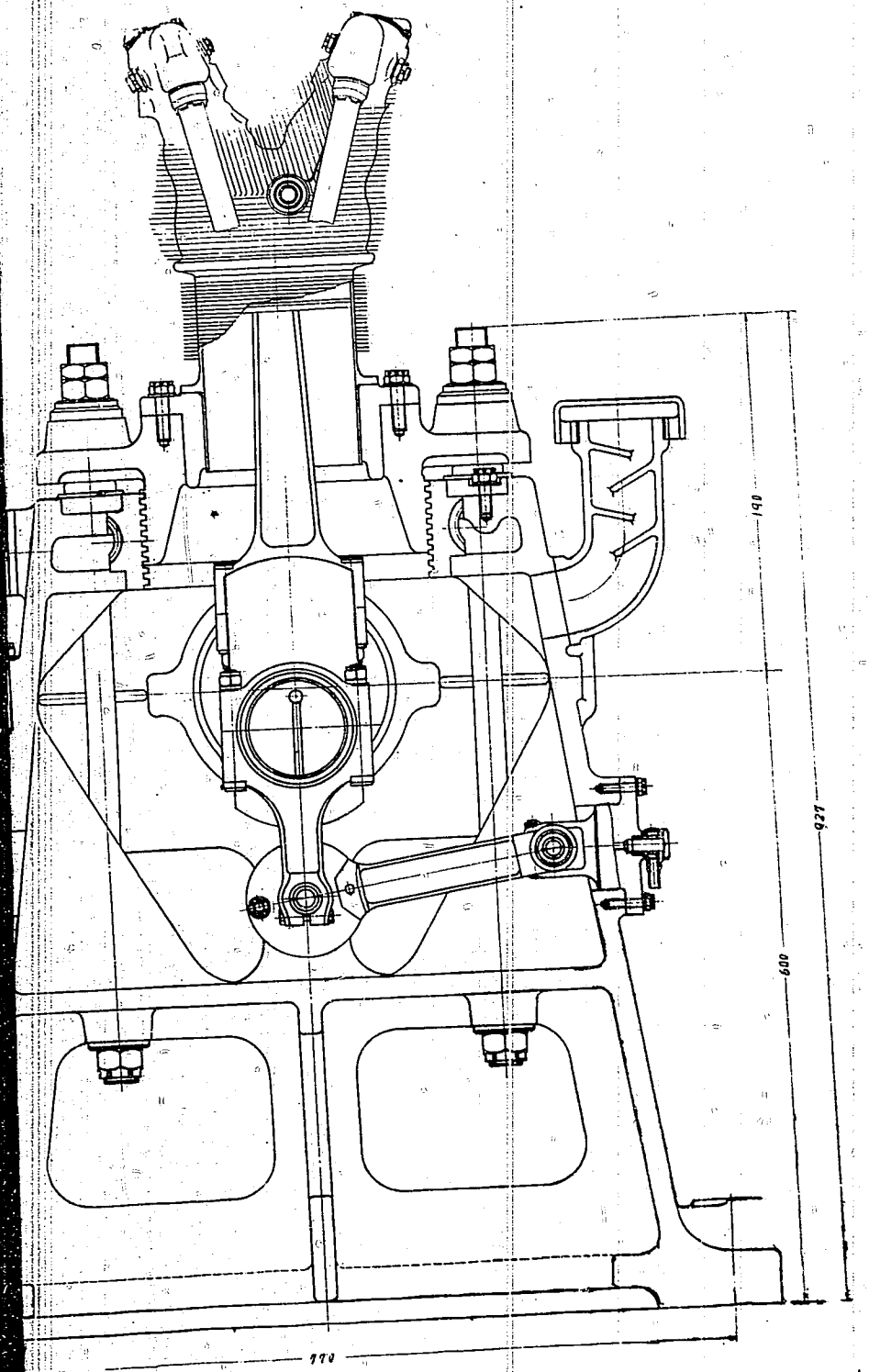

Air
NOZZLE
1ST. SURGE TANK
BY-PASS
GATE VALVE
180φ
Superheated
Steam
MAIN
GATE-VALVE
FLOW METER
(GÖTTINGEN-TYPE)
180φ
SUPERCHARGER
(τ) 350m.m.Hg Max.
AIR HEATER
MOTOR 50 HP
WIRE
LOAD RESISTANCE
ELECTRIC DY
INPUT
OUTPUT
MOTOR
60HP
500φ
BLOWER
850 m³/min.
PRESSURE GAUGE



U.S. NAVAL TECHNICAL MISSION TO JAPAN	RESTRICTED
FLOW SHEET OF MONO-CYLINDER TESTING APPARATUS	
DEC. 5, 1945	PLATE III(B) 33	X-38(N)-2

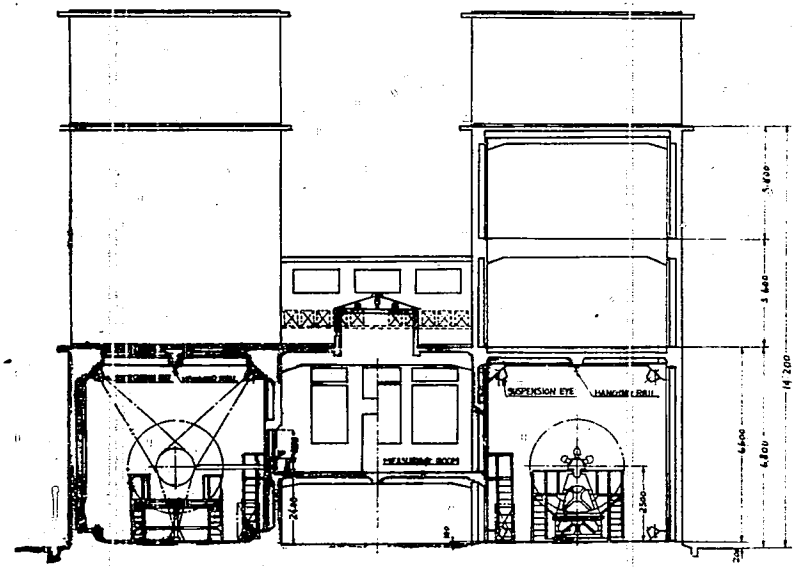

865
1620

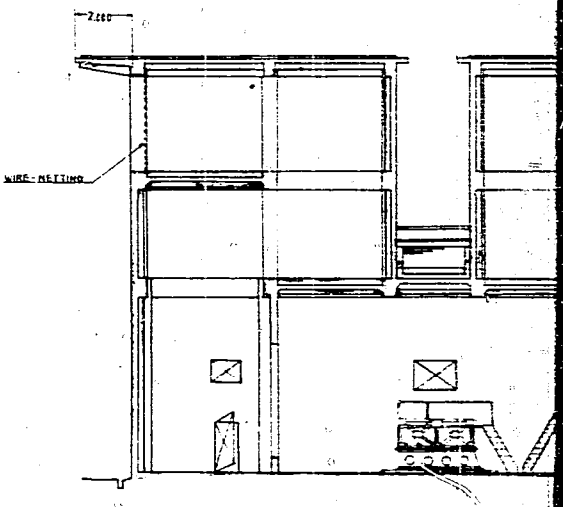

400
756
1620

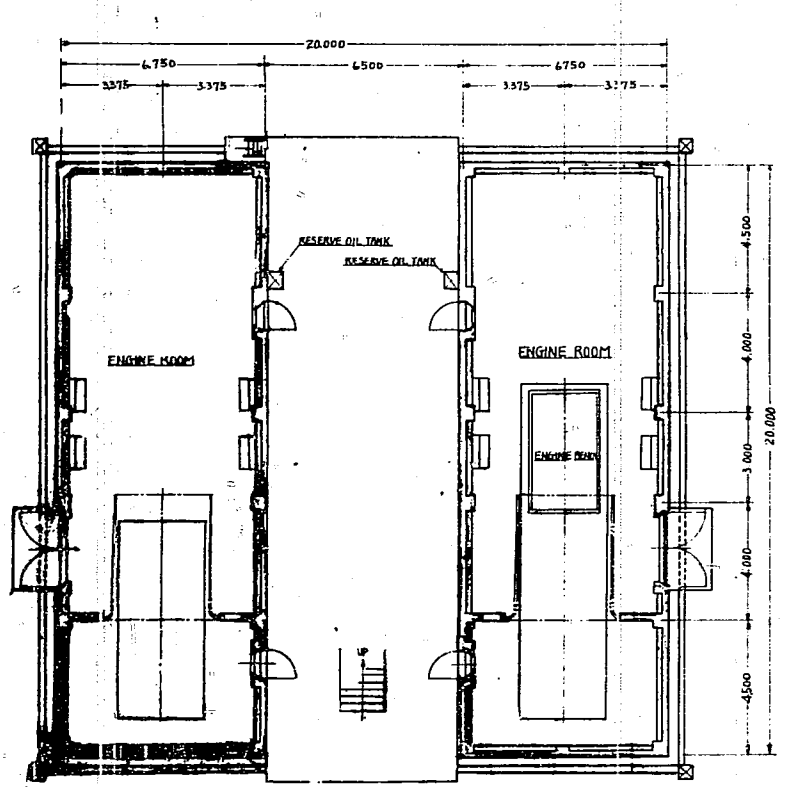


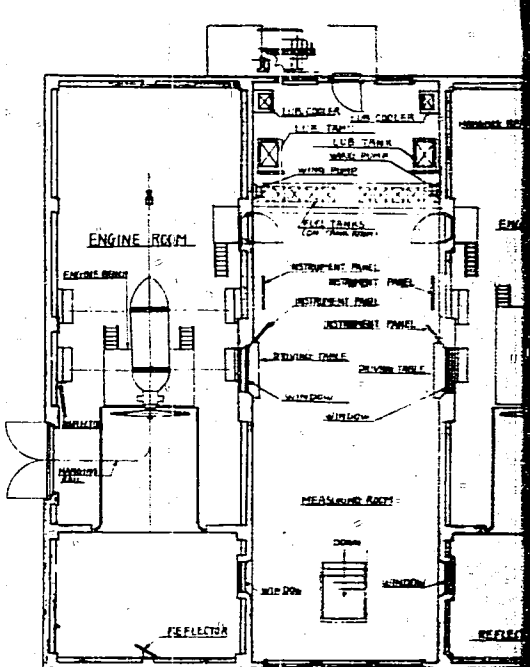
U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
SINGLE CYLINDER TESTING ENGINE		
DEC. 22, 45	PLATE IV(B)33	X-38(N)-2

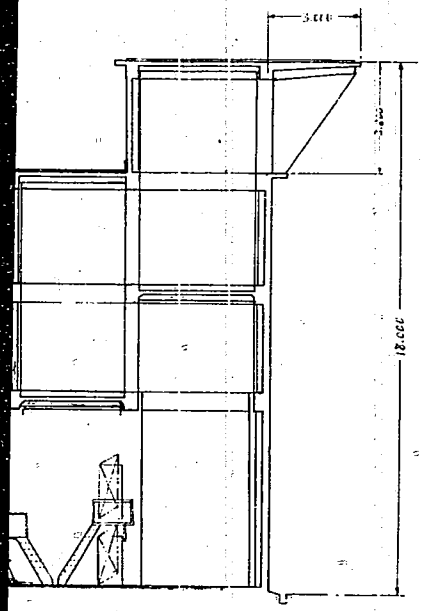
RESTRICTED

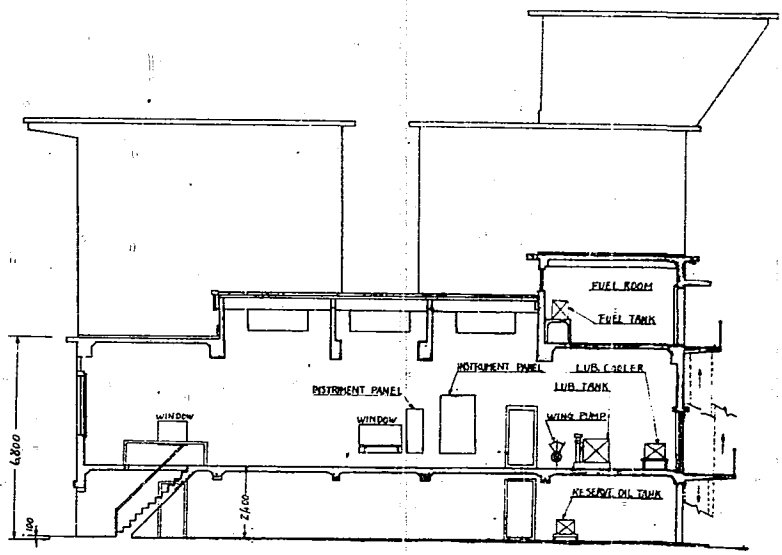

SUSPENSION EYE
HANGER (RAIL)
MEASURING ROOM
14 200
6 400
6 600
1 800
1 400
2 440
2 500

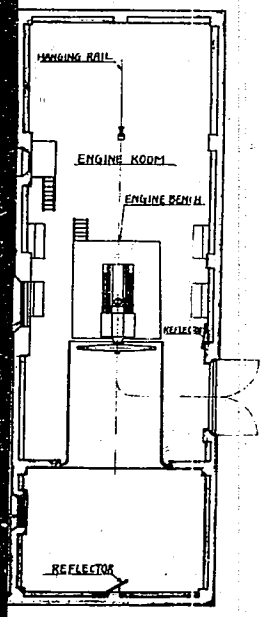

2 200
WIRE-NETTING


20 000
6 750
6 500
6 750
3 375
3 375
3 375
3 375
RESERVE OIL TANK
RESERVE OIL TANK
ENGINE ROOM
ENGINE ROOM
ENGINE BEDS
4 500
4 000
3 000
4 000
4 500
20 000

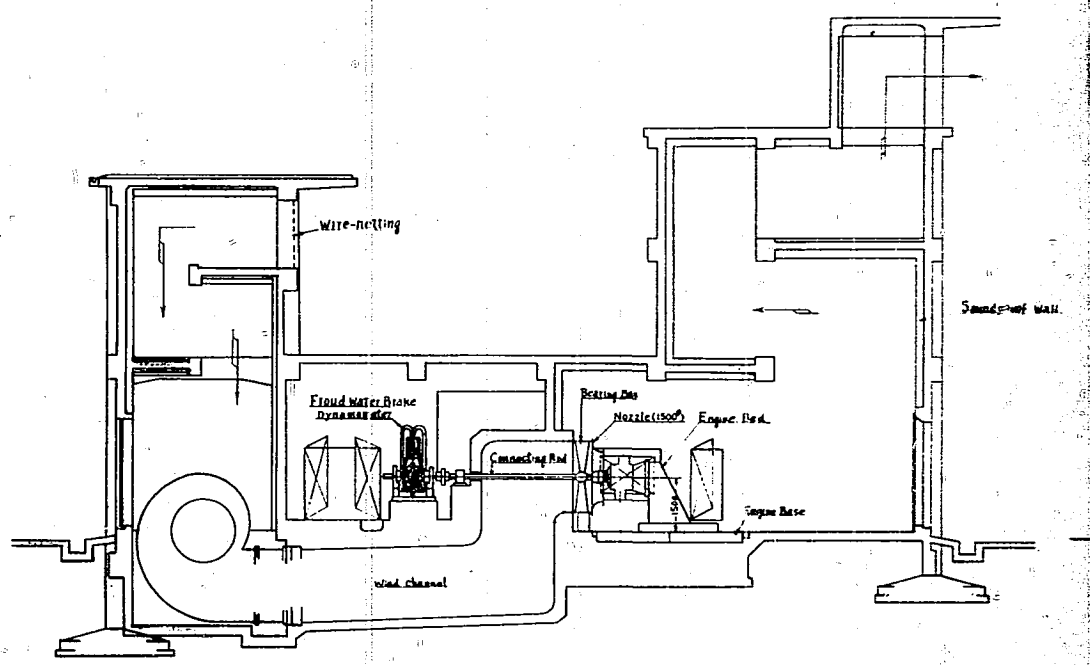

L.O. COOLER
L.O. COOLER
L.O. TANK
L.O. TANK
WING PUMP
WING PUMP
ENGINE ROOM
INSTRUMENT PANEL
INSTRUMENT PANEL
INSTRUMENT PANEL
INSTRUMENT PANEL
STEERING TABLE
STEERING TABLE
WINDOW
WINDOW
MEASURING ROOM
DOWN
WINDOW
REFLECTOR

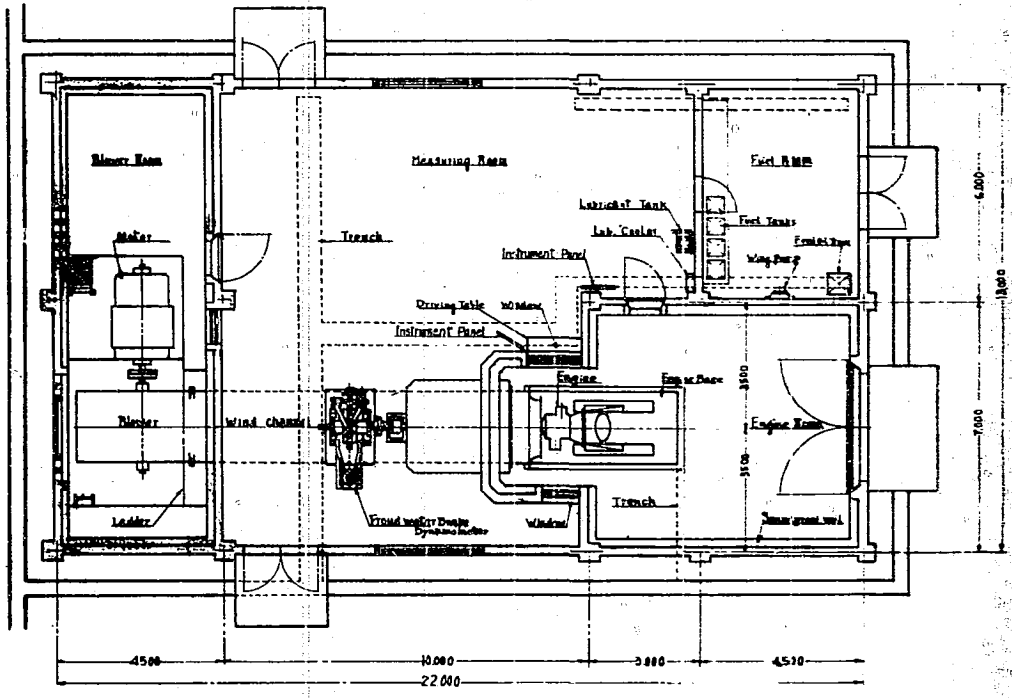


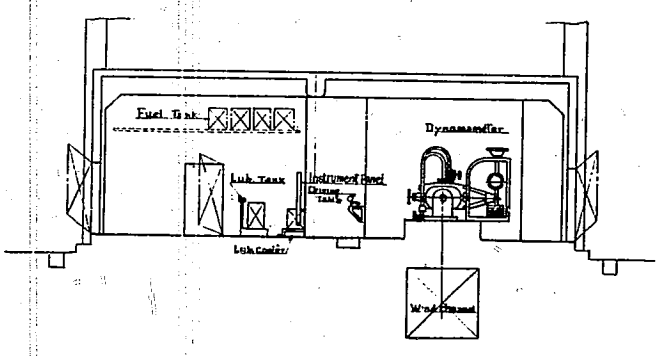


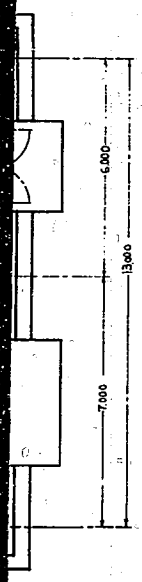


U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
FIRST EXPERIMENTAL LABORATORY FOR		
AEROENGINES		
DEC. 8, 1945	PLATE V(B)33	X-38(N)-2


Wire-netting
Sound-proof wall
Froud Water Brake Dynamometer
Bearing Box
Nozzle(1500)
Engine Bed
Connecting Rod
Engine Base
Wind Channel


Blower Room
Measuring Room
Fuel Room
Motor
Trench
Lubricat Tank
Fuel Tanks
Lub. Cooler
Fuel Pump
Instrument Panel
Wing Pump
Driving Table
Window
Instrument Panel
Engine
Engine Base
Blower
Wind Channel
Engine Room
Trench
Ladder
Froud water Dynamometer
Window
4500
10.000
3.000
4500
22.000
6.000
10.000
7.600
3500
3500





U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
SECOND EXPERIMENTAL LABORATORY FOR		
AEROENGINES		
DEC. 8, 1945	PLATE VI(B) 33	X-38(N)-2

ENCLOSURE (B) 34

LOW TEMPERATURE AND LOW PRESSURE EXPERIMENTAL LABORATORY

by

Chem. Eng. Lieut. Comdr.
T. NAKAYAMA

Prepared for and Reviewed With Author by the U.S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)34

LIST OF TABLES AND ILLUSTRATIONS

Figure 1(B)34 Insulation of Low Temperature Room ..... Page 399

Figure 2(B)34 General View of the Experimental Laboratory for Low Temperature and Low Pressure ..... Page 400

Figure 3(B)34 Low Temperature and Low Pressure Testing Room ..... Page 401

Figure 4(B)34 Freon Refrigerator ..... Page 402

Plate I(B)34 General View of Experimental Laboratory for Low Temperature and Pressure

Plate II(B)34 Flow Sheet of Experimental Laboratory for Low Temperature and Pressure

Plate III(B)34 Flow Sheet of Low Pressure and Low Temperature Engine Testing Plant

ENCLOSURE (B)34

OBJECT

The object of constructing this building was to conduct research on fuels, lubricating oils and hydraulic oils under the condition of 10,000-20,000 meters altitude and temperature down to -55°C.

I. INTRODUCTION

The maker and designer of this plant was Ebara Co. Ltd. at Hanedacho, Kamadaku, TOKYO and its cost of construction was ¥23,000,000 (in 1943). This plant was commenced December 1943 and was not completed (Oct. 1945). This plant consists of two parts: one part comprises the rooms of low temperature and low pressure and the refrigerator using Freon-12 and Freon-11 as cooling media, Part 2 consists of a single cylinder (aircraft engine) testing plant designed for low temperature and pressure operation. The first part is about 80% completed, while only the rooms of low pressure and temperature have not been completed; the second part has reached the design stage only except for the concrete foundation which had been built. The construction was discontinued because of the bombing and destruction of the Ebara Co. Ltd. at which time the designer was killed, and the machines, the design papers, the wooden models of the castings, and many parts of the uncompleted machines, were destroyed or burned.

II. DESCRIPTION OF APPARATUS

A. The Rooms of Low Temperature and Low Pressure (See Plates I(B)34, II(B)34, III(B)34, and Fig. 1(B)34)

1. Dimension and condition of the rooms are shown in Plate I(B)34.

The insulation of the wall of the rooms and iron structure of the low pressure rooms is shown in Plate II(B)34, and Fig. 1(B)34. These rooms were to be cooled by Freon refrigerating machine to the desired temperature within two hours from atmospheric temperature. The low pressure rooms are evacuated by means of a 20 hp rotary vacuum pump.

2. Refrigerating machine: (Plate III(B)34) The machines which use Freon-12 (F-12, CF_2Cl_2) and Freon-11 (F-11, $CFCl_3$) are constructed, with two stages, each stage comprising the turbo compressors and evaporators.

Freon-11 is used at the first stage, which cool both the Freon-12 and the Brine ($CaCl_2$ saturated aq. solution). Freon-12 is used at the second stage, and cold liquid Freon-12 and Brine cool the low temperature rooms and observation rooms.

The operating condition, cooling media and capacities are shown in Plate III(B)34.

3. CO_2 Fire extinguisher system (Plate III(B)34)

Ten carbon dioxide pressure cylinders were installed outside of the low temperature rooms. Pipes filled with CO_2 were led into each of the low temperature rooms and are there shut off by valves. In case of fire in any room, the workmen first open the valve, leave the room, and shut the air-tight door, thus smothering the fire.

ENCLOSURE (B)34

B. Single Cylinder Engine Testing Plant at Low Temperature and Pressure (See Plate I(B)34)

This plant consisted of the single cylinder test engine (which is the same type of single cylinder test engine reported in engine test of aviation fuel), air cooling system, and vacuum system. The engine was to be installed in a steel housing and this vessel was to be evacuated (but not cooled) by means of two vacuum pumps. Intake air was to be cooled by brine and one part of the air was to be used for engine intake air and the other part further cooled by the air expansion turbine and then used for cooling air of the cylinder.

The test engine was to be attached to the electric dynamometer. Thus only the cylinder cooling air and intake air for the combustion in the cylinder was to be cooled and single cylinder test engine was to be put in vacuum state vessel but not cooled itself.

ENCLOSURE (B)34

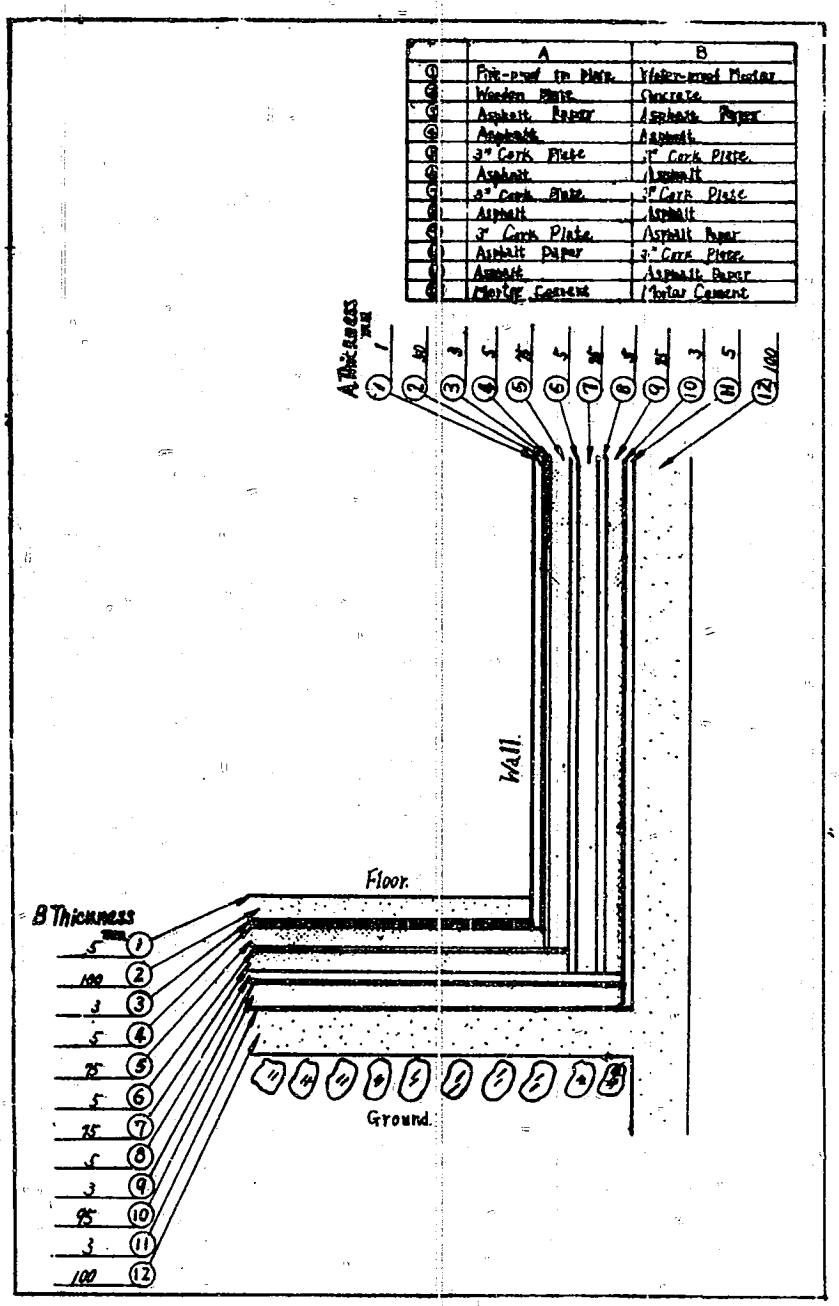


Figure 1(B)34

INSULATION OF
LOW TEMPERATURE ROOM

ENCLOSURE (B)34

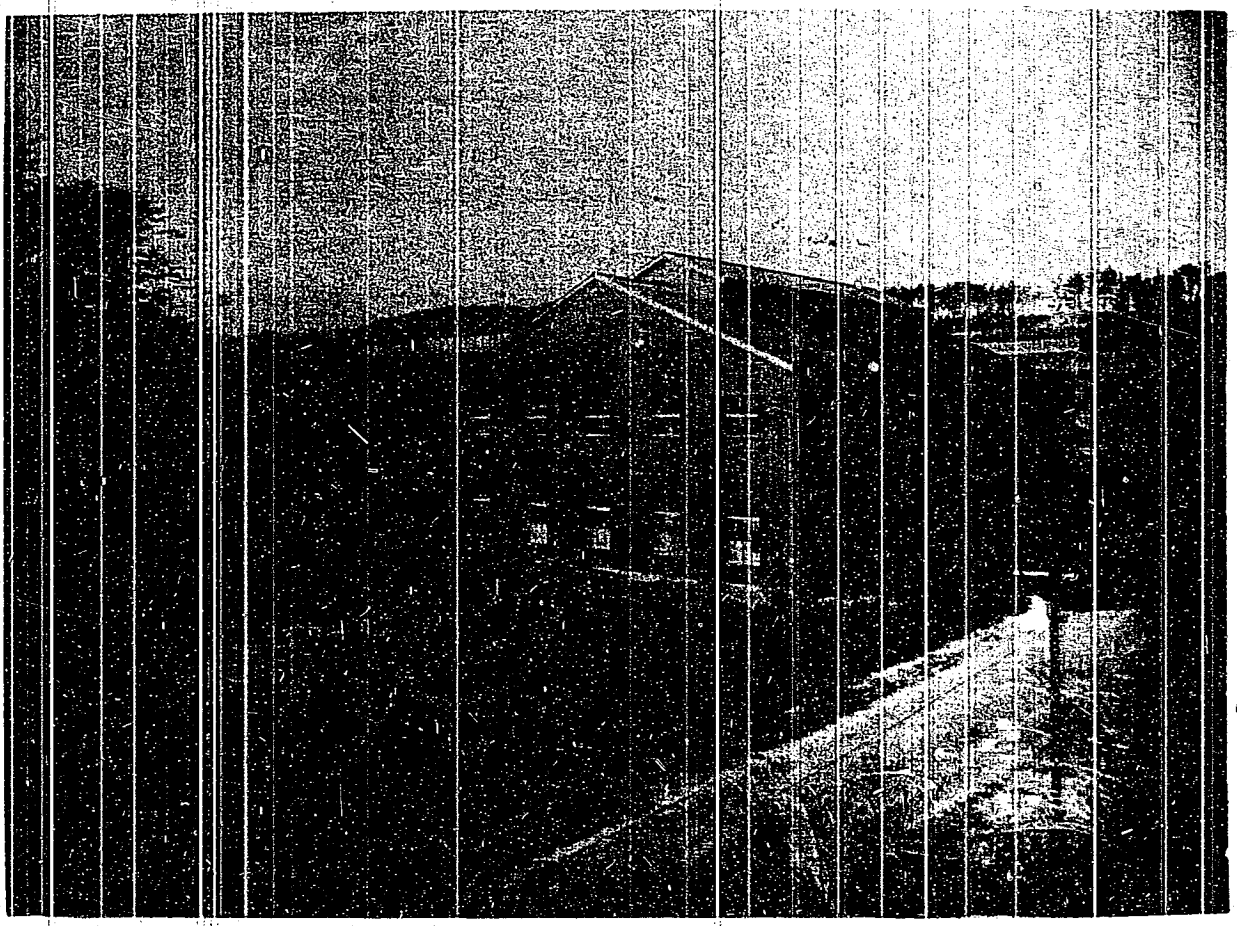


Figure 2(B)34

GENERAL VIEW OF THE EXPERIMENTAL LABORATORY FOR LOW TEMPERATURE AND LOW PRESSURE

ENCLOSURE (B)34

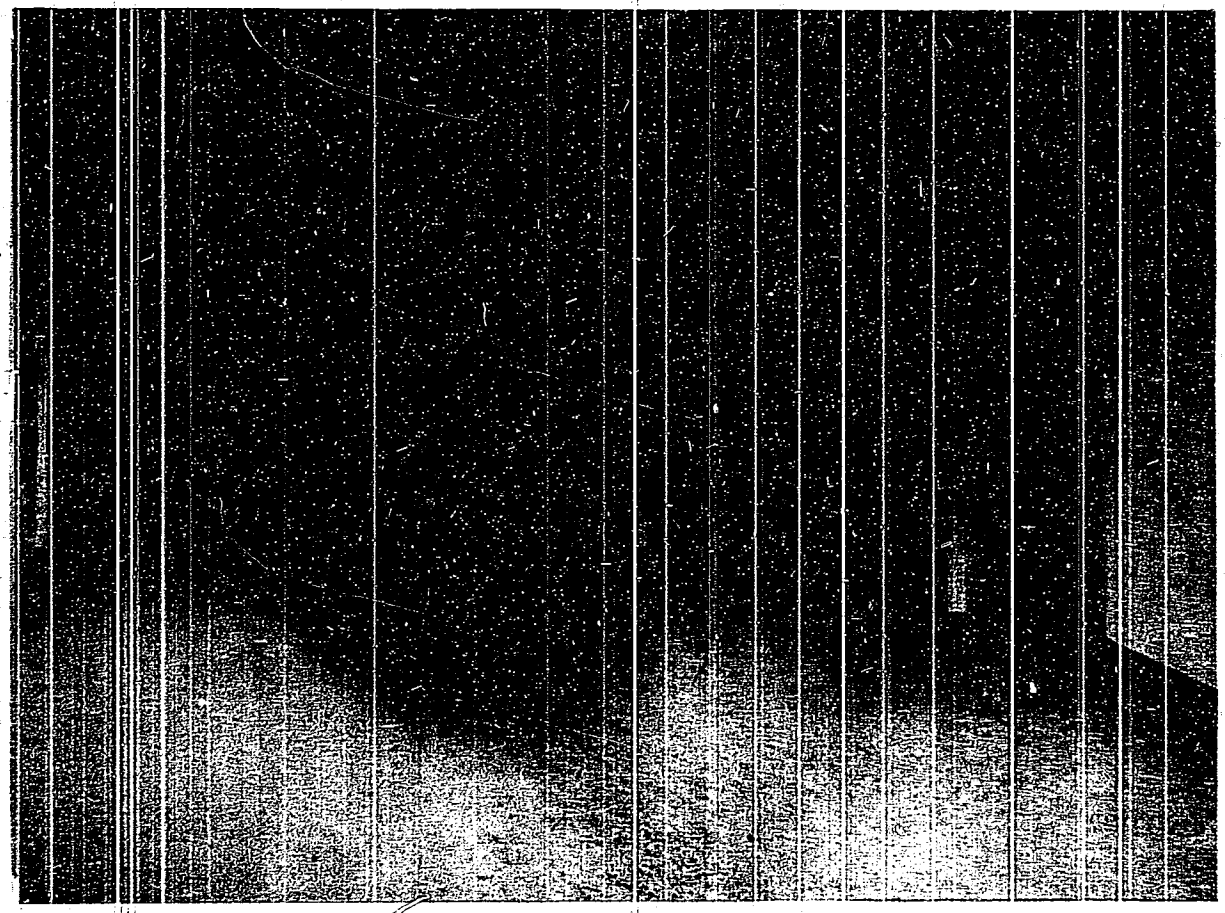


Figure 3(B)34
LOW TEMPERATURE AND LOW PRESSURE TESTING ROOM

ENCLOSURE (B)34

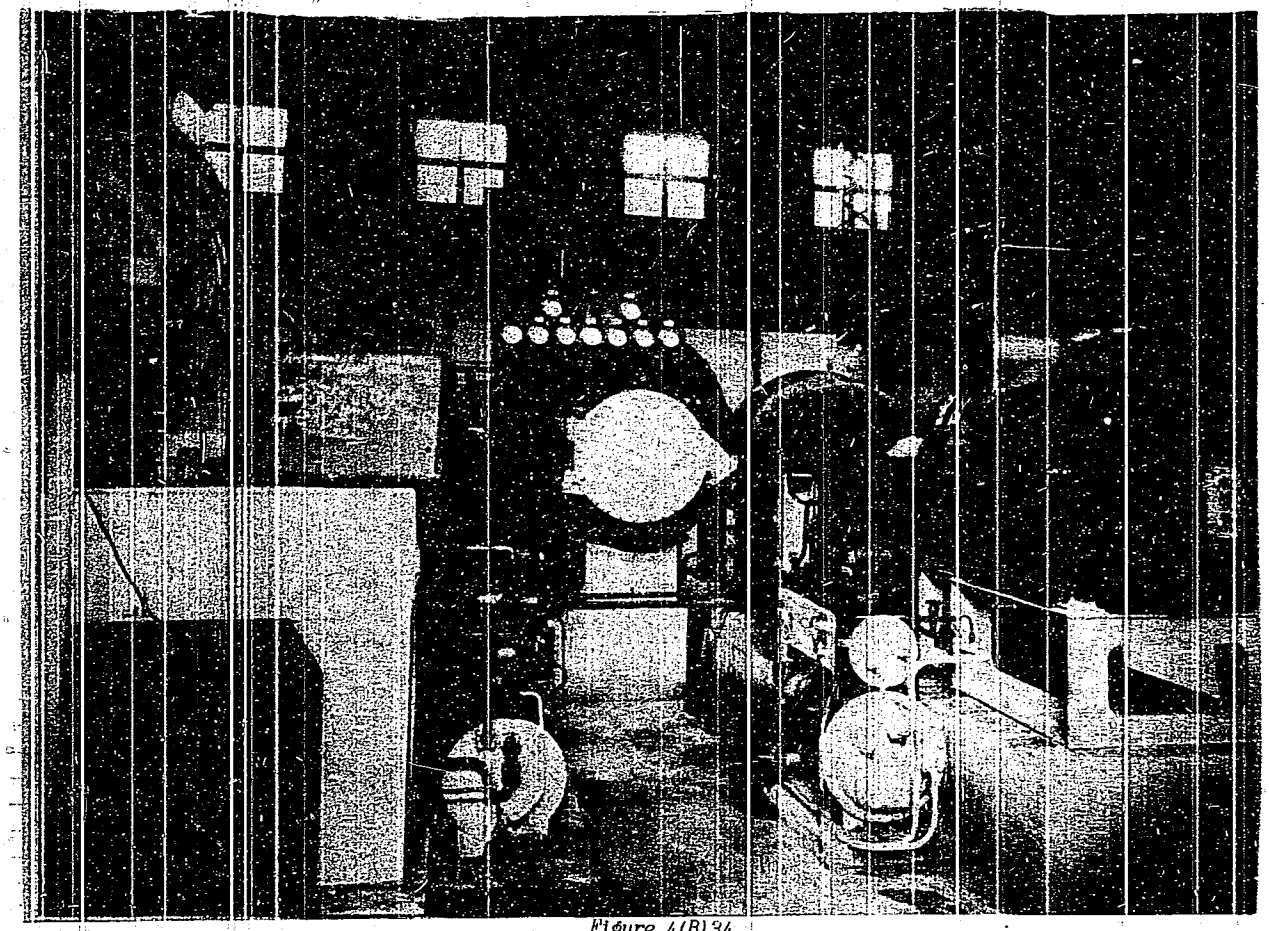
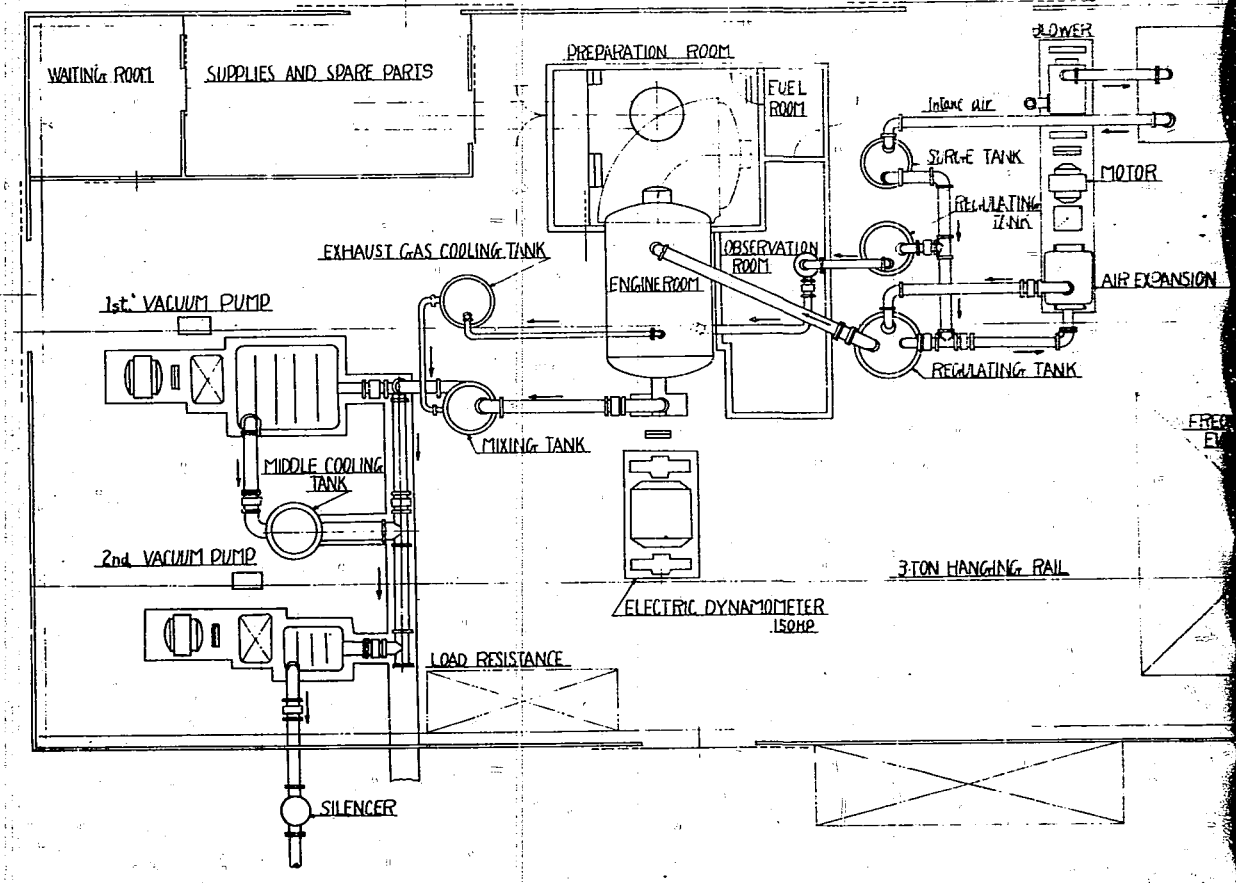
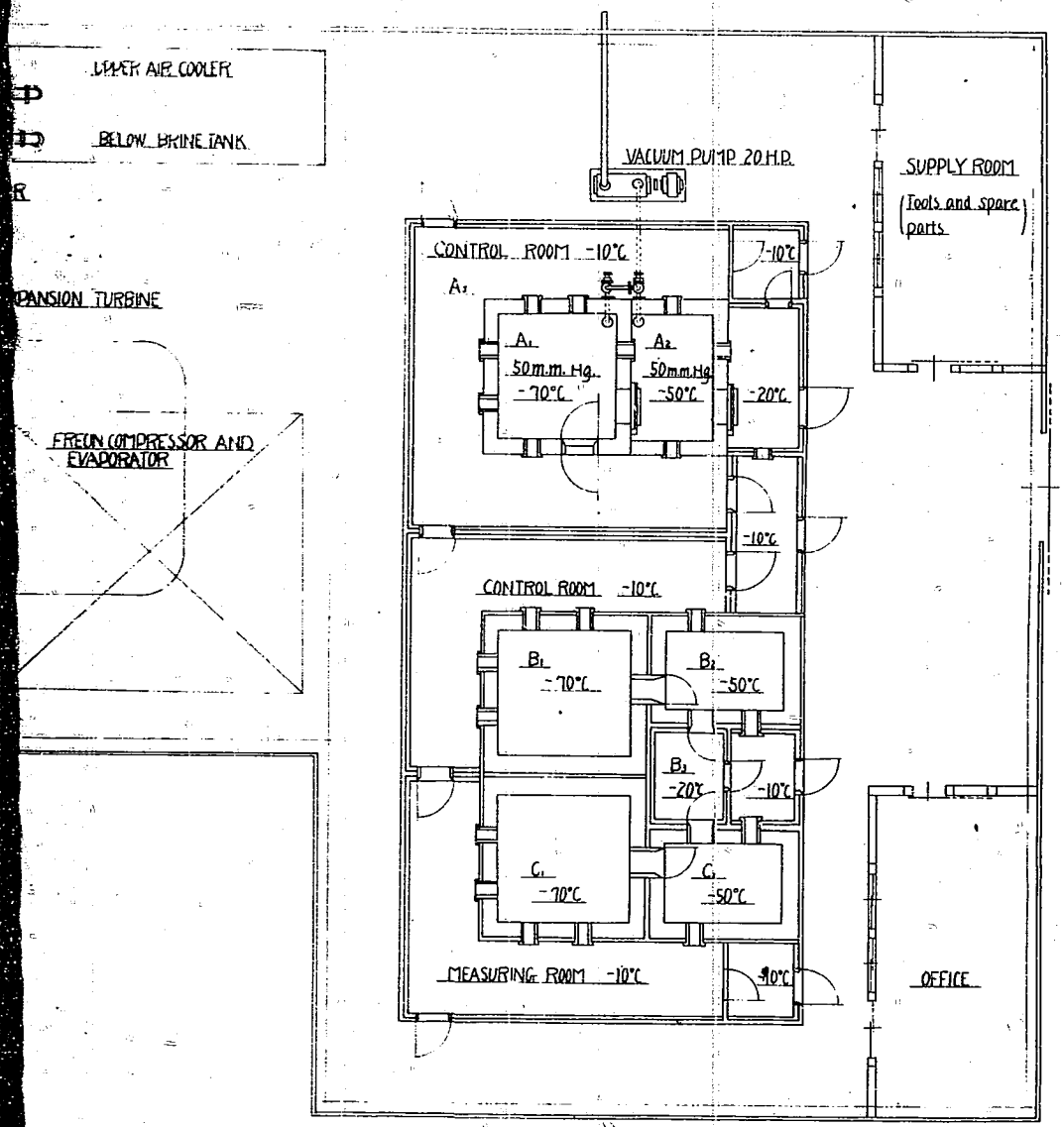
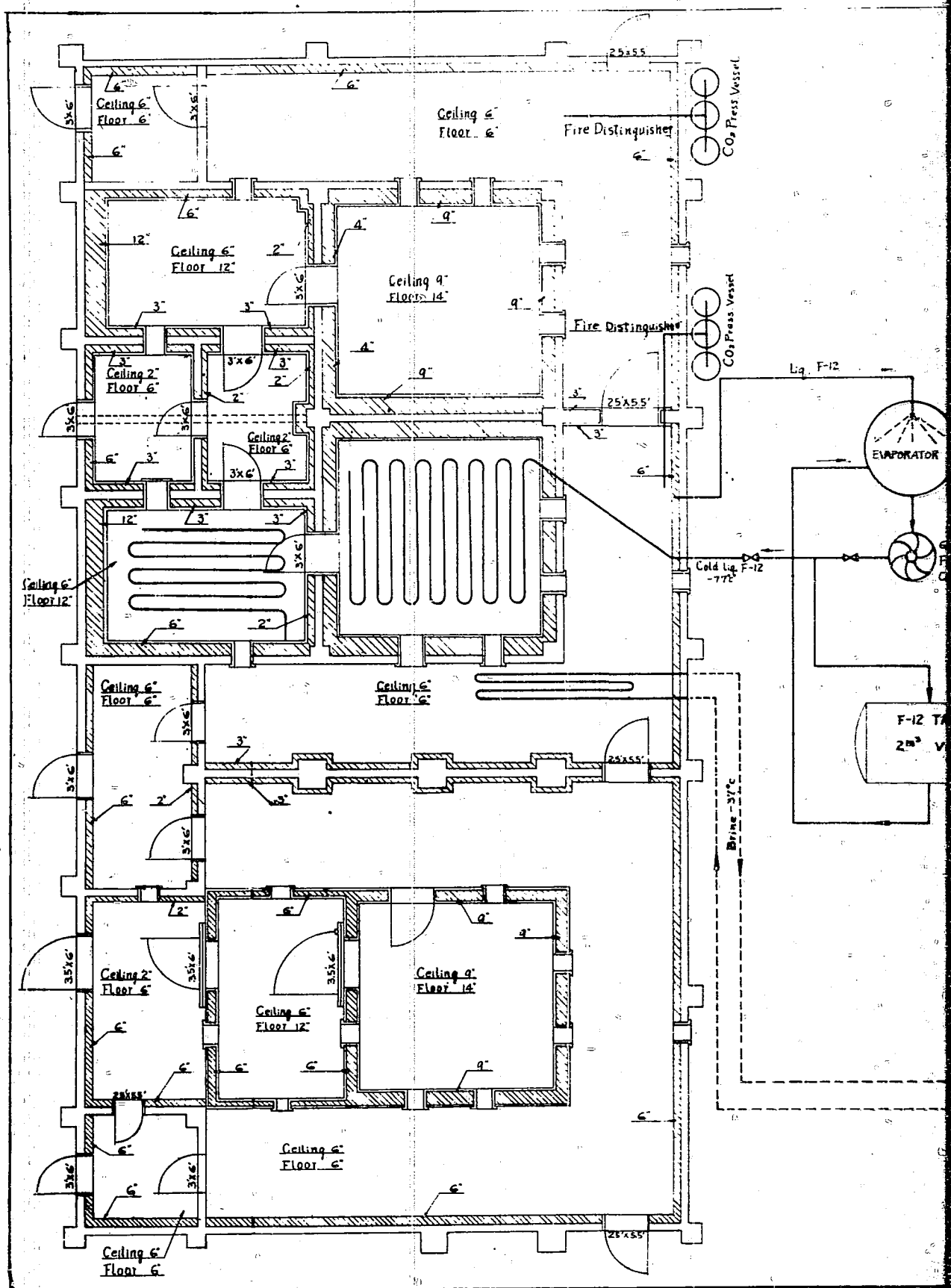


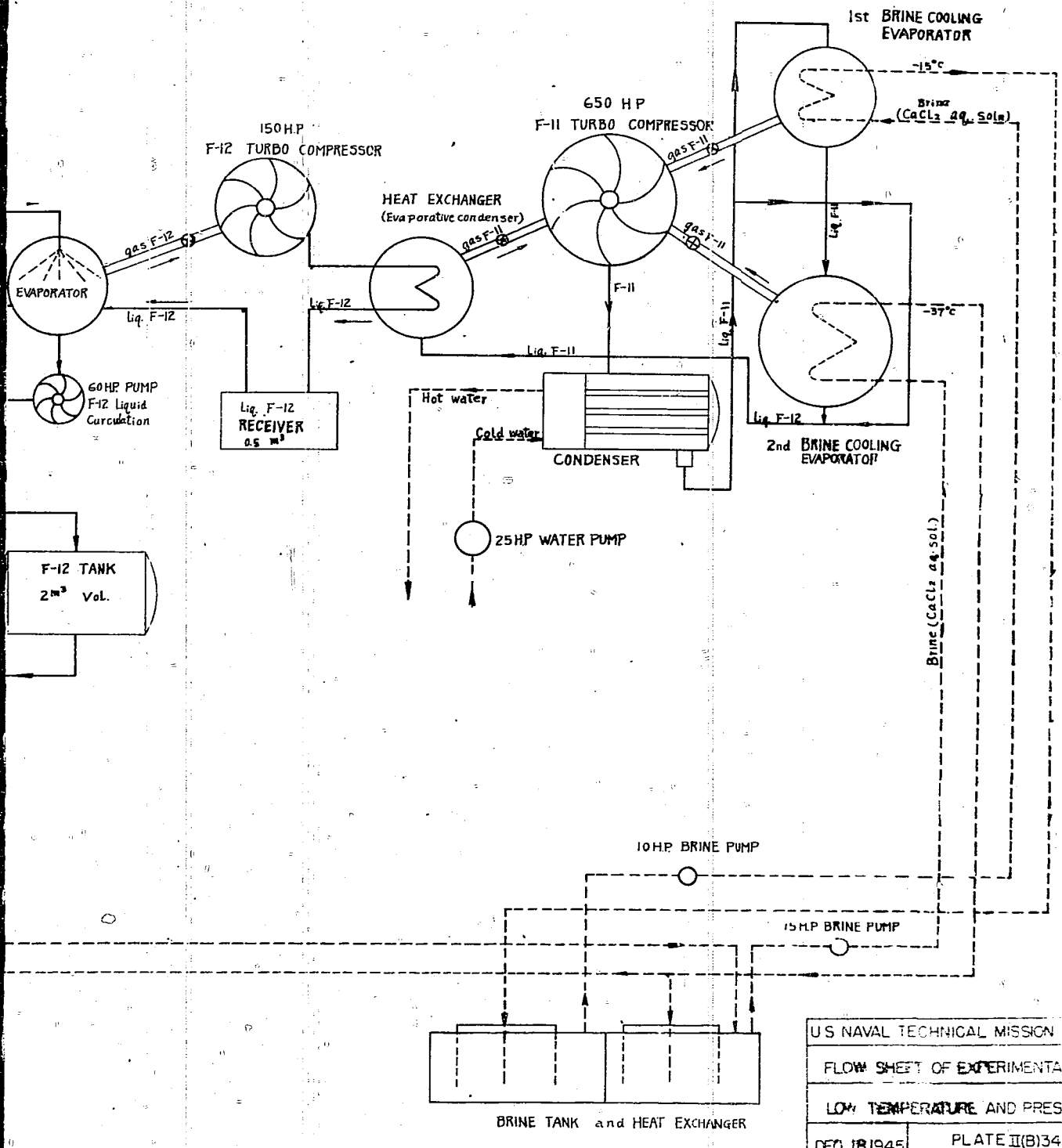
Figure 4(B)34
FREON REFRIGERATOR


WAITING ROOM
SUPPLIES AND SPARE PARTS
PREPARATION ROOM
FUEL ROOM
BLOWER
Intake air
SURGE TANK
MOTOR
REGULATING TANK
OBSERVATION ROOM
ENGINE ROOM
EXHAUST GAS COOLING TANK
AIR EXPANSION
REGULATING TANK
1st. VACUUM PUMP
MIXING TANK
MIDDLE COOLING TANK
2nd. VACUUM PUMP
3-TON HANGING RAIL
ELECTRIC DYNAMOMETER
150HP
LOAD RESISTANCE
SILENCER

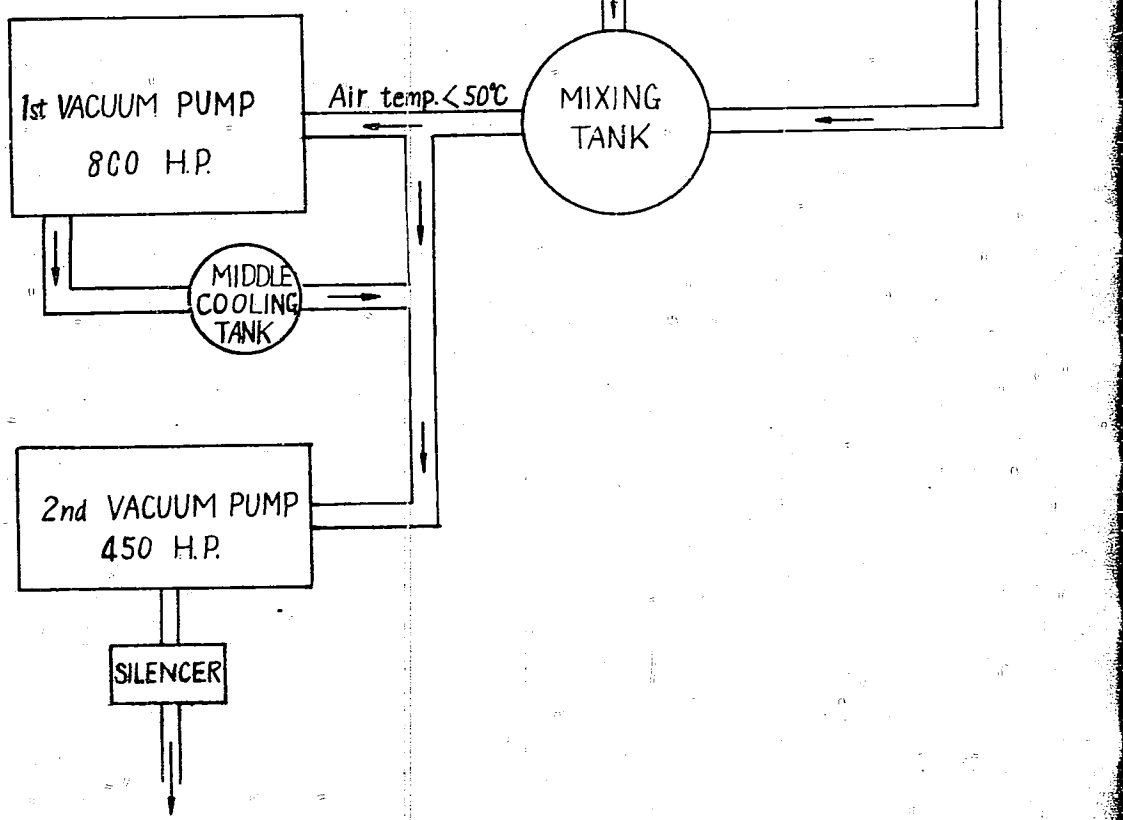


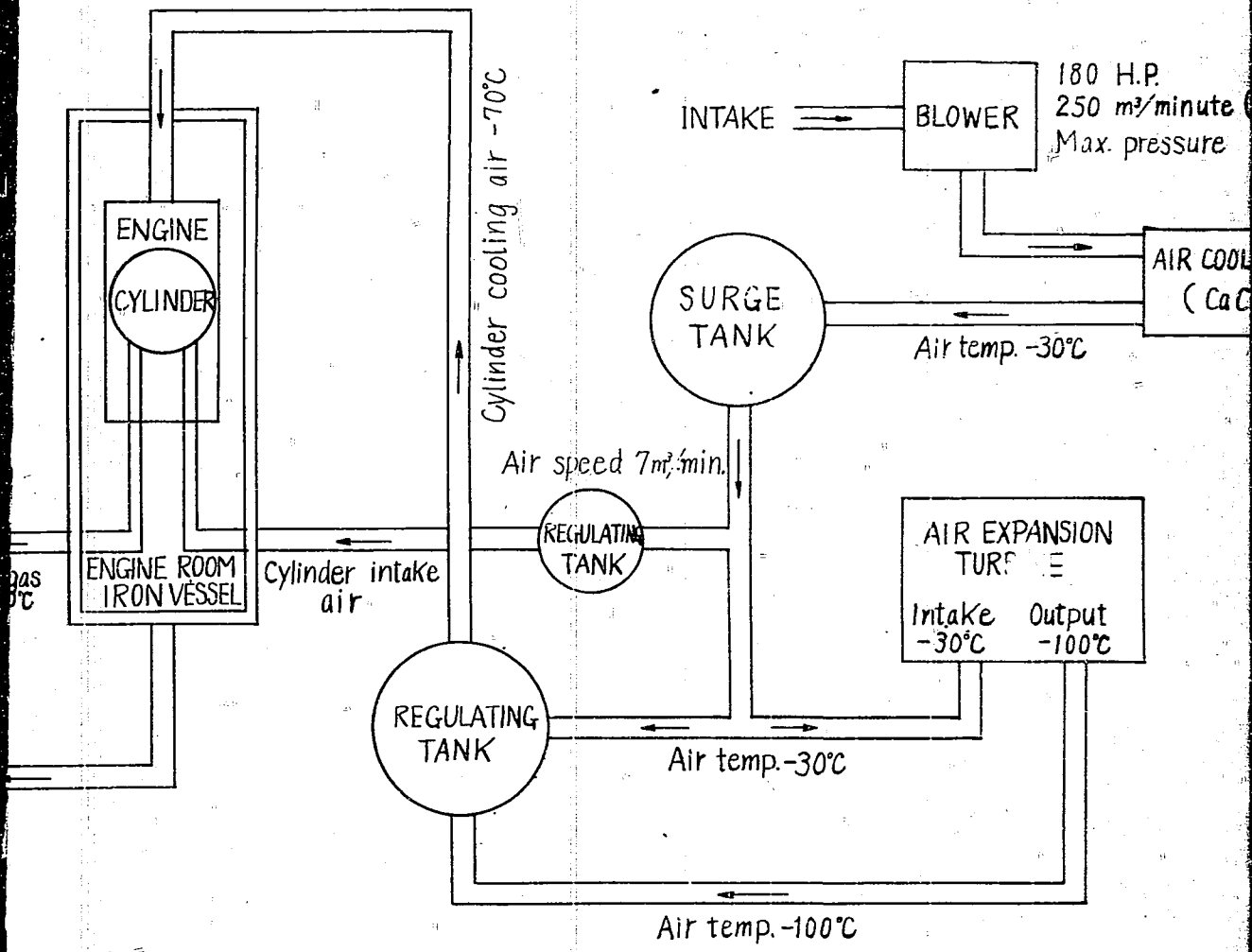
U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
GENERAL VIEW OF EXPERIMENTAL LABORATORY FOR		
LOW TEMPEATURE AND PRESSURE		
DEC. 14 1945	PLATE I(B)34	X-38(N)-2


Ceiling 6"
Floor 6"
Ceiling 6"
Floor 12"
Ceiling 9"
Floor 14"
Ceiling 2"
Floor 6"
Fire Distinguisher
CO_2 Press Vessel
Liq. F-12
EVAPORATOR
Cold liq. F-12
-7°C
Brine -3°C
F-12 T
2m³ V
25'x5.5'
3'x6'
3.5'x6'



U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
FLOW SHEET OF EXPERIMENTAL LABORATORY FOR		
LOW TEMPERATURE AND PRESSURE		
DEC 18,1945	PLATE II(B)34	X-38(N)-2


Engine room pressure reduced to 100 m.m. Hg. temperature not cooled directly.
ENGINE
CYLINDER
EXHAUST GAS COOLING TANK
Exhaust gas 600~700℃
ENGINE ROOM IRON VESSEL
1st VACUUM PUMP 800 H.P.
Air temp.<50℃
MIXING TANK
MIDDLE COOLING TANK
2nd VACUUM PUMP 450 H.P.
SILENCER



Air speed is shown by m³/minute, its volume data being converted to the state of 25°C and 760 m.m. Hg.

U.S. NAV
FLOW
ERATE
DEC 21,

180 H.P.
250 m³/minute (at 25℃, 760 m.m.Hg.)
Max. pressure 1000 m.m. Hg.

AIR COOLER BY BRINE
($CaCl_2$ aq. soln.)

30℃

NSION
E
utput
-100℃

lume
5℃

U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
FLOW SHEET OF LOW PRESSURE AND LOW TEMP-		
ERATURE ENGINE TESTING PLANT		
DEC 21,1945	PLATE III(B) 34	X-38(N)-2

ENCLOSURE (B) 35

PHOTOGRAPHIC INVESTIGATIONS OF FLAME PROPAGATION AND DETONATION IN ENGINE CYLINDERS

by

ENG. COMMANDER
K. NAKATA

Research Period 1933-1935

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

Dec. 1945

ENCLOSURE (B)35

LIST OF TABLES AND ILLUSTRATIONS

Figure 1(B)35 Schematic Diagram of the Test Apparatus ..... Page 407
Figure 2(B)35 Cylinder Head ..... Page 408
Figure 3(B)35 No Knock ..... Page 409
Figure 4(B)35 Incipient Knock ..... Page 409
Figure 5(B)35 Moderate Knock ..... Page 410
Figure 6(B)35 Severe Knock ..... Page 410

ENCLOSURE (B)35

SUMMARY

A small L-head single-cylinder testing engine was prepared for this work. It had a narrow quartz window as shown in Figure 2(B)35. Flame propagation in the cylinder was studied by photographs taken through the window.

I. INTRODUCTION

A. History of Project

These studies on engine combustion were started in March, 1933.

A small L-head, air-cooled single cylinder engine for agricultural use was installed. Its maximum speed was 2,500 RPM and the power about 1.5 hp.

A new cylinder head was designed, with a narrow slit along the center line of the head. A quartz window was made on this slit. It was constructed by the Hinode Co. in October 1933, and the experiments were performed during the period from April 1934 to March 1935.

B. Key Personnel Working on Project

Civil Eng. K. NAKATA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

Schematic figure of the test apparatus is shown in Figure 1(B)35. A film drum was mounted above the engine upon which a film of standard size (35mm) was wound. This drum was driven by a small motor of variable speed. A "Tessor" photographic lens of the aperture of $f \fallingdotseq 2.0$ and the focal length of 7cm was inserted between the engine and the film drum so as to be moved vertically by adjusting screws. The engine was connected with a D.C. motor of about 2 hp. This was used to start the engine and to give a load to it. Details of the cylinder head are shown in Figure 2(B)35. The window was made of transparent fused quartz. It was a square bar of 13mm x 13mm x 150mm.

B. Test Procedure

The engine was started by the motor. When all the engine conditions were settled after several minutes' running, a small quantity of sodium bicarbonate was put in the air intake to color the flame yellow. The film drum was rotated by the motor and the speed was adjusted to get a satisfactory figure. The cover of the film drum was opened and the shutter was operated.

When the knocking flames were to be photographed, 20-30% of ethyl nitrate was added to the fuel. As the compression ratio of the engine was small (≈ 4.0), no knocking occurred although an ordinary gasoline of low octane value (O.N.$\fallingdotseq 45$) was used.

C. Experimental Results

Many photographs were taken at different degrees of severity of detonation. This was done by the quantity of ethyl nitrate added to the fuel.

The reproductive sketch of these photographs are shown in Figures 3,4,5,6.

Flame speed was calculated from the slope of the flame front, and was the order of 10 m/sec at the middle portion of the combustion chamber. No flame was observed immediately after the ignition, i.e., the induction period was observed and this sometimes amounted to about 10 degrees of crank shaft revolution. This was equal to about 1/1500 second.

Flame velocities of knocking condition and non-knocking condition were compared but no difference was recognized between the portion from the spark position to the knocking position.

Flame speed at the knocking portion was intended to be measured, and the speed of revolution of the film drum was increased 2 or 3 fold, but the flame front was always vertical to the time axis in the knocking region. When the speed was increased, the result was that the image of the flame was faint and that it was difficult to determine the flame speed in the knocking region by such a method.

Vertically striped bright flame patterns were observed in the detonation region. The frequency of the patterns was measured and found to decrease as the piston went down in the cylinder. It was about 6,000 cycles near the T.D.C, and 5,000 at the end of combustion.

III. CONCLUSION

For the first time the author conducted an experiment on the study of combustion. In performing the above mentioned experiment he had not intended to draw any important conclusion from it but chiefly to enlighten himself. At first he was afraid whether such an engine which was designed by a physicist like himself could run satisfactorily.

But the engine ran successfully and was not destroyed by a severe detonation. He took many photographs of flame propagation. Thus, he became familiar with the engine combustion and also learned how to operate a gasoline engine. The flame speed of the order of 10 m/sec. at the center of the combustion chamber was smaller than he had expected. That was due to the flat combustion chamber and low compression ratio.

At that time there were many theories on detonation. One of them was that the flame propagation velocity before the occurrence of knocking would be faster in the case of the knocking condition than in the non-knocking condition, so the unburnt charge would be compressed adiabatically more in the case of the former than in the latter, and this caused the spontaneous ignition. The results of the author's experiment did not verify this fact. The flame velocities were the same in both cases.

The frequency of knocking sound was determined by tuning forks and decided to be nearly 6,000 cycles.

This coincided with the frequency of striped patterns observed in the knocking flame.

These patterns were supposed to appear by the adiabatic compression of burnt gas due to detonation waves. The next step of his work was to proceed to measure the pressure changes in the engine cylinder.

ENCLOSURE (B)35

FIG. 1. SCHEMATIC DIAGRAM OF THE TEST APPARATUS

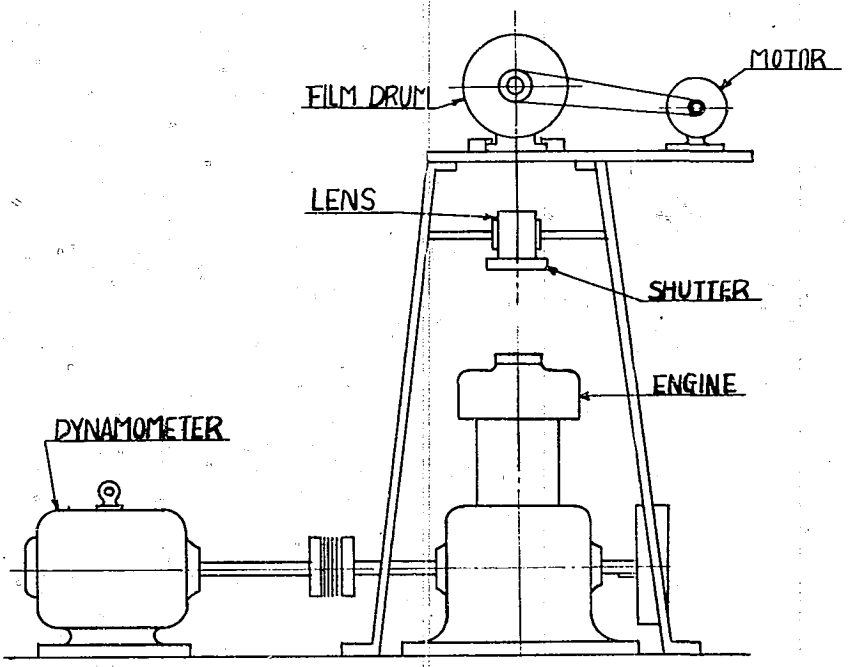


Figure 1(B)35

SCHEMATIC DIAGRAM OF THE TEST APPARATUS

ENCLOSURE (B)35

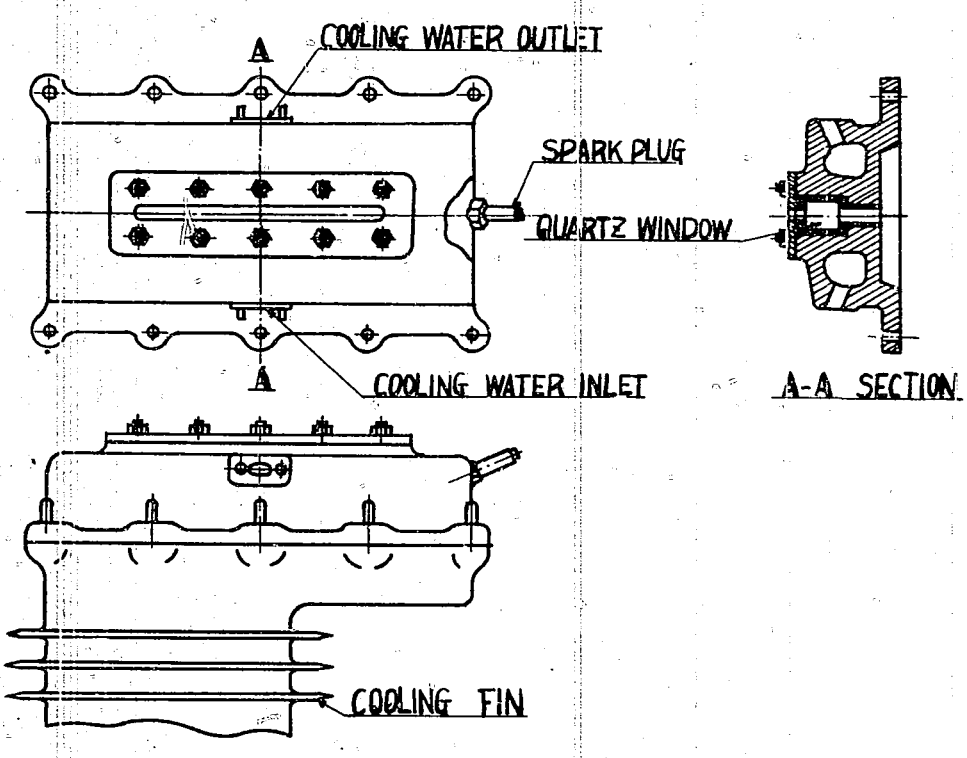


Figure 2(P)35
CYLINDER HEAD

ENCLOSURE (B)35

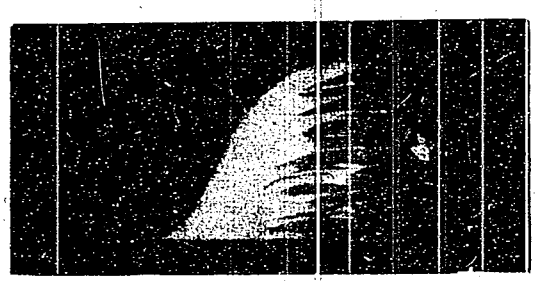


Figure 3(B)35
NO KNOCK

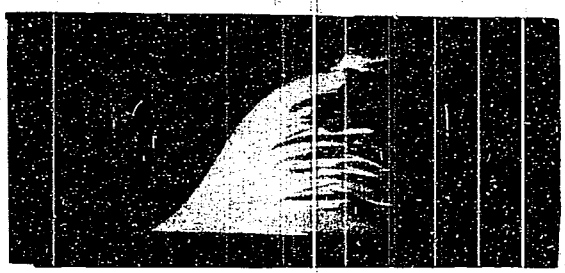


Figure 4(B)35
INCIPIENT KNOCK

ENCLOSURE (B)35

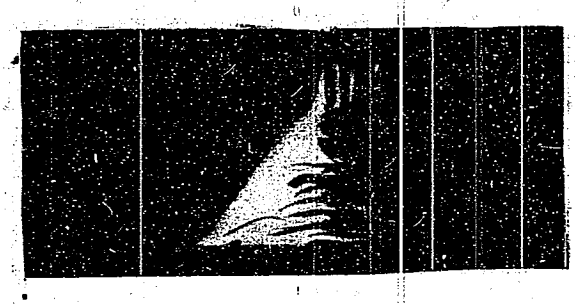


Figure 5(B)35
MODERATE KNOCK

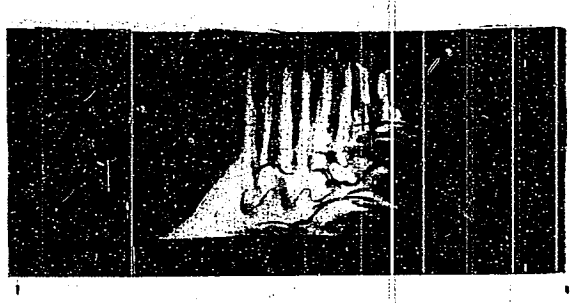


Figure 6(B)35
SEVERE KNOCK

ENCLOSURE (B) 36

ENGINE DETONATION STUDIED BY PIEZOELECTRIC INDICATOR

by

ENG. COMMANDER
K. NAKATA

Research Period: 1935-1939

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

Dec. 1945

ENCLOSURE (B)36

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ENCLOSURE (B)36

SUMMARY

To catch precisely the detonation waves in engine cylinders a pressure indicator of high natural frequency must be used. For this purpose, piezoelectric indicator was most suitable, but there was no reliable one in Japan when this work started. An effort was made to make this. Many types were made. Some types gave a good indicator card but they were innient in practical use, and some were rather brittle. The best one is shown in Figure 3(B)36. Tests were performed by C.F.R. engine, L-head engine with quartz window and B.M.W. single cylinder testing engine and they were proved to be satisfactory. It was used in many full scale engines including HOMARE, 2000 hp class engine to find detonation or to explore combustion phenomena.

Although it gave good indicator cards for small engines, there appeared vibrations on pressure line when used in high power engines. Since the frequency of these vibrations was not so high, it was not due to the defect of pick-up itself. Perhaps it was due to the vibration of amplifier valves caused by the severe pressure changes of surrounding air due to exhaust gas pulsation. This is unavoidable unless the amplifier is put in a sound-proof box. But these vibrations were not troublesome to find out detention or to calculate indicated horse power from the indicator card.

I. INTRODUCTION

A. History of Project

In the previous work in which flame propagation was photographed, bright striped patterns were found in the detonation flame. To determine whether this is due to the adiabatic compression or rarefaction in the detonation waves, it is necessary to measure the pressure inside the cylinder with an indicator of small inertia and high natural frequency. At that time, the Maihak indicator (spring type), the Farnbore indicator (balanced pressure type) and the Nakanishi indicator (optical type) were used at the First Technical Depot at YOKOSUKA. The Maihak indicator is not suitable for high speed engines. With the Farnbore indicator, one indicator card is obtained by a great many explosions and it is difficult to examine vibrations on the indicator card. With the Nakanishi indicator, the pressure line is broadened and faint. So it is not suitable for accurate measurement.

A piezoelectric indicator had been used at the Aeronautical Institute of Tokyo Imperial University. It was a water cooled type and as the rod which transfers pressure from diaphragm to quartz was long and the natural frequency was so low that undesirable vibrations were observed on the pressure line, even used on a small engine. It is necessary to give to the moving part a natural frequency of the order of 50,000 cycle. From April 1935 onwards the author tried to make an indicator of the air cooled type. So, many types were constructed, and many experiments were performed by many kinds of engines. These experiments were completed in the year 1939.

B. Key Research Personnel Working on Project

Naval Engineer K. NAKATA.

ENCLOSURE (B)36

II. DETAILED DESCRIPTION

A. Description of Test Apparatus and Test Procedure

The structure of the indicator designed at the outset is shown in Figure 1(B)36. The author was not free from the idea of old type using steel ball and lead wire conducted from the side of the case. The diaphragm was made from the same block as the case but the supporter of the quartz was a different piece from the diaphragm, so undesirable vibration appeared on the pressure line in the indicator card. So the second type was made, the structure of which is shown in Figure 2(B)36. In this type, the quartz supporter and the diaphragm were made in one piece and this was screwed in the case with a heated fitness. Four quartz pieces were used to get high sensitivity. This type gave a satisfactory results in regard to the smoothness of the pressure line, but as the height of the quartz was small, it had the tendency of leakage in a hot, humid season. After many trials, a type was reached which is shown in Figure 3(B)36. This type gave satisfactory results and preferably used in all cases.

Lead wire from the indicator to the amplifier must be shielded to avoid the disturbances from the ignition spark. When the wire vibrates, the distributed capacity between the wire and the shielding metal changes and this causes vibrations on the pressure line, so the wire must be kept rigidly in the center of the shielding metal. The wire, the structure of which is shown in Figure 4(B)36, gave the best results.

The vacuum tubes used in the amplifier was U X 54 for the first stage and six U X 171 A tubes in parallel for the second stage. Batteries were used as electrical source. These were put in a steel case to protect from electromagnetic disturbances.

The output from the amplifier was put in YOKOGAWA'S 6 element electromagnetic oscillograph, and the pressure-time curve in the engine cylinder was observed on the rotating mirror or photographed on the rotating film. A-type vibrator whose natural frequency in air is 6000 cycles was generally used.

The time mark on the film was made by the alternating current wave from the 1000 cycle vibrator.

A small hole was drilled at the periphery of the fly wheel. Light from a small pealamp was so arranged to pass through this hole when the piston was at Top Dead Center. The light which came through the hole fell on a photocell and the photocurrent flowed at the instant when the piston was T.D.C. The photocurrent was amplified by vacuum tubes and led to the oscillograph to give a T.D.C. mark on the film.

Ignition timing was marked on the film in the following manner. A wire was wound 2 or 3 times on the high tension wire used for spark ignition. Electric inductions were caused in this wire when ignition spark passed through the spark plug. These inductions were amplified and led to the oscillograph.

The indicator was always calibrated before and just after it was used by a gauge tester of the oil pressure type.

Cooling air for the indicator was sent from a small compressor. The oil vapour and the humidity in the cooling air were removed by the oil separator and $CaCl_2$ respectively.

B. EXPERIMENTAL RESULTS

1. Indicator Cards of C.F.R. engine. Figures 5(B)36 and 6(B)36 show the indicator cards taken with the C.F.R. engine and the former corresponds to no knocking and the latter knocking conditions. As the engine is small and the speed is low, the pressure lines are smooth. There are vibrations of small amplitude on the expansion line of the knocking indicator card. The frequency is measured and plotted against the crank angle shown in Figure 7(B)36. This is over 7000 cycle at T.D.C. and decreases as the piston goes down from T.D.C.

2. Indicator Cards of "Hinode" L-head Engine with the Quartz Window. By this engine, the indicator card and the photograph of flame propagation were taken simultaneously. A new cylinder head was constructed which had two plug holes, one of which was used for the ignition plug and the other for the indicator pick-up. In Figure 8(B)36, the indicator card and flame photograph corresponding to detonation are shown while in Figure 9(B)36 those corresponding to preignition. In the case of normal combustion, the pressure curve in the indicator card is smooth and no striped patterns were observed in the flame photographs. But in the case of detonation or preignition, pulsating pressure changes are observed corresponding to the striped patterns in the flame photographs.

Figure 10(B)36 is the plot of this frequency against the crank angle. The frequency of the striped patterns is also plotoed in the same figure. It is very curious that the frequency of the vibration in the pressure line is almost double that of the flame.

3. Indicator Cards of B.M.W. Testing Engine. This testing engine was constructed at the D.V.L. Laboratory in Germany. It has a water cooled B.M.W. single cylinder and is a variable compression type. In Figures 11(B)36 and 12(B)36 are shown some indicator cards of this engine. Figure 11(B)36 shows the normal combustion. Knocking occurred occasionally in the case of Figure 12(B)36. These indicator cards were taken in the early stage of this work (1937) and the indicator was not refined and so we find unfavourable vibrations on the pressure lines. The frequency of the knock vibration is plotted against the crank angle in Figure 13(B)36. The frequency is small compared with those observed in the C.F.R. engine or other small engines. This is due to the larger bore of this engine.

4. Indicator Cards of Kinsei, Homare, and other Full Scale Aero Engines. Many indicator cards were taken for the study of combustion and detection of detonation in full scale aero engines such as "Kinsei" and Homare. But none of them was left to-day. They were more improved than those shown in Figure 11(B)36 or 12(B)36. But when the engine was running with high power, vibrations began to appear on the pressure line. Judging from the nature of these vibrations it was supposed to be due to the vibrations of amplifier tubes which were compelled to vibrate by the severe pulsations of exhaust gas.

III. CONCLUSION

Piezoelectric indicator of the air cooled type was constructed and tested on every kind of engine. After many improvements the best type was determined.

There appeared vibrations in the pressure line when the engine detonated. The frequency of the vibration was larger when the engine was smaller and smaller

when a large cylinder was used. The frequency decreased as the piston went down from T.D.C.

When the indicator card was taken simltaneously with the photograph of engine flame, the number of vibration on pressure line was almost twice the number of bright striped patterns in the detonating flame.

As to the absolute value of the pressure, it was not satisfactory to use such an oscillograph of low natural frequency as was used in this work. It was preferable to use cathode ray oscillograph. The author had been preparing a cathode ray oscillograph but had no time to use it.

Figure 1(B)36

PIEZOELECTRIC INDICATOR - TYPE I

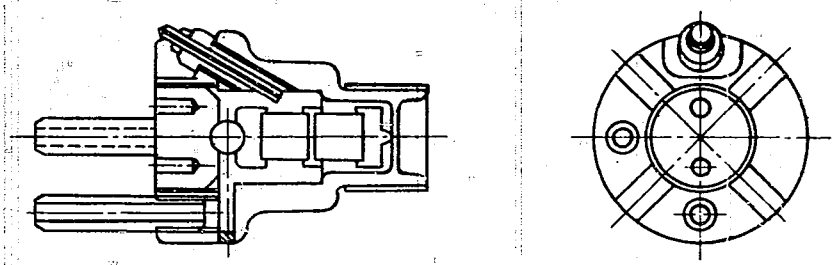
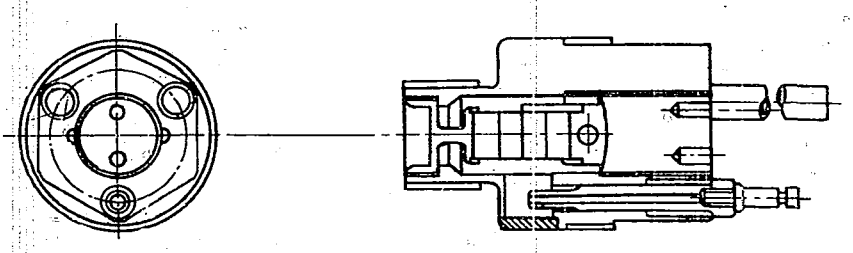


Figure 2(B)36

PIEZOELECTRIC INDICATOR - TYPE II



ENCLOSURE (B)36

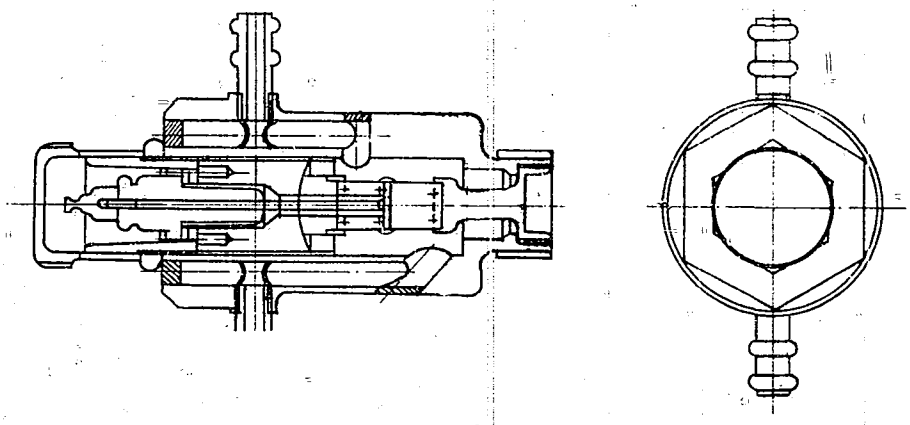


Figure 3(B)36
PIEZOELECTRIC INDICATOR - TYPE VII

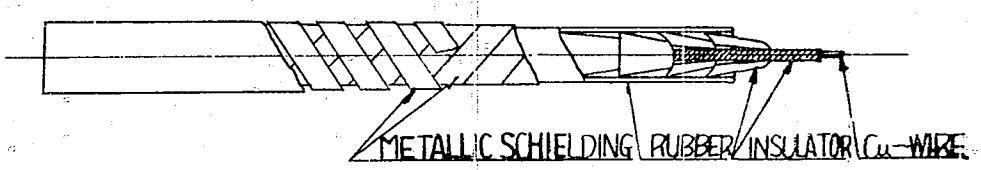


Figure 4(B)36
LEAD WIRE

ENCLOSURE (B)36

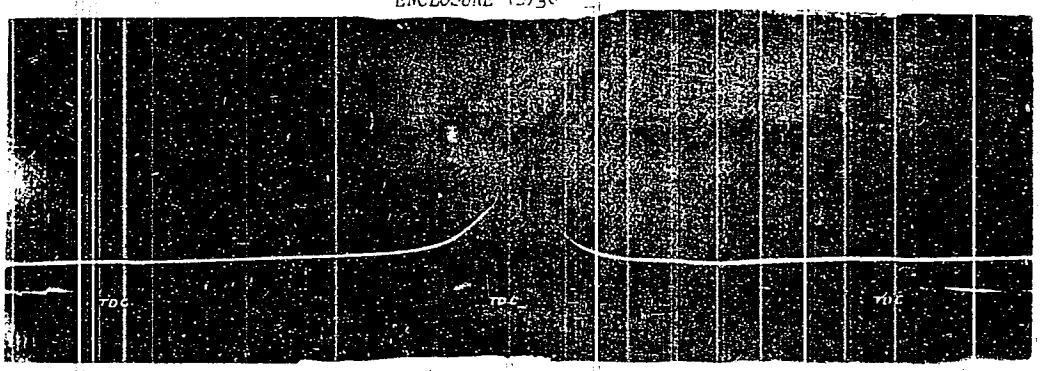


Figure 6(B)36

INDICATOR CARD OF A C.F.R. ENGINE
NORMAL COMBUSTION

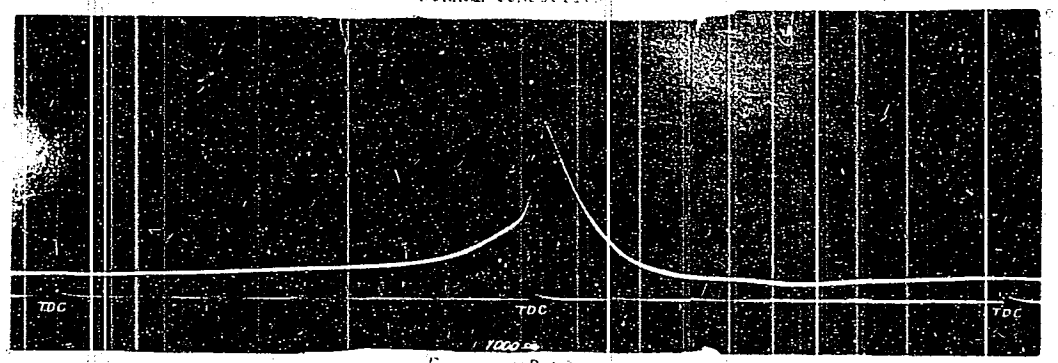


Figure 6(B)36

INDICATOR CARD OF A C.F.R. ENGINE
KNOCK CONDITIONS

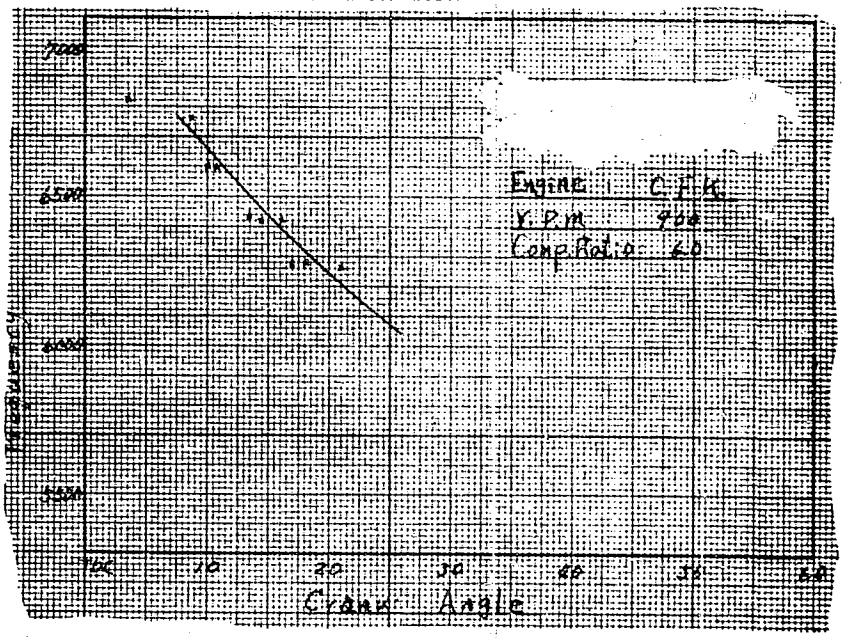


Figure 7(B)36

FREQUENCY OF DETONATION WAVES

ENCLOSURE (B)36

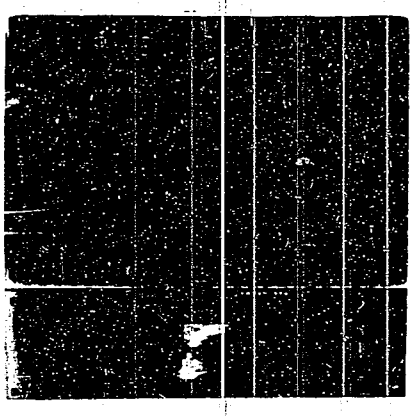


Figure 8(B)36

INDICATOR CARD TAKEN WITH HINODE L-HEAD ENGINE
FLAME PHOTOGRAPH CORRESPONDS TO DETONATION

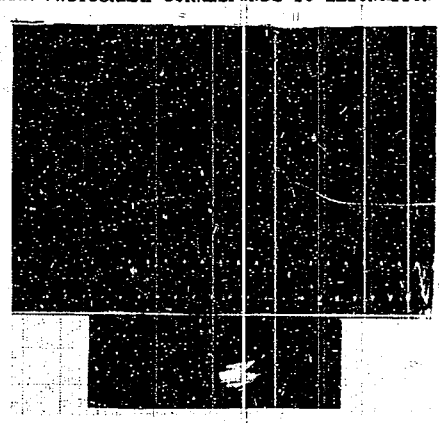


Figure 9(B)36

INDICATOR CARD TAKEN WITH HINODE L-HEAD ENGINE
FLAME PHOTOGRAPH CORRESPONDS TO PREIGNITION

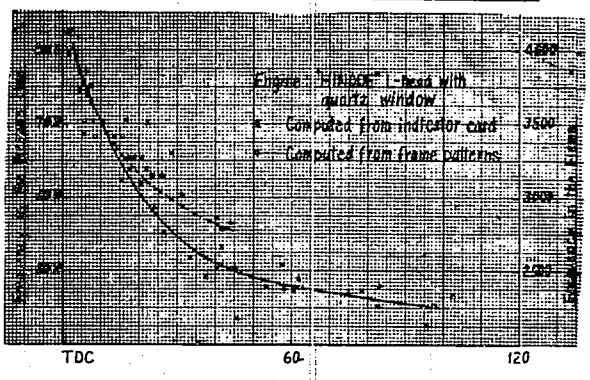


Figure 10(B)36

FREQUENCY OF DETONATION WAVES

ENCLOSURE (B)36

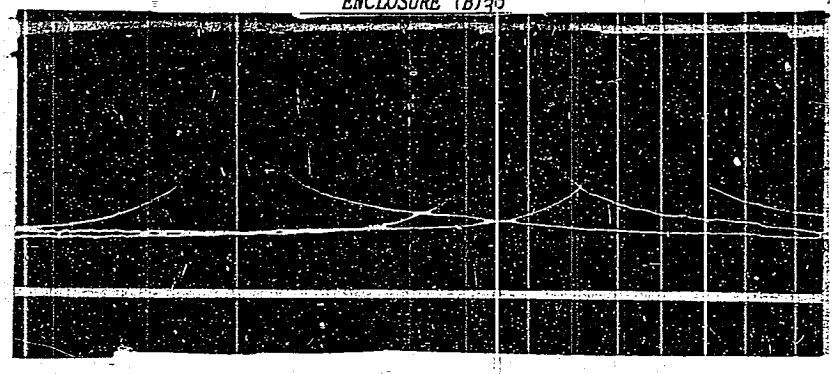


Figure 11(B)36

INDICATOR CARD OF B.M.W. SINGLE CYLINDER ENGINE
NORMAL COMBUSTION

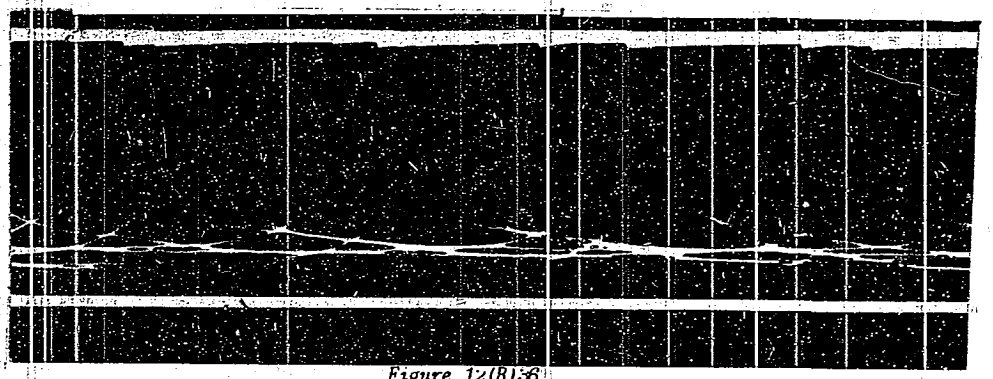


Figure 12(B)36

INDICATOR CARD OF B.M.W. SINGLE CYLINDER ENGINE
OCCASIONAL KNOCKING

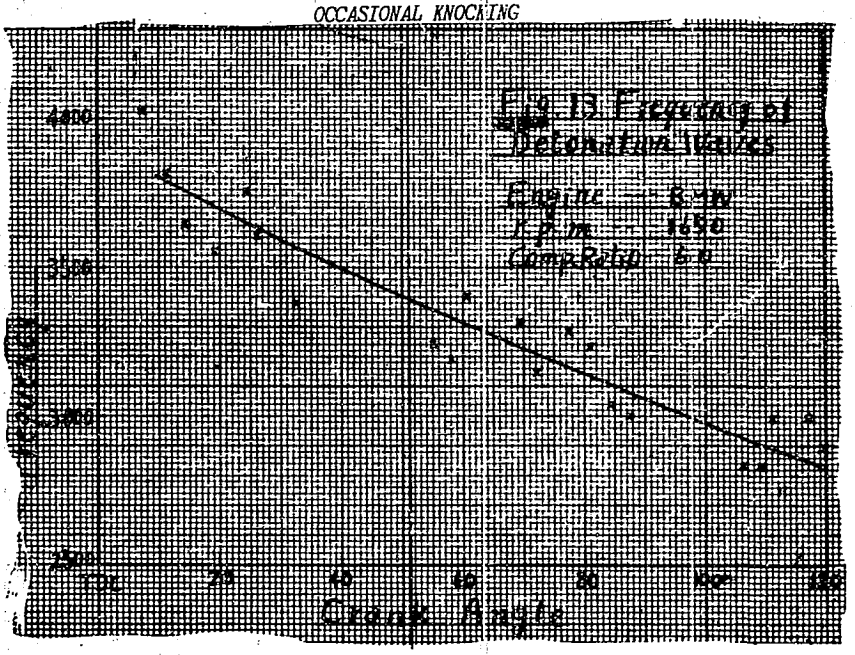


Figure 13(B)36

FREQUENCY OF DETONATION WAVES

ENCLOSURE (B) 37

FLAME PROPAGATION IN ENGINE CYLINDERS STUDIED BY THE IONIZATION METHOD

by

ENG. COMDR. K. NAKATA

Research Period: 1935-1940

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

December 1945

ENCLOSURE (B)37

LIST OF TABLES AND ILLUSTRATIONS

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Figure 5(B)37 Change of Flame Speed with Engine Speed ..... Page 428

ENCLOSURE (B)37

SUMMARY

Flame propagation in aero engine cylinders was studied by the ionization gap method. For an air cooled engine, the Kotobuki 9 cylinder radial engine was used and for a water cooled engine, the BMW single cylinder testing engine was used. Running conditions were varied and their effects upon speed were determined.

I. INTRODUCTION

A. History of Project

This work was carried out during the period from April, 1935 to March, 1940. There were still problems to be investigated with small testing engines, but our interest was directed to the study in full scale engines. As it was very difficult to put a quartz window over the head of a full scale engine, the ionization gap method was used. For this purpose, a specially designed small plug was prepared by the Tachikawa factory for the air cooled engine. As the engine did not belong to our party, experiments were performed intermittently when the engine was not occupied by other persons. For the water cooled engine, usual spark plugs were used as ionization gaps.

B. Key Research Personnel Working on Project

Eng. Lt. Comdr. K. NAKATA

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

For an air cooled aero engine, the Kotobuki nine cylinder radial engine was used Its essential dimensions were as follows:

Bore	146mm
Stroke	160mm
Compression ratio	5.25
Rated hp	460 hp
Rated revolution	2100 RPM

One cylinder was installed with one indicator and eight ionization plugs as shown in Figure 1(B)37. The structure of the ionization gap is shown in Figure 2(B)37.

For a water cooled engine, the D.V.L. variable compression testing engine was used. B.M.W. engine single cylinder was installed in this engine. Its main dimensions were as follows:

Bore	100mm
Stroke	180mm
Compression ratio	7.0
Speed	1400 RPM

Six holes were drilled equidistantly around the combustion chamber, as shown in Figure 3(B)37. One or two holes were used for ignition spark plugs and the remainder for ionization plugs.

ENCLOSURE (B)37

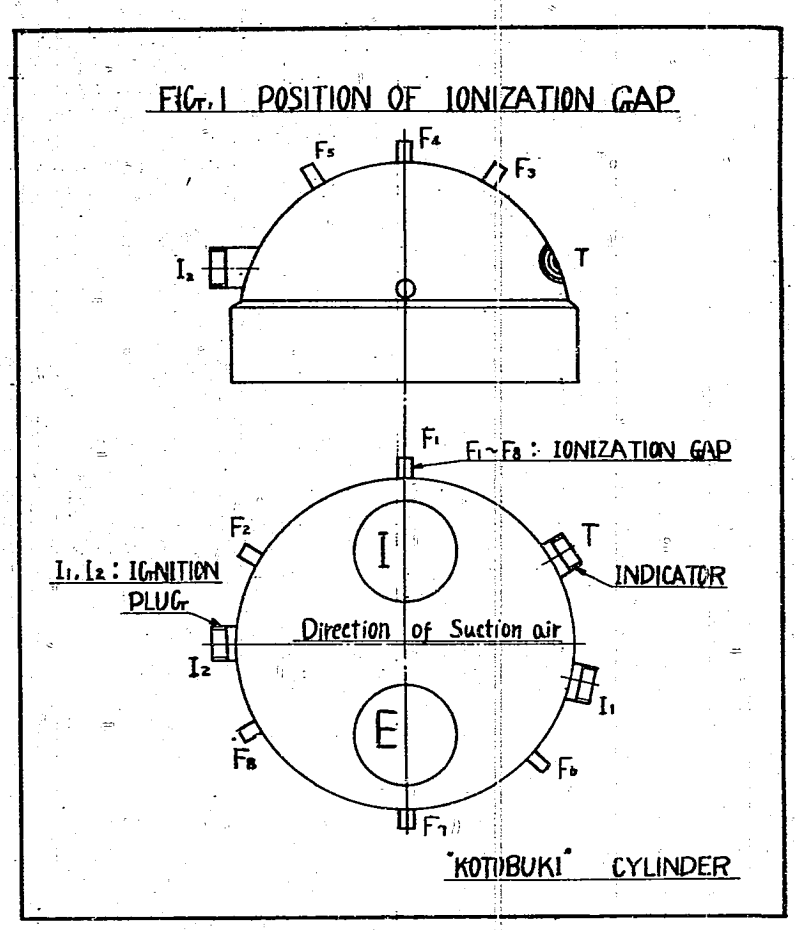

Figure 1(B)37
POSITION OF IONIZATION GAP

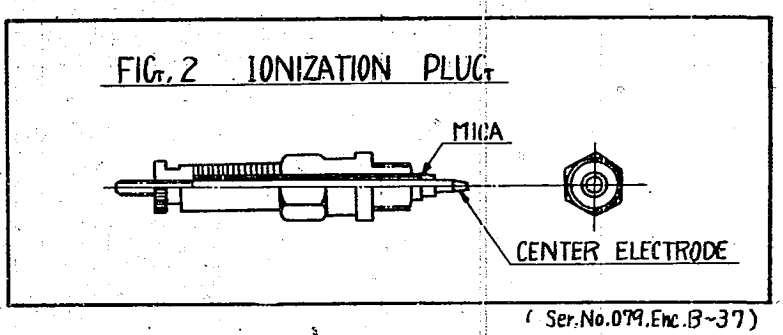

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Figure 2(B)37
IONIZATION PLUG

ENCLOSURE (B)37

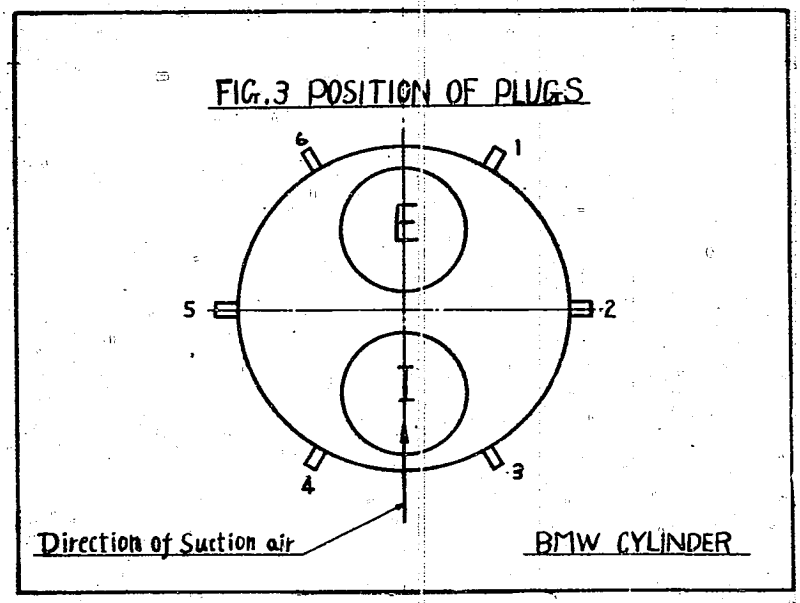

Figure 3(B)37
POSITION OF PLUGS

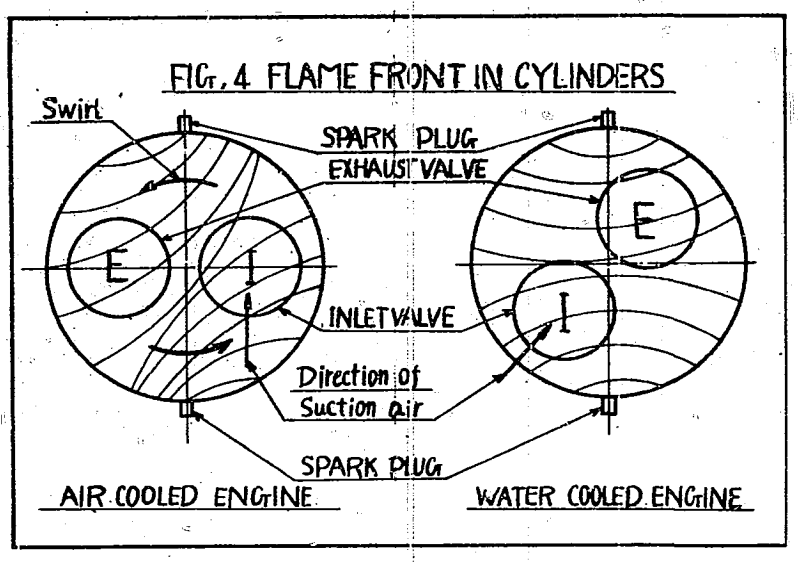

Figure 4(B)37
FLAME FRONT IN CYLINDERS

ENCLOSURE (B)37

B. Test Procedures

Experiments were performed as experimental conditions were varied as follows.

1. With Kotobuki engine

a. Three fuels of different octane values
b. Boost pressure
c. Mixture strength

2. With BMW engine

a. Engine speed
b. Number and position of spark plugs

The ionization current which flowed when the flame reached the ionization plug was the order of microamperes, so a X171A amplifier was used. The amplified current was led to an electromagnetic oscillograph. Fifty cycle AC waves were used for a time scale.

Oscillograms were developed and the distances between spark timing marks and ionization current marks were measured with a comparator. These were changed to propagation time using the time scale recorded on the same film.

C. Experimental Results

1. Kotobuki engine

a. Three fuels, with octane values 87, 85, 65 respectively, were tested under the same running conditions. It was found that the higher the octane value, the faster the velocity of flame propagation.

b. The effect of boost pressure on the flame propagation velocity was not remarkable. It was frequently masked by the effect of other running factors and could not be determined decisively, but it can be said that the higher the boost pressure, the greater the flame velocity.

c. The fuel supply was altered by operating an AC lever, but no air-fuel ratio meter, such as a Cambridge gas analyser was used at that time. Therefore, the accurate mixture strength could not be determined. The flame velocity was greatest when the output of the engine was largest. The flame velocity was greatly reduced with both rich and lean mixtures.

The flame ignited with two plugs, filled up the cylinder when the crank shaft was at an angle of 40-50 degrees. The mean velocity of flame propagation, calculated from this value, was about 20 m/sec. This was about twice the velocity obtained by the small L-head engine with a quartz window.

2. BMW engine

a. Revolution of the engine was varied from 500 RPM to 1400 RPM and the effect of engine velocity upon flame velocity was examined. Flame velocity was greatly increased with the engine speed. When the time for the flame to travel through the cylinder was plotted against the engine speed, a straight line

inclined to the right hand side as shown in Figure 5(B)37 (drawn from memory) was obtained. This must be due to the increase of vaporization of fuel in the carburetor and of the turbulence in the cylinder.

b. The mean flame propagation velocity, ignited by a single spark, was about 35 m/sec, and about 50 m/sec when ignited by two plugs. The effect of the position of the spark plug upon the flame velocity was also examined. The flame velocity was maximum when the plugs were situated between the inlet and exhaust valves.

c. When detonation occurred, it was also ascertained by this method that the last charge was burnt vigorously.

The flame front in the cylinder is supposed to be as in Figure 4(B)37. In the water cooled engine cylinder the flame propagated symmetrically referring to the line connecting two plugs, but in the air cooled engine it was distorted as shown in the figure. With the air cooled engine cylinder, the intake tube was connected tangentially to the cylinder, and the vortex was generated in the anticlockwise direction. The side of the flame assisted by this vortex went far from the plug, while the procedure of the side against the vortex was hindered. The intake tube to the water cooled engine was perpendicular to the cylinder; thus, no general circulation of the charge in the cylinder was generated. This was the reason why there was a difference in flame propagation between the air cooled and water cooled engine cylinders. The position of the last portion where detonation occurred was determined by drawing imaginary flame fronts. When unsuitable fuel was used, foreboding of piston burning was noticed in every cylinder at this portion, showing rough and granular appearances.

III. CONCLUSIONS

From the above results, the following conclusions were derived:

1. The velocity of flame propagation is increased with the speed of engine revolution.
2. The effect of boost pressure is not remarkable, but there is a tendency of increase of flame speed with boost pressure.
3. The flame velocity is much reduced by rich or lean mixture.
4. The flame velocity is higher with high octane fuels than with low octane fuels (within the limits of this experiment).
5. The last portion is instantaneously burnt when knocking occurs.
6. In a cylinder which has a tangential intake tube, the flame front is distorted by swirls.

In conclusion, the ion gap method is very convenient to investigate flame propagation in the cylinder of a full scale engine.

ENCLOSURE (B)37

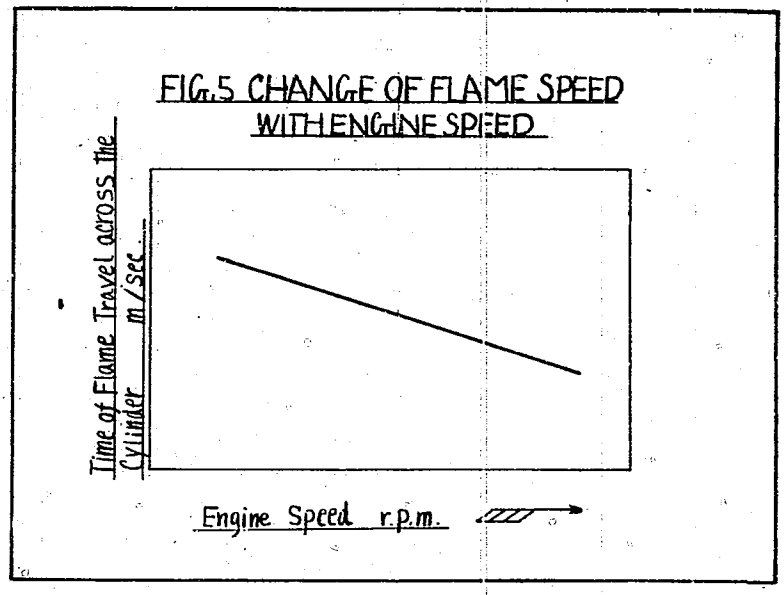

Figure 5(B)37
CHANGE OF FLAME SPEED WITH ENGINE SPEED

ENCLOSURE (B) 38

STUDIES OF SLOW OXIDATION OF HYDROCARBONS BY ABSORPTION SPECTRA

by

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Research Period 1939-1944

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U.S. Naval Technical Mission to Japan

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ENCLOSURE (B)38

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ENCLOSURE (B)38

SUMMARY

It is well known that the antiknock property of iso-octane is very good while that of normal heptane is very poor. To clarify the cause of this difference the slow oxidation method was adopted. The mixtures of these fuels and air were heated in a quartz tube, and their activities were examined by absorption spectra. Normal heptane reacted with oxygen at lower temperature and gave peculiar continuous absorption band, while isooctane was inactive with oxygen up to higher temperature.

I. INTRODUCTION

A. History of Project

Excellent reports were written by Withrow and Rassweiler on the subject of the mechanism of engine detonation. Nakata also constructed in 1938 an engine which had two quartz windows on both sides of the engine and a stroboscopic plate which enabled the flame to be observed at any phase of revolution. The object of this work was to study the mechanism of engine combustion by observing emission or absorption spectra of engine flame. As the engine was constructed unsatisfactorily, he began the work of slow oxydation in a quartz tube as Ubbelohde and Egerton had performed. This work was done from 1939 to 1944 when he came to the First Naval Fuel Depot at OFUNA.

B. Key Research Personnel Working on Project

Eng. Comdr. K. Nakata.

II. DETAILED DESCRIPTION

A. Description of Test Apparatus and Test Procedure

Schematic figure of the test apparatus is shown in Figure 1(B)38. Reaction vessel is a quartz tube with flat windows at both ends. The internal diameter and the length of the tube are 15mm and 800mm respectively. It has two side tubes with a stop cock near both ends and serve as mixture inlet and exhaust. Inside of them are two more small tubes inside of which are thermojunctions to measure the temperature of the reaction vessel. This vessel is surrounded by an electric furnace and the temperature of the quartz tube is to be raised up to 1,000°C. The distribution of the temperature inside of the reaction tube was measured by moving a thermojunction throughout the tube and was found to be almost constant. The maximum deviation was only 2°C.

Hydrocarbon air mixture was made by passing air bubble through the liquid hydrocarbon contained in a glass bottle which was kept in a thermostat. Misture strength was controlled by the temperature of the thermostat and examined by "Doi" type refractometer and was kept constant to be 13:1.

In the case of the flow method 60cc of the mixture was passed through the reaction tube per minute. In the case of the stagnant method, the temperature of the reaction tube was kept constant at the desired temperature, the tube was evacuated by a vacuum pump, and the tube was filled with the mixture at atmospheric pressure.

Adam Hilger's hydrogen discharge tube was used as the source of continu-

ous ultraviolet rays. Shimadu's small quartz spectrograph was used to take absorption spectra.

B. Experimental Results

1. Relationship between reaction temperature and octane number

a. Flow Method: Each of Isooctane, normal heptane and cyclohexane were each mixed with air, the mixture strength being 1:13, and the mixture was flown through the reaction tube. The temperature of the tube was raised slowly from room temperature, and the absorption spectrum was taken at every 10°C rise of temperature. These are shown in Figures 2(B)38 and 4(B)38.

(1) Isooctane Figure 2(B)38: No absorption nor any reaction examined by gas analysis was recognized till 450°C. At 460°C, the edge of the shortest wave length was absorbed faintly. If the temperature was higher than 460°C, the region of absorption became larger and the mixture was burnt with a blue flame.

(2) Normal heptane Figure 3(B)38: No absorption and no reaction till 200°C. At 210°C, reaction occurred and a peculiar continuous absorption band, the center of which being 2,600 Å, appeared. This has no structure in it. The nature of this band is not yet known and is called U-band for the present. The absorption area was broadened with a rise of temperature. A wave length shorter than the band remained till 230°C. At 240°C all under 3000 Å was absorbed and faint formaldehyde bands appeared at the edge of the spectrum. Formaldehyde bands became clear with the rise of temperature but they began to disappear above 470°C and a combustion took place with a blue flame.

(3) Cyclohexane Figure 4(B)38: No reaction took place till 300°C. At 310°C, the edge of the shortest wave length was absorbed like isooctane. At 320°C, the region of shorter wave length than 3,000 Å was absorbed and formaldehyde bands appeared near the end of the spectrum. This state continued till 370°C and then above this temperature the spectrum began to become longer. Above 450°C, the absorption reappeared but no formaldehyde band was observed. At 520°C the mixture began to burn with a blue flame and the spectrum became longer again.

From these results, it may be concluded that isooctane is stable with the temperature but low octane fuel such as normal heptane is active with oxygen at relatively low temperature. The absorption of cyclohexane at 310°C may take place in the form of a ring, but the absorption above 450°C may be due to a chain compound like isooctane resulting from the bond breaking. In the region between 380°C and 440°C no reaction was recognized both by spectrum and gas analysis. Oxygen which coupled loosely to the cyclohexane molecule below 370°C may be supposed to detach the molecule in the region of temperature between 380°C to 440°C.

b. Stagnant Method: To determine the accurate temperature at which reaction takes place, experiments were performed by the stagnat method. The reaction tube was heated at fixed temperature and evacuated, then the mixture was sent in and the cock was closed at the atmospheric pressure.

At every 5 minutes, absorption spectrum was taken, and for 2 hours kept constant at the same temperature. Internal pressure of the reaction tube was measured by the mercury manometer simultaneously. Gas analysis was also conducted after 2 hours' exposure if necessary. The same experiments were repeated by changing the temperature. At first normal heptane was mainly used as its reaction temperature was relatively low. Air-fuel ratio was kept constant to 13:1. Experimental results are shown in Figures 5(B)38 to 14(B)38. In these figures, pressure changes in the reaction tube measured at every 10 minutes are shown on the right hand side of the photographs. The explanation of these figures is as follow:

(1) Figure 5(B)38: Below 120°C, no absorption and no pressure change were observed.

(2) Figure 6(B)38: At 130°C, after heating 80 minutes a faint U-absorption band appeared and became darker as time elapsed. No pressure change was observed.

(3) Figure 7(B)38: At 150°C, after heating 25 minutes U-band began to appear and became evident as time went on. A slight depression in pressure was observed.

(4) Figure 8(B)38: At 160°C, after heating 15 minutes U-band began to appear and was clearer than that which was shown in Figure 7(B)38. The short wave portion below 2,400 Å still remained. Pressure change was still a depression.

(5) Figure 9(B)38: At 180°C, U-band appeared after heating 10 minutes. After 25 minutes all the spectrum below 2,900 Å disappeared. At this stage, faint formaldehyde bands could be detected near the edge of the spectrum (3,000 Å). These were scarcely recognized on the negative plate. At first the pressure decreased but after 30 minutes it increased.

(6) Figure 10(B)38: At 190°C, the portion of the spectrum below 2,900 Å was absorbed after heating it 5 minutes, without the appearance of the U-band. Formaldehyde bands were recognized faintly. Pressure in the reaction tube increased without initial depression.

(7) Figure 11(B)38: At 200°C, the spectrum was the same as in Figure 10(B)38 but the pressure increase was remarkable.

(8) Figure 12(B)38: At 230°C, reaction took place immediately after the mixture had been introduced into the reaction tube. After 5 minutes, all below 2,900 Å disappeared. Formaldehyde bands were clearly observed even on the positive print. But as time elapsed spectrum became longer and showed the disappearance of such substances which absorbed these portions of the spectrum. Pressure increased remarkably but it was interesting to observe its depression after 100 minutes.

(9) Figure 13(B)38: At 250°C, the reaction took place vigorously, immediately after the mixture had been introduced into the tube and below 2,900 Å was entirely absorbed. As time elapsed, spectrum became longer and formaldehyde absorption bands appeared clearly. Pressure increased for 30 minutes and remained constant for about 30 minutes: then

it began to decrease. The maximum and the last pressures were lower than in the case shown in Figure 12(B)38

(10) Figure 14(B)38: At 280°C, the reaction very abruptly occurred, but the recovery of the spectrum was remarkable and after 100 minutes the mixture was almost transparent down to 2,300 Å. The pressure of the mixture rose initially but decreased after 60 minutes and the last pressure was slightly higher than the atmospheric pressure.

From the above results the following conclusions may be drawn:

(1) The appearance of U-band is accompanied by the depression of the pressure.

(2) When formaldehyde bands appear, the portion of the spectrum below 2,900 Å is also absorbed and the pressure increases. With the rise of temperature, the pressure increases more and more, perhaps according to the decomposition of the substances which absorb light.

(3) At higher temperatures, these substances oxidized and polymerized, so the pressure decreases and the absorption disappears.

It is natural that in the stagnant method reaction occurs at lower temperature compared with the flow method.

Next, 6 samples of fuel whose octane values are 0, 20, 40, 60, 80, 100 respectively were obtained by mixing isooctane and normal heptane. The reaction temperatures of these samples were observed by the stagnant method. When they are plotted taking octane value as abscissae, a curve is obtained as shown in Figure 15(B)38. The reaction temperatures of hexane, isopentane, cyclohexane, benzene and isopropyl ether as representatives of normal paraffins, isoparaffins, naphthenics, aromatics and fuels which have oxygen in their molecules were measured by the same method. They are shown in the second column of the following table.

Table I(B)38

Reaction Temperatures and Octane Numbers

	Reaction Temp.	Octane No. from Reaction Temp.	C.F.R. Octane Number
Hexane	230°C	60	59
Isopentane	270°C	86	86
Cyclohexane	260°C	80	79
Benzene			130(?)
Isopropyl ether	210°C	48	98

Octane numbers obtained by the curve in Figure 15(B)38 are shown in the third column. In the fourth column, octane values obtained by C.F.R. motor method are shown as comparison. Except for isopropyl ether, octane numbers obtained by reaction temperatures agree well with those obtained by the C.F.R. motor method. Benzene itself has selective absorption in the region of 2,600 Å, so the reaction temperature can not be determined. The C.F.R. octane value of isopropyl ether is very high but that obtained by the reac-

tion temperature is very low. This must be due to the difference of combustion mechanisms, and be thought as the means of studying combustion mechanism.

2. Gas analysis

To investigate the substance which gives U-band i.e., the substance which gives continuous absorption band, its center being at 2,600 Å, the mixture of normal heptane and air was taken out of the reaction vessel after two hours' exposure at the temperature between 130° and 150°C and the consumptions of O_2, C_7H_{16} and production of CO_2 etc. were measured by gas analysis. CO_2 was not generated and the same number of mols of O_2 and C_7H_{16} was found to be consumed. Judging from the fact that when U-absorption band occurs, the pressure of the mixture decreases, the substance which gives U-band may be a peroxide of some sort composed of one molecule of normal heptane which is coupled with one molecule of O_2 loosely. The examination of the existence of peroxide by acidic solution of potassium iodide and starch revealed to be positive. 170°C is the temperature at which the portion below 2,900 Å is absorbed, the formaldehyde bands appear faintly and pressure of the mixture rises slightly. The result of the test for the existence of formaldehyde at this temperature was positive.

These relations are shown in Figure 16(B)38.

The supposed mechanism of slow oxidation of normal heptane at the initial stage may be as follows.

$$C_7H_{16} + O_2 \rightarrow C_7H_{16}.O_2 \rightarrow \overset{H}{H}>C=O + H_2 + C_{5H11}\overset{H}{>}C=O.$$

U-band — Formaldehyde band — Absorbs below 2,900 Å

3. Effect of tetra ethyl lead

Three samples of normal heptane and air mixture, one of which being normal heptane only and the others containing tetra ethyl lead 0.1% and 0.2% respectively, were experimented in the same way as is shown in (1). The temperature at which the U-absorption band appears was the same with or without tetra ethyl lead. The remarkable difference was that at higher temperatures absorbed spectrum became transparent as time elapsed when normal heptane alone is used as shown in Figures 13(B)38 and 14(B)38, but when a small quantity of tetra ethyl lead was contained in normal heptane, absorption continued up to higher temperatures.

4. Engine test of fuel which contains small quantity of substence which gives U-band

A small quantity of the substance which gives the U-absorption band was taken out of the reaction vessel by cooling the exhaust gas with ice. This was mixed with a gasoline and a test was conducted so as to see whether it was easy to detonate by the C.F.R. engine and it was found that this was true.

III. CONCLUSION

A. If a fuel of low octane value such as normal heptane is mixed with air and heated to commence slow oxidation in a quartz tube, reaction takes place at a very low temperature, say 130°C, and some substance is generated which gives a continuous absorption band in the region of wave length 2,600 Å

As the temperature rises the portion of the spectrum below 2,900 $\mathring{A}$ is absorbed and formaldehyde bands appear in the region of 3,000 $\mathring{A}$.

B. High octane fuels such as isooctane do not give such absorption, and at relatively higher temperature, say 300°C, absorption occurs at the shortest wave length region and gives formaldehyde bands.

C. At still higher temperatures, formaldehyde bands begin to disappear and by and by the spectrum recovers its length.

D. The first absorption of cyclonexane-air mixture begins at a temperature between that of normal heptane and isooctane and the form of absorption differs from both. If the temperature is increased above this, absorption disappears but at higher temperatures absorption occurs again and this resembles the absorption of isooctane.

E. Octane numbers of hydrocarbons except aromatics can be determined by the reaction temperature thus determined.

F. In the case of normal heptane, the appearance of the peculiar absorption band accompanies the depression of the pressure of the mixture and this is due to the formation of a peroxide which is composed of one molecule of normal heptane and oxygen.

G. At the stage when formaldehyde bands appear, all the shorter wave length portions are absorbed and the pressure in the reaction vessel increases.

H. At higher temperatures, these absorptions disappear by and by and the pressure in the reaction vessel which have been increased by the appearance of formaldehyde bands begins to decrease.

I. There is an indication of peroxide when the U-band appears in the spectrum and of formaldehyde when its bands are recognized. The slow oxidation of normal heptane is supposed to be as follows.

$$C_7H_{16} + O_2 \rightarrow C_7H_{16}\cdot O_2 \rightarrow \overset{H}{H} > C = O + H_2 + C_5\overset{H}{H}_{11} > C = O.$$

J. The existence of tetra ethyl lead in normal heptane does not suppress the formation of the substance which gives the U-band, but it has some effect on the recovery of spectrum (i.e., decomposition of polymerization of absorbing substances) at higher temperature.

ENCLOSURE (B)38

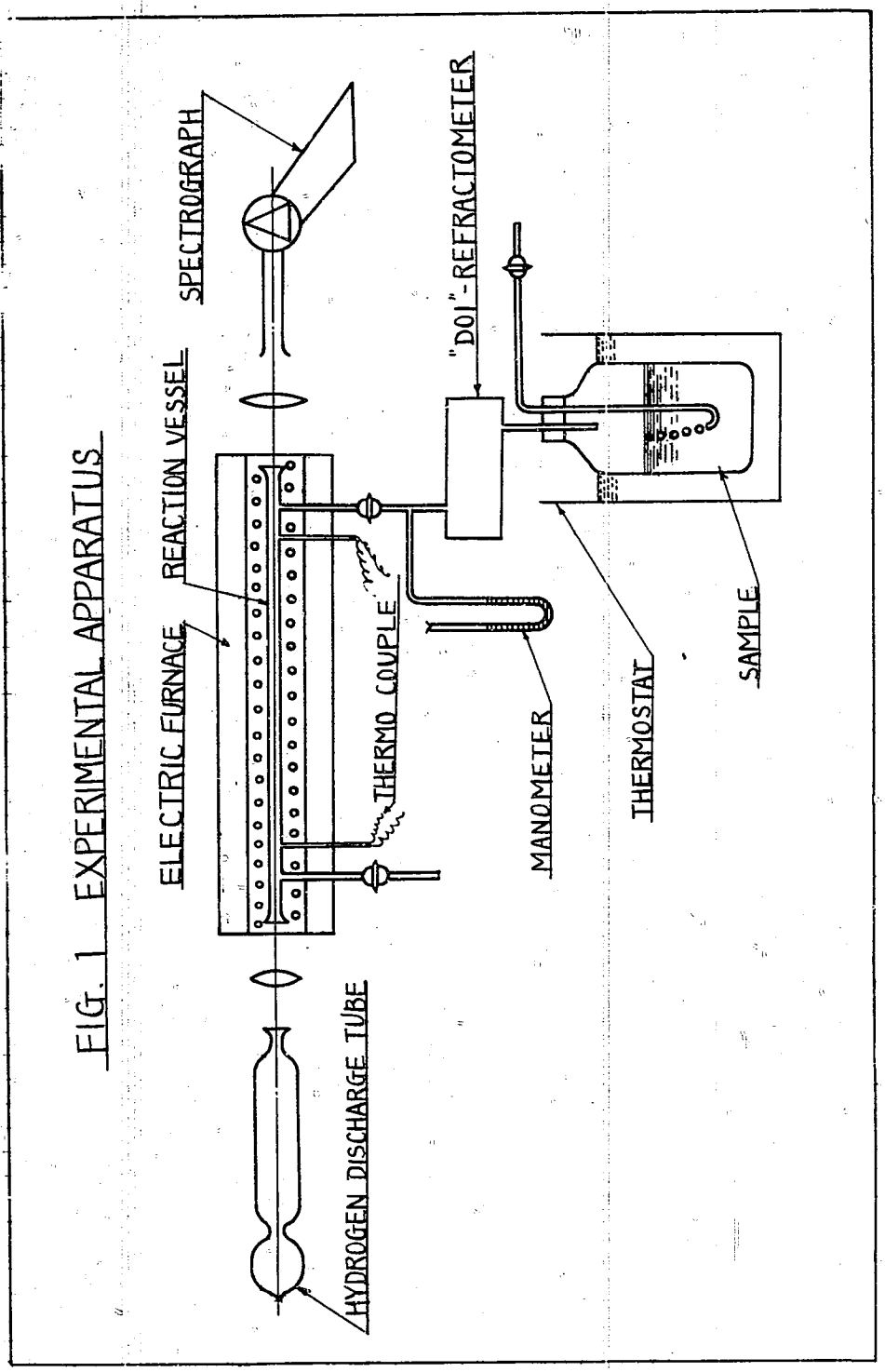


Figure 1(B)38
EXPERIMENTAL APPARATUS

ENCLOSURE (B)38

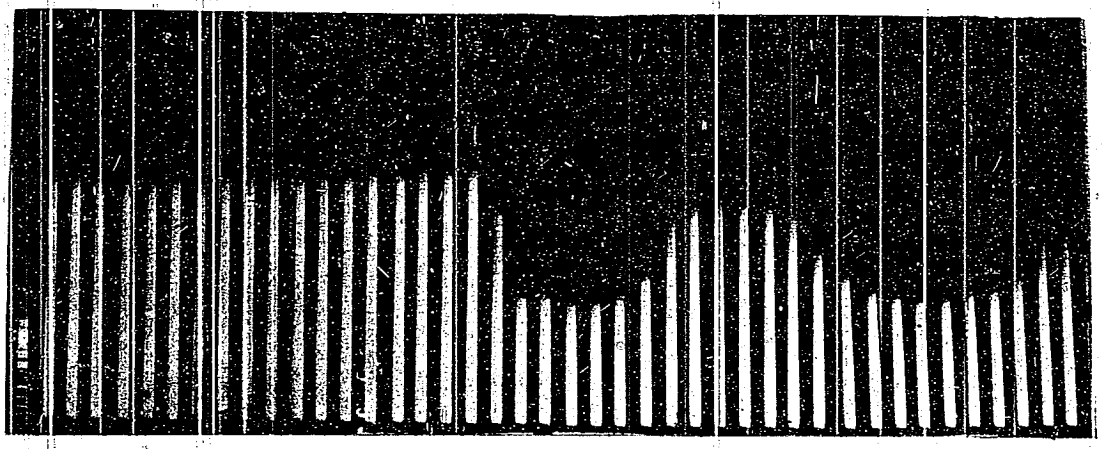


Figure 1(B)38
ABSORPTION SPECTRA OF CYCLOHEXANE

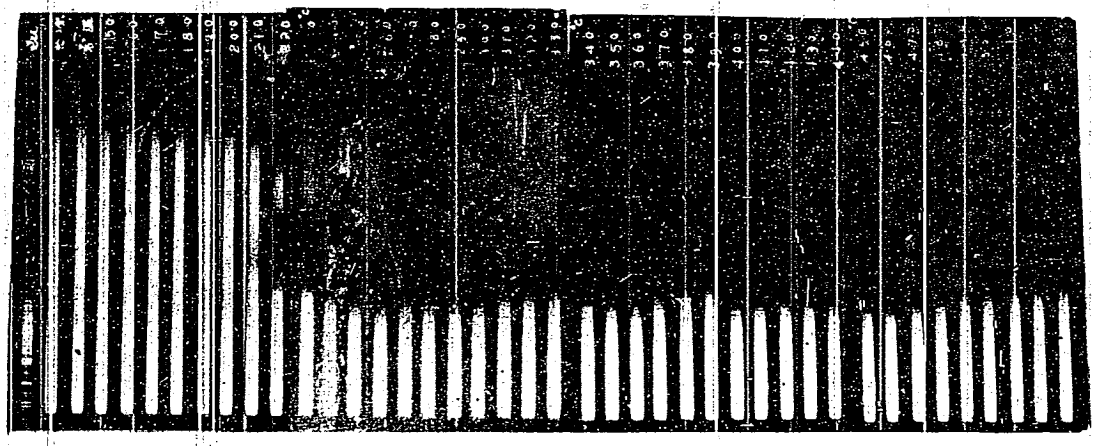


Figure 3(B)38
ABSORPTION SPECTRA OF NORMAL HEPTANE

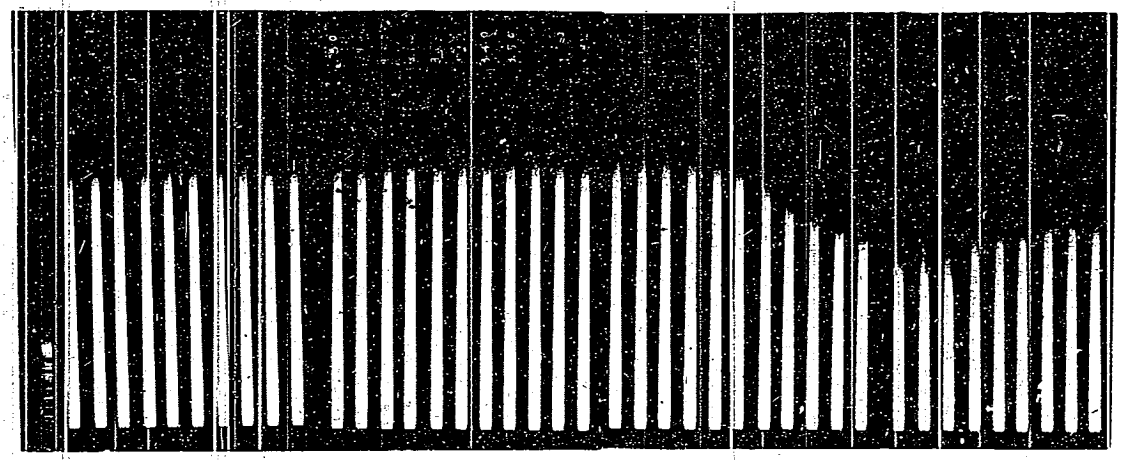


Figure 2(B)38
ABSORPTION SPECTRA OF ISO-OCTANE

ENCLOSURE (B)38

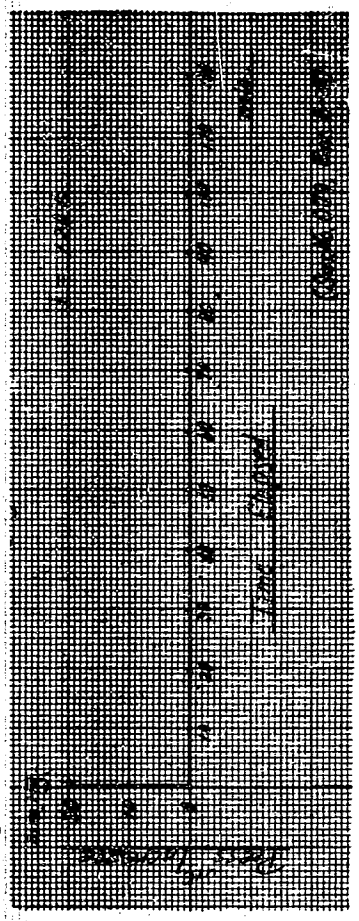


Figure 5(B)38
n-HEPTANE, REACTION TEMP. = 120°C

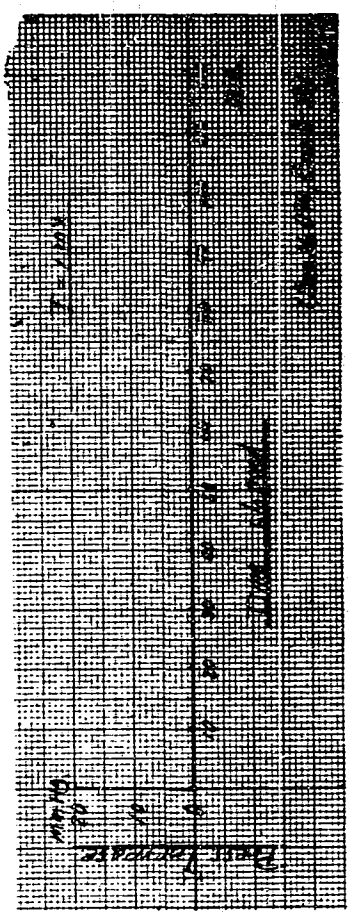
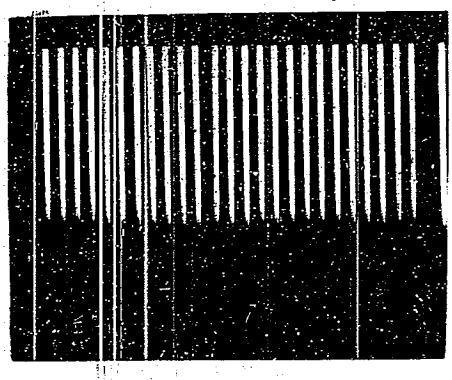
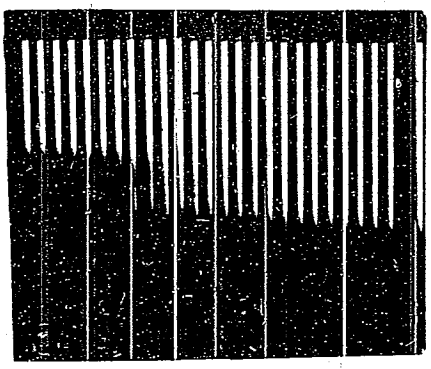


Figure 6(B)38
n-HEPTANE, REACTION TEMP. = 130°C





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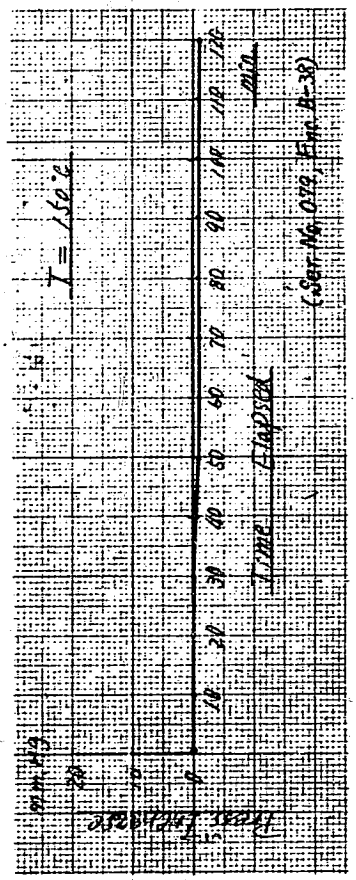


Figure 7(B)38
n-HEPTANE, REACTION TEMP. = 160°C

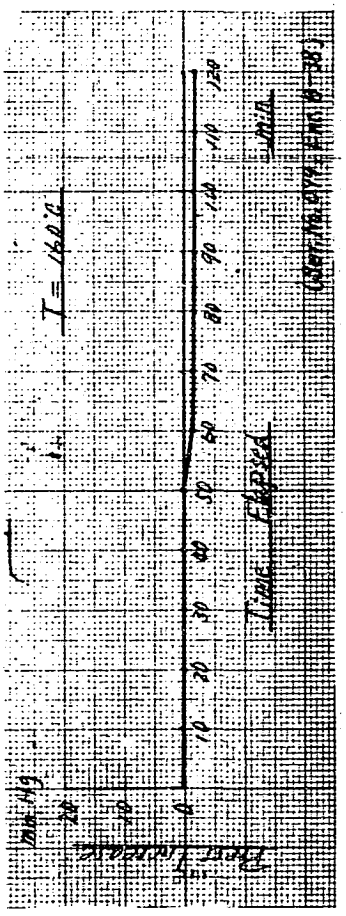
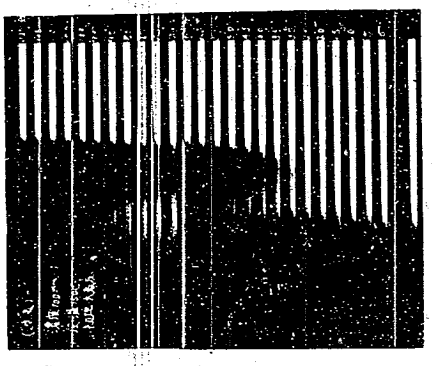
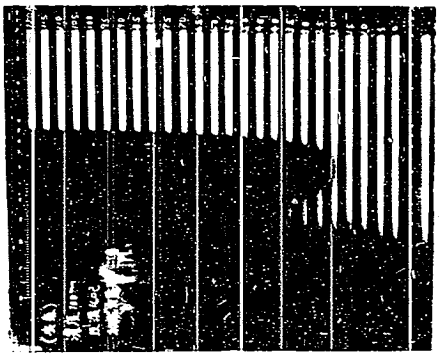


Figure 8(B)38
n-HEPTANE, REACTION TEMP. = 160°C





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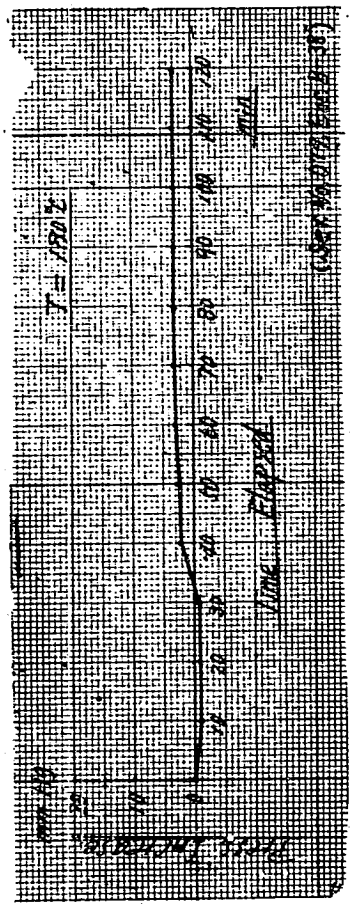


Figure 9(B)38
n-HEPTANE, REACTION TEMP. = 180°C

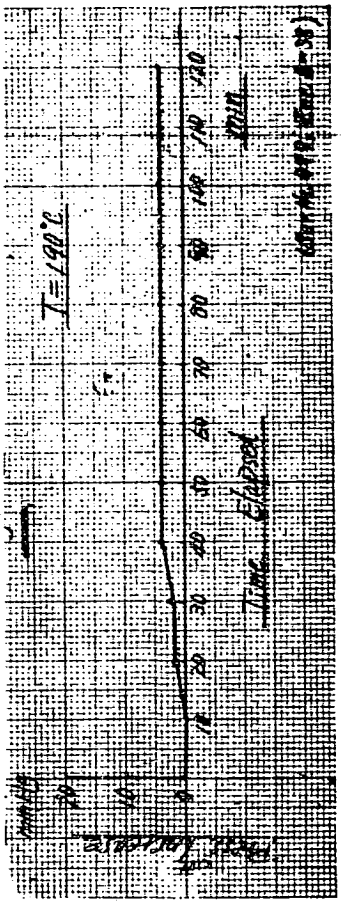
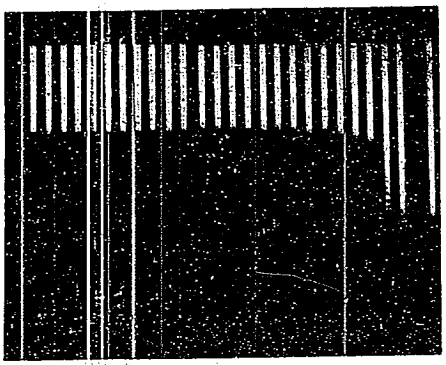
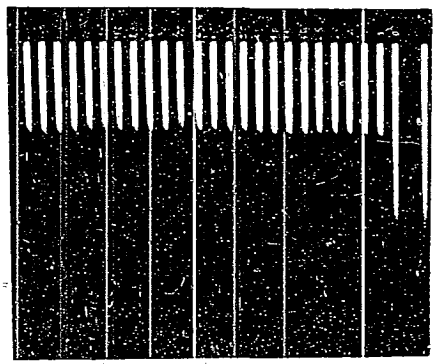


Figure 10(B)38
n-HEPTANE, REACTION TEMP. = 190°C





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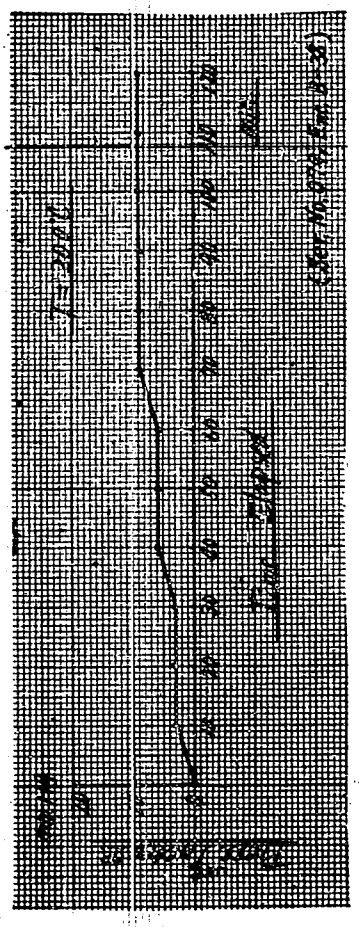


Figure 11(B)38
n-HEPTANE, REACTION TEMP. = 200°C

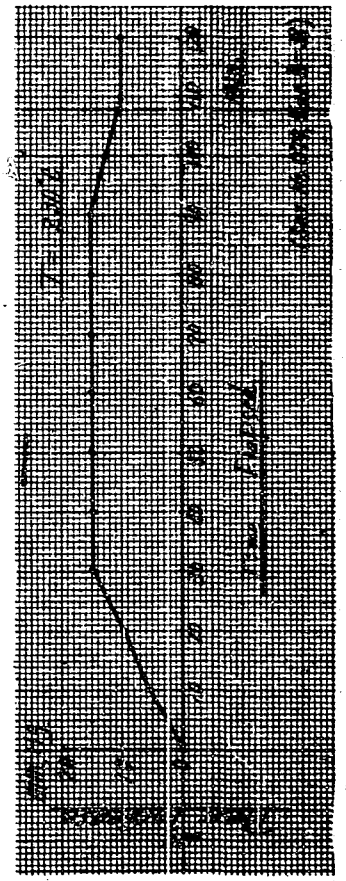
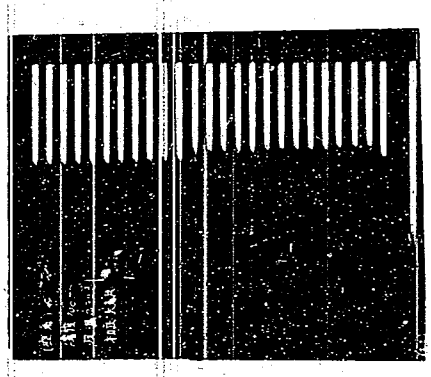
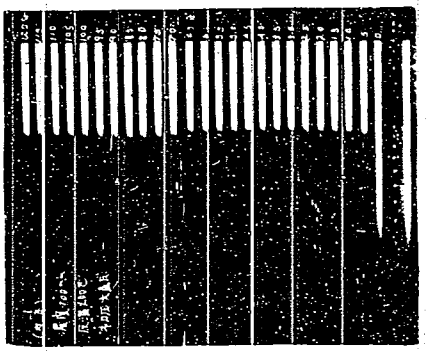


Figure 12(B)38
n-HEPTANE, REACTION TEMP. = 250°C





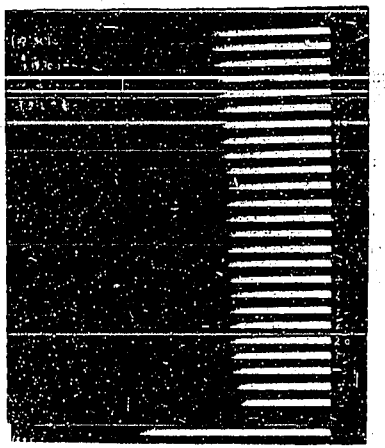
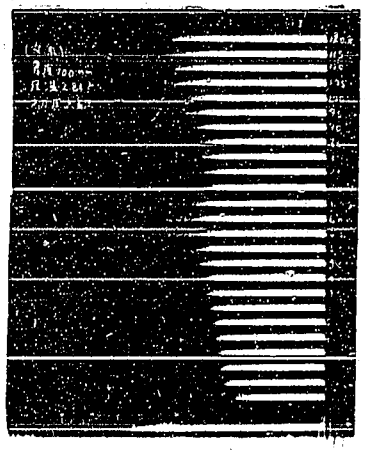


Figure 15(B)38
n-HEPTANE, REACTION TEMP. = 250°C



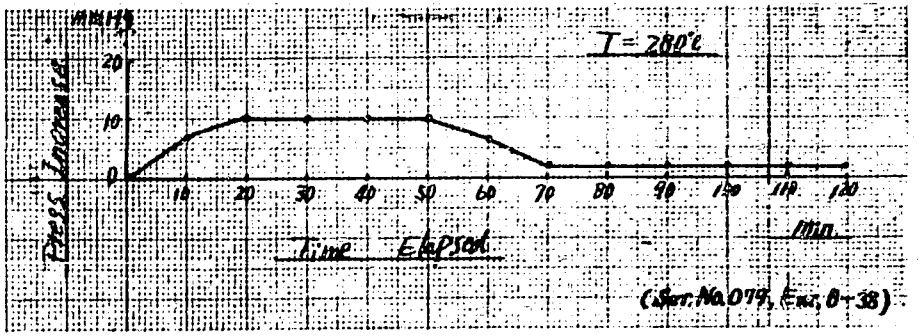


Figure 14(B)38
n-HEPTANE, REACTION TEMP. = 280°C

ENCLOSURE (B)38

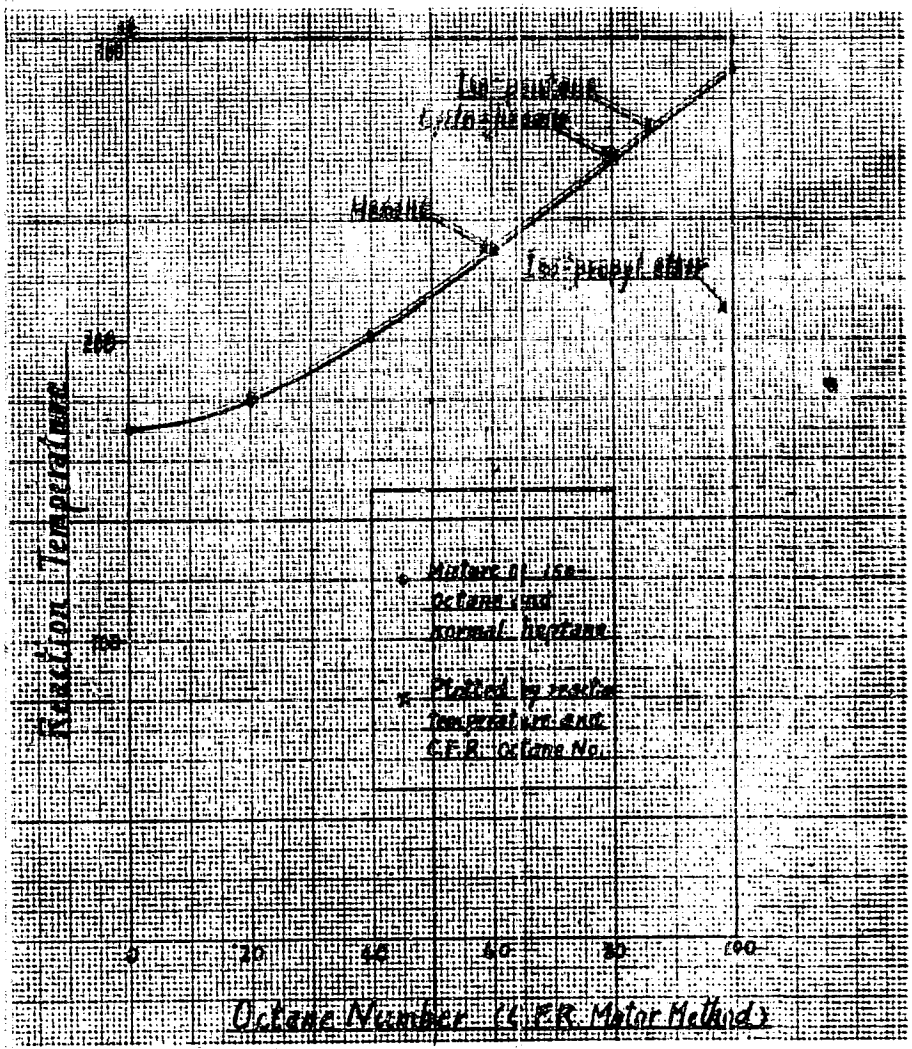


Figure 15(B)38

RELATION BETWEEN REACTION TEMP. AND OCTANE NO.

ENCLOSURE (B)38

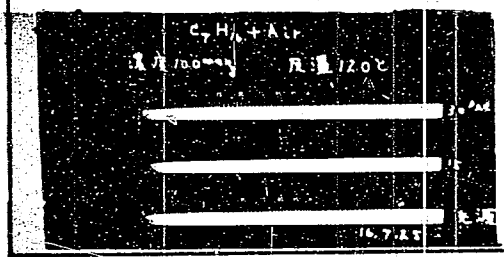
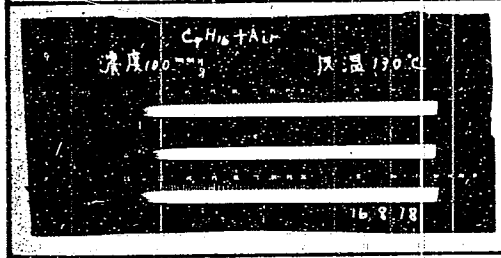
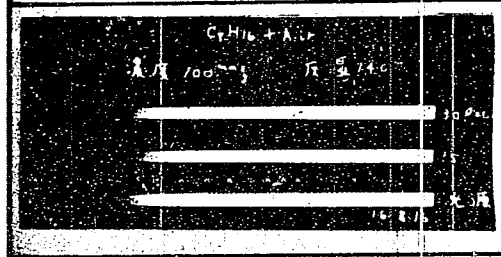
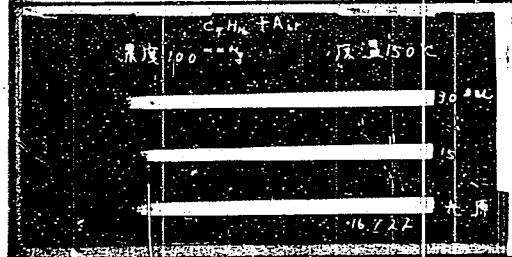
ABSORPTION SPECTRUM OF C_7H_{16}+AIR MIXTURE UPPER 30 SEC. EXPOSURE MIDDLE 15 " " LOWER LIGHT SOURCE	TEMP.	PEROXIDE
	120°C	NONE
	130°C	TRACE
	140°C	PRESENT
	150°C	"

Figure 16(B)56

ENCLOSURE (B)38

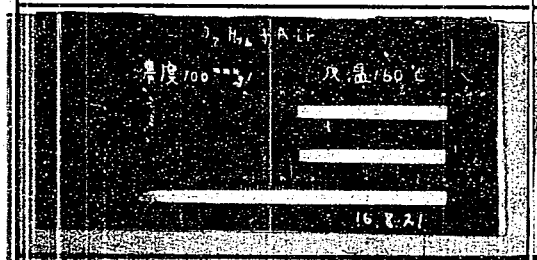
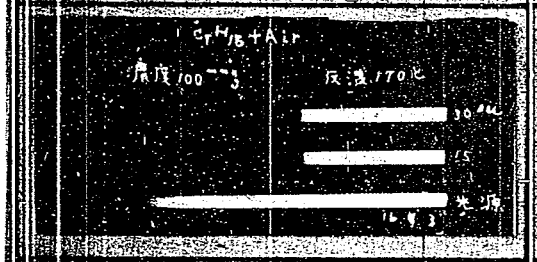
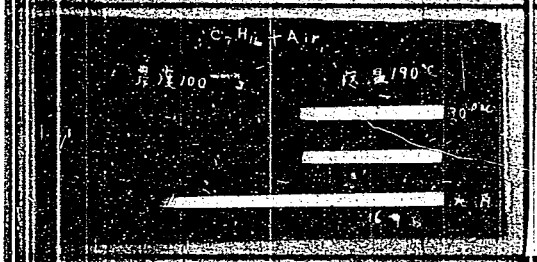
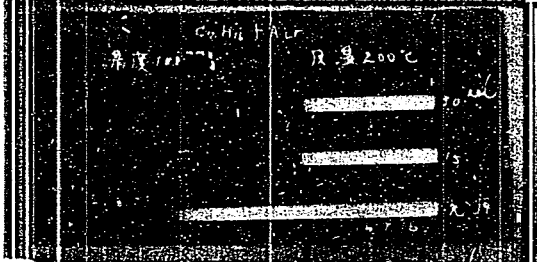
ABSORPTION SPECTRUM OF C_7H_6+AIR MIXTURE UPPER 30 SEC. EXPOSURE MIDDLE 15 " " LOWER LIGHT SOURCE	TEMP.	PEROXIDE
	160°C	PRESENT
	170°C	"
	180°C	"
	200°C	"

Figure 17(B)38

ENCLOSURE (C)

LIST OF JAPANESE DOCUMENTS PERTAINING TO GASOLINE RESEARCH

(Obtained from the first Naval Fuel Depot OFUNA and Kyushu Imperial University, FUKUOKA, and forwarded through ATIS to the Washington Document Center)

I. Gasoline Research Documents from the First Naval Fuel Depot, OFUNA. ATIS No. 4576.

NavTechJap No.	Title	Author	Date
ND26-0005.1	Studies on the Synthesis of Liquid Fuel from Acetylene.	C. FUJIO	12/26
0005.2	Studies on the Synthesis of Liquid Fuel from Acetylene, Effect of Metallic Reaction Tubes on the Polymerization of Acetylene.	C. FUJIO A. SHIRAI	11/27
0005.3	Corrosion of Metal by Commercial Benzol.	C. FUJIO	12/27
0005.4	Effect of Room Temperature on the First Drop in the A.S.T.M. Fractional Distillation Method.	M. AKITA I. HARADA	1/28
0005.5	Studies on the Composition of Gasoline Obtained from Japanese Crude Oil.	M. AKITA G. NOMURA	3/28
0005.6	On the Cracking of Methane.	C. FUJIO A. SHIRAI	5/29
0005.7	Composition and Properties of Commercial Gasolines.	M. AKITA I. HARADA G. NOMURA T. WADA	12/29
0005.8	The Sulphur Compounds in Gasoline.	M. AKITA	11/10/31
0005.9	Thermal Polymerization of CH_4 to Aromatic Hydrocarbons.	T. FUJIO	6/13/32
0005.10	Vapour Pressure of Gasoline.	M. AKITA	9/8/32
0005.11	Gasoline from Petroleum.	M. AKITA	10/1/32
0005.12	Blending of Motor Benzol in Gasoline.	Y. AKITA T. NAKAHARA H. SUGIHARA	11/11/32
0005.13	Experiments on the Poisonous Effects of Gasoline on Animals.	INADA	3/14/33
0005.14	Testing Method for Sulphur in Gasoline by Silver Nitrate.	T. NAMIKAWA F. NAKAMURA	9/34
0005.15	Studies on the Ignition Delay Time of Liquid Fuel by Dropping Method, Part II, Cyclic Hydrocarbons.	N. ISOGAYA Y. NISHIDA	11/34

ENCLOSURE (C), continued

NavTechJap No.	Title	Author	Date
ND26-0005.16	Properties of Motor Benzol and Various Aviation Gasolines.	M. AKITA H. SHINOYAMA	10/35
0005.17	Properties of Various Aviation Gasolines.	M. AKITA T. YOSHIHIRO N. ISOYA H. KONISHI H. SUGIHARA T. WADA	11/35
0005.18	Gummy Substances in Gasolines.	Y. AKITA	6/1/37
0005.19	Influence of Intake Air Temperature on the Antiknock Properties of Fuel.	M. AKITA N. ISOYA H. SUGIHARA	7/37
0005.20	Octane Values of n-Paraffines by The C.F.R. Motor Method.	M. AKITA N. ISOGAI H. SUGIHARA	7/37
0005.21	Octane Values of Hydrocarbon Mixture.	M. AKITA N. ISOGAI H. SUGIHARA	8/37
0005.22	Measuring Method for Octane Value Over 100.	M. AKITA	12/37
0005.23	On the Influence of Vapour Pressure of Gasoline upon the Starting of Engines.	T. NAKAYAMA	3/15/41
0005.24	On the Influence of Some Chlorides on the Octane-Value of Gasoline.	N. ISOGAI M. UEHARA H. SUGIHARA S. FUKAMI M. INADA	12/3/42
0005.25	On the Solubility of Water in the Unsaturated Hydrocarbons of Gasoline.	H. ASADA	10/27/43
0005.26	On the Influence of Moisture upon the Octane Value of Gasoline.	M. UEHARA	12/28/43
0005.27	Influence of Some Bromides and Iodides on the Octane-Value of Gasoline.	H. ISOGAI M. UEHARA H. SUGIHARA S. FUKAMI M. INADA	4/13/44

ENCLOSURE (C), continued

II. Combustion Research Documents from the First Naval Fuel Depot, OFUNA. ATIS No. 4584.

NavTechRep No.	Title	Author	Date
ND26-0013.3	Combustion.	N. ISOGAI	8/30
0013.5	Influence of Non-Combustible Gas on the Combustion of Hydrocarbons.	E. ISOGAI	3/33
0013.8	Studies on the Combustion of Hydrocarbon under Constant Volume. Part II. Combustion of Aromatic Hydrocarbons.	M. AKITA S. IGASAKI	6/34
0013.9	Relation between the Residual Gas of Flame and Explosive Limits of Gas.	M. AKITA N. ISOGAI	4/35
0013.14	The Explosive Limit of Hydrocarbons under High Pressure and the Mechanism of Combustion.	H. HONDA	3/42
0013.22	On the Combustion of Butane and Isobutane.	M. HAGIHARA H. HONDA	1/44

III. Technology Reports of Kyushu Imperial University, FUKUOKA, 1940-1945. (Including reports relative to the synthesis of gasoline from rubber). ND26-0011.1 to ND26-0011.26, ATIS No. 4582.