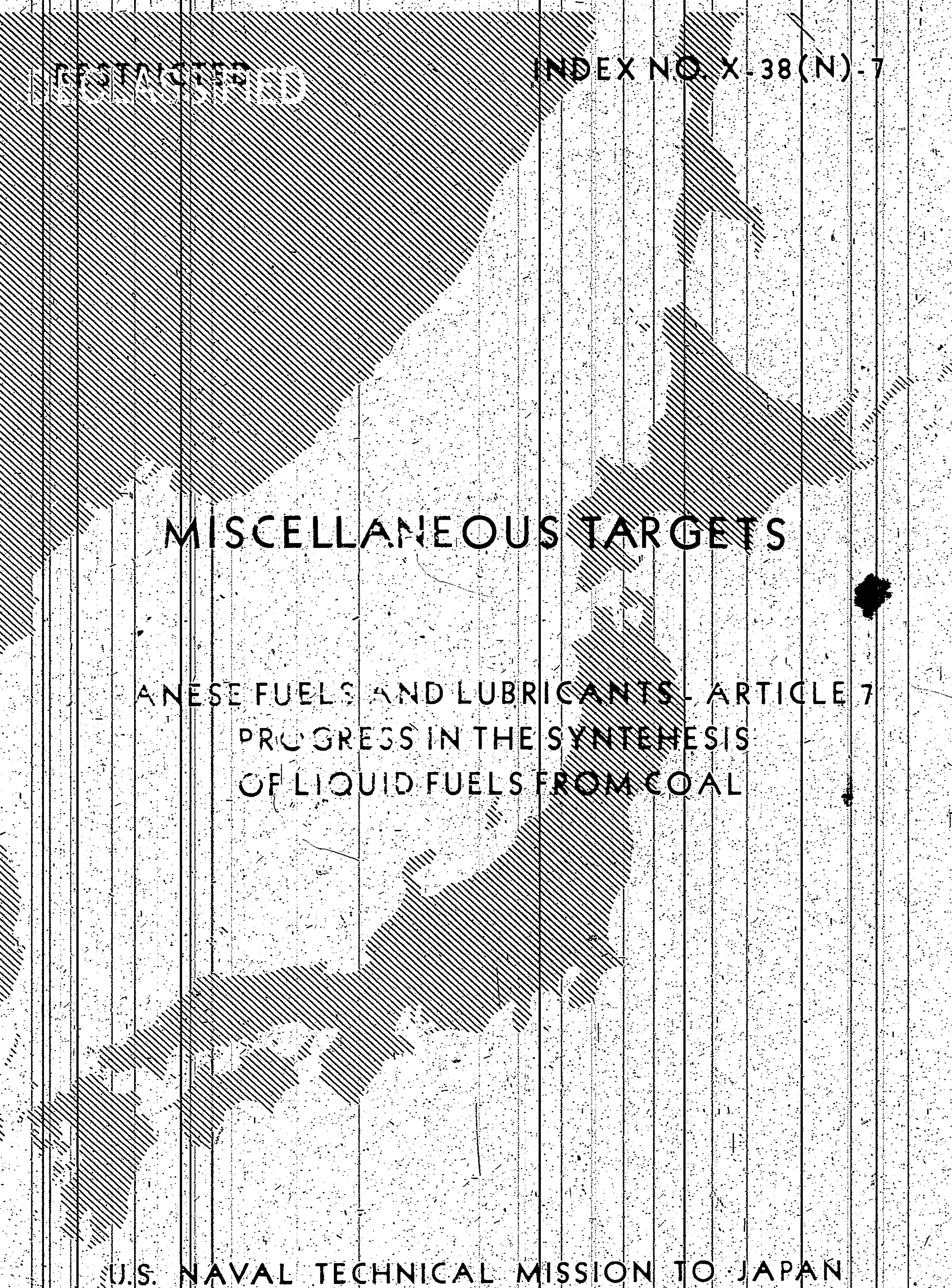

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INDEX NO. X-38(N)-7

MISCELLANEOUS TARGETS

ANESE FUELS AND LUBRICANTS - ARTICLE 7
PROGRESS IN THE SYNTEHESIS
OF LIQUID FUELS FROM COAL

U.S. NAVAL TECHNICAL MISSION TO JAPAN

ERRATA

"Japanese Fuels and Lubricants, Article 7 - Progress in the Synthesis of Liquid Fuels from Coal", - Index No. X-38(N)-7.

Page 15 Insert following after second paragraph:

> "Information obtained from the Imperial Fuel Institute indicated that the design capacity, or intended capacity, of the AGOCHI plant was 50,000 metric tons of "oil" per year. On the basis of the size of the converter given by SHONO, it appears that the figure of 20,000 tons of oil processed per year would apply to a single converter at the AGOCHI plant".

Page 18 In the sixth line of fifth paragraph under "Plant Development", delete "by thermo - syphon action".

Page 256 In third line of eighth paragraph change "pan mill" to "ball mill".

Page 280 Delete text commencing "This represents --- "and ending" --- hydrogenation of coal". Substitute therefor:

> "MIYAMA was unable to give accurate figures or product distribution for the FUSHUN plant".

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 7 - Progress in the Synthesis of Liquid Fuels from Coal.

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

1. Subject report, covering the synthesis of oil outlined by Targets X-09, X-10, and X-38 of Fascicle X-1 of reference (a), is submitted herewith.

2. The investigation of the target and the target report were accomplished by Comdr. G. L. Neely, USNR, Lt. Comdr. C. S. Goddin, USNR, Lieut. W. H. Millet, USNR, Mr. C. O. Hawk, Technical Representative from the U.S. Bureau of Mines, and Ens. E. R. Dalbey, USNR, as interpreter and translator.

C. G. GRIMES
Captain, USN

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X-38(N)-7

JAPANESE FUELS AND LUBRICANTS - ARTICLE 7
PROGRESS IN THE SYNTHESIS OF LIQUID FUELS FROM COAL

"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 7
PROGRESS IN THE SYNTHESIS OF LIQUID FUELS FROM COAL

Impelled by the lack of petroleum resources, Japan made a determined effort to develop an industry for converting coal into oil. Paralleling the program in Germany, emphasis was placed on three primary coal conversion processes: high pressure hydrogenation, the Fischer-Tropsch Synthesis, and low-temperature carbonization.

Although the Japanese Navy initiated research on coal hydrogenation in 1925, only two commercial-scale coal hydrogenation plants were installed in the Japanese Empire. These plants were based on the Japanese Navy's 200-Atmosphere process with modifications by the respective operating companies. The actual production of oil from coal was insignificant, since one plant, at AGOCHI, Korea, never achieved continuous operation, and the other, at FUSHUN, Manchuria, operated only intermittently. Visits to these plants by The U. S. Naval Technical Mission to Japan were not feasible in view of the unsettled military conditions in those areas.

The Fischer-Tropsch industry in Japan was based primarily on Ruhrchemie patents purchased by the MITSUI interests in 1936. Only three plants ever produced oil and the actual output of each was well below design capacity. Two of these plants operated at normal pressure and utilized a cobalt catalyst, while the other operated at middle pressure and used both cobalt and iron catalysts. The iron catalysts were the product of Japanese research, the manufacturing details of which are fully described herein.

The most important source of liquid fuels from coal was the low-temperature carbonization process. Most of the installations were Lurgi or Koppers ovens, and all evidence indicated that no coal carbonization process of Japanese design was successfully operated.

The Japanese "Seven-Year Plan" called for production of 2,000,000 kiloliters of liquid fuels from coal by 1943. Actual production in the peak year, 1944, was only 113,000 kiloliters. The plan was a failure due to stoppage of foreign machinery imports by the war, diversion of critical materials during the war, and technical difficulties encountered with the coal hydrogenation and the Fischer-Tropsch processes. As a matter of interest, the output of oil from shale at FUSHUN, until 1944, exceeded the combined output from all coal conversion processes.

TABLE OF CONTENTS

The Report

LIST OF ENCLOSURES

REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA.
Third Naval Fuel Depot, TOKUYAMA.
Army Fuel Research Institute, FUCHU.
Kyoto Imperial University, KYOTO.
Imperial Fuel Research Institute, KAWAGUCHI, Saitama Pref.
TEIKOKU NENRYO KOGYO K.K., TOKYO.
Miike Synthetic Oil Co., OMUTA.
NISSAN EKITAI NENRYO K.K., Wakamatsu Works, WAKAMATSU.
TEIKOKU NENRYO KOGYO Ube Works, UBE.

Japanese Personnel Interviewed:

S. KOMATSU, Ph. D., Civilian Advisor to the Department of Fuel Research, First Naval Fuel Depot, OFUNA, (formerly Professor of Bio-Chemistry at Kyoto Imperial University).
K. MITSUI, Ph. D., Engineering Commander Japanese Navy, First Naval Fuel Depot, OFUNA, (key research man on coal hydrogenation research).
A. NAKEI, Engineering Lieutenant-Commander, Japanese Navy, First Naval Fuel Depot, OFUNA, (key research man on the Fischer-Tropsch Process).
I. WATANABE, Engineering Rear-Admiral, Japanese Navy, Superintendent of the Third Naval Fuel Depot, TOKUYAMA.
G. KITA, Ph. D., Retired Professor of the Institute of Physical and Chemical Research, at the Kyoto Imperial University, (pioneered research on the Fischer-Tropsch Process in Japan; especially development of iron catalysts).
S. KODAMA, Ph. D., Professor in the Institute of Physical and Chemical Research at the Kyoto Imperial University (is now actively in charge of Fischer-Tropsch research at the University).
Y. BAN, Director of the Imperial Fuel Research Institute, (has been associated with the Institute for 25 years, is competent, and thoroughly familiar with Japanese coal resources and problems of utilization).
T. MIYATA, Technical Director of TEIKOKU NENRYO KOGYO K.K., TOKYO, (formerly with Manchurian Chemical Industries Co. at DAIREN, working on ammonia synthesis, then became General Manager of the coal hydrogenation plant at FUSHUN from 1937-1942 prior to present assignment).
N. SHONO, Assistant to Chief Engineer of TEIKOKU NENRYO KOGYO K.K., TOKYO, (formerly Chief Engineer with the Toho Kagaku Kogyo Co. at NAGOYA up to 1944, especially familiar with hydro-cracking).
N. NAKAHARA, President of the Toa Nenryo (Oil) Co., (especially familiar with catalytic cracking development in Japan).
T. MITSUI, President of the Miike Synthetic Oil Co., (a Dartmouth graduate and closely related to the development of the plant at MIIKE, primarily a businessman, and not highly informed technically).
M. TAKEI, Head of the Chemical Department of the Miike Synthetic Oil Co., (a graduate chemist, well informed on details of the Fischer-Tropsch Process at MIIKE).
N. YAMADA, Director of the Nissan Ekitai Nenryo Plant at WAKAMATSU, unusually well-informed on the technical details of the low-temperature process employed at this plant).

continued

IWAMOTO, Director of the Ube Works of the TEIKOKU NENRYO KOGYO K.K., (well-informed technically on the operations of this plant).

In addition to the key personnel listed above, a number of other plant executives and research assistants were interviewed, and are listed in the enclosures contained in this report.

Referenced Japanese Reports.

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

INTRODUCTION

Recognizing her critical lack of an adequate domestic or a dependable foreign source of petroleum, Japan has intensively endeavored to overcome this deficiency by developing an industry for conversion of extensive reserves of low grade coals into oil. Three processes for converting coal into oil have been studied and expanded to industrial scale operation:

1. High-Pressure Hydrogenation.
2. Fischer-Tropsch Synthesis.
3. Low-Temperature Carbonization.

This report summarizes the findings of the Petroleum Section of the U. S. Naval Technical Mission to Japan relative to research and industrial developments on the above processes. A general history of the synthetic fuels program in Japan is also presented.

To obtain this information, important Japanese oil research institutions were inspected, including the Naval Research Laboratory at OFUNA, the Army Fuel Research Institute at FUCHU, the Imperial Fuel Research Institute at KAWAGUCHI, and the laboratories of Professor KITA at the Imperial University, KYOTO. Typical commercial scale installations visited were the Fischer-Tropsch plant at MIIKE, the low-temperature carbonization works at WAKAMATSU and the low temperature carbonization and high pressure oil hydrogenation units at UBE.

Semi-commercial coal hydrogenation units at OFUNA and KAWAGUCHI were also inspected. Interviews were held with representatives of TEIKOKU NENRYO KOGYO, K.K., (Imperial Fuel Industries Co.), a government agency established to promote development of the synthetic liquid fuel industry in Japan.

Particular attention was devoted to evaluation of the research carried on at the First Naval Fuel Depot, OFUNA. Detailed research reports of the work on coal conversion were prepared (in English) by technical personnel of the Depot and are submitted as Enclosures (B)1 to (B)25, inclusive. Since the original research reports, drawings and documents had been burned in August, 1945, it was necessary to recall Japanese personnel to reassemble this information from laboratory notebooks and miscellaneous records.

It is recognized that the data secured do not completely cover Japan's program with respect to the production of oils from coal. However, it is believed that there is sufficient material to permit at least a rough appraisal of the extent and nature of her synthetic fuel developments.

THE REPORT

Part I - HISTORY

Research on coal conversion was begun in Japan as early as 1921 by the Imperial Fuel Research Institute, which at that time initiated studies on low-temperature carbonization of Japanese coals. The Japanese Navy, in 1925, started laboratory studies at TOKUYAMA on high-pressure hydrogenation and low-temperature carbonization. This work was stimulated by the fact that units of the fleet were then in process of converting from coal to liquid bunker fuels. In 1926, Dr. OGAWA, of the Tokuyama Naval Research Laboratory, visited the I. G. Farbenindustries A. G. at LEUNA, taking with him samples of Fushun and Japanese coals for hydrogenation tests. Upon his return, work on the hydrogenation process was intensified, and in 1930, the decision was made to build the first semi-commercial coal hydrogenation unit in Japan. This unit, of seven tons per day paste throughput capacity, was completed in 1932, and experiments were continued at TOKUYAMA until 1939, when the unit was transferred to OFUNA.

In 1928 the South Manchurian Railway Co. started experiments on coal hydrogenation in their Central Research Laboratory at DAIREN, Manchuria.

In 1931, the Imperial Fuel Research Institute at KAWAGUCHI also began research on high-pressure hydrogenation of coal, and in 1934 constructed a simplified pilot plant of 3-5 tons per day paste charge capacity. The work, however, apparently did not play an important part in industrial development of the process.

The information obtained by NavTechJap indicates that only two commercial-scale coal hydrogenation plants were ever installed in the Japanese Empire. In 1936, the South Manchurian Railway Co. began construction of a unit of about 10,000 tons per year coal charge capacity at FUSHUN, Manchuria, which was jointly designed by the Navy and the South Manchurian Railway Co. In 1937, the Korean Nitrogen Fertilizer Co. began construction of a plant at AGOCHI, Korea, with a coal charge capacity of 20,000 tons per year. This plant was also based on the Navy process, but with modifications, especially in reactor design, which reflected the experience of the parent company in ammonia synthesis.

Both these plants commenced operations in 1939. Apparently the Agochi plant was never able to achieve continuous operation on coal, due to excessive coking and to plugging difficulties. Experiments were continued on hydrogenation of low-temperature tar and coal until 1942, when the plant was converted to methanol synthesis. The Fushun plant is reported to have been somewhat more successful, although many process and design changes on which the Navy and the South Manchurian Railway Co. cooperated, were required. From 1940 to 1942 the plant was alternately operated on coal and hydrocracking of low-temperature tar and in July, 1942, was completely converted to hydrocracking of low-temperature tar and petroleum oils for production of aviation gasoline.

In the meantime other agencies, impatient with delays in development of the Japanese coal hydrogenation process, attempted negotiations with Germany. In 1937, the Ogura Oil Co. reached a price agreement with I. G. Farbenindustries for licensing rights to the Bergius Process. However, the Japanese Navy prevented completion of the deal, apparently on the basis that development of a satisfactory Japanese process was imminent. The Japanese Army, on the other hand, continued negotiations with the German Government until 1945, but it is reported that no actual technical data were secured.

Beginning in 1939, the Japanese Army in its extensive laboratories at FUCHU, conducted research on hydrocracking various oils for production of aviation gasoline, and constructed kerosene hydrocracking units in its refineries at IWAKUNI and SHIHEIGAI. There is no indication, however, that the Army investigated the high-pressure hydrogenation of coal.

Although a number of oil hydrocracking units were successfully operated for production of aviation gasoline, the production of liquid fuels by the high pressure hydrogenation of coal in the Japanese Empire was negligible.

Research on the Fischer-Tropsch Process for synthesis of oil from carbon monoxide and hydrogen was pioneered in Japan by Professor G. KITA at the Institute of Physical and Chemical Research at the Imperial University, KYOTO. This work was started in 1927, one year after the appearance of Franz Fischer's first paper on the subject, and was centered primarily on development of cheap iron catalysts for use in both normal and middle-pressure synthesis.

The Imperial Fuel Research Institute at KAWAGUCHI also conducted research from 1933 to 1940, especially on nickel substitute catalysts, but made no significant contributions to the industry. Professor MATSUBARA, at the Tokyo Imperial University, also worked on catalysts for this process and developed a natural iron catalyst in 1943-44. Iron catalysts from both Tokyo and Kyoto Universities were tested on plant scale at the Takikawa middle pressure Fischer-Tropsch plant.

In 1936, the Mitsui interests purchased rights to the Fischer-Tropsch Process from Ruhrchemie, and in the same year, commenced construction of a normal-pressure cobalt plant at MIIKE, near OMUTA. This plant was designed to have an output capacity of 30,000 tons of crude product per year. Operational difficulties were encountered and actual production was substantially less than this figure. Two other Fischer-Tropsch plants were built in Japan under the joint management of MITSUI and TEIKOKU NENRYO K.K. One of these was the middle pressure plant at TAKIKAWA, employing both cobalt and iron catalysts, which started operations in December, 1942; the other was a normal pressure plant at AMAGASAKI, employing a cobalt catalyst, which started in September, 1943. Two other plants in Manchuria, one at CHIELIN and the other at CHINCHU, were under construction at the end of the war.

The Mitsui interests, at their laboratory in TOKYO, conducted some research, especially on iron catalysts and the manufacture of lubricating oils and chemicals from Fischer-Tropsch liquids. The Army and Navy also conducted a small amount of research on the process, but made no significant contributions to the technology.

The most successful method for production of oil from coal in Japan, with respect to volume and cost of production, was low-temperature carbonization. Although studies of the process were started in 1921 by the Imperial Fuel Research Institute, difficulties of marketing the semi-coke prevented any substantial development of the industry under peace-time conditions.

In 1936, the Japanese Government established a petroleum substitutes policy as a war measure, which included indemnities for losses suffered in the production of such fuels. With the establishment of this policy, the low-temperature carbonization industry expanded rapidly.

In January, 1938, the Imperial Fuel Industries Co. (TEIKOKU NENRYO KOGYO K.K.) was established under the Japanese "Seven Year Plan" for synthetic oil development. Under this plan, annual production of 1,000,000 kl each of synthetic gasoline and fuel oil was to be achieved by 1943 (See Enclosure I). TEIKOKU NENRYO K.K. was authorized to finance synthetic oil enterprises and to manufacture and sell synthetic oils. Companies engaging in synthetic oil production were exempted from income, import, and profit taxes, and were given subsidies based on oil output. In 1942, however, subsidies were eliminated and the government purchased all oil from the synthetic oil companies at favorable fixed prices.

Under the "Seven Year Plan," the synthetic oil industry was to be developed to include 10 high-pressure coal hydrogenation units, each of 100,000 kl per year oil output capacity, 11 Fischer-Tropsch units, each of 50,000 kl per year capacity, and 66 low-temperature carbonization units, each charging 100,000 tons per year of coal. The actual plants constructed in the empire, and their outputs during the war years, are given in Table I, which is based on data supplied by TEIKOKU NENRYO K.K. It will be noted that the peak annual output of oil from all coal conversion processes amounted to only 114,000 kl compared with the 2,000,000 kl called for in the plan. This performance was due mainly to (1) the effect of the Moral Embargo and declaration of the European War in 1939 which stopped shipment of equipment from the United States and Germany, (2) the curtailment in the plant construction program in Japan, after the attack on Pearl Harbor, due to diversion of critical materials for more pressing military requirements, and (3) the operating difficulties and low outputs from both Fischer-Tropsch and coal-hydrogenation plants.

Part II
HIGH PRESSURE HYDROGENATION

A. DIRECT HYDROGENATION OF COAL

1. General Remarks. Studies on the direct hydrogenation of coal in Japan began as early as 1925, at the Japanese Naval Research Laboratory at TOKUYAMA (Enclosure (A)). The first experiments were carried out in small high pressure autoclaves for assay purposes, that is, to qualitatively determine the suitability of coal to liquefaction by hydrogenation. In 1926, Shimbara and Oyama coals were sent to Germany for confirmatory assay and for study in a small continuous plant at LEUNA.

The Japanese were attracted to coal hydrogenation as a possible source of liquid fuels because of their extremely poor position with respect to native petroleum. They had acquired some knowledge of low-temperature carbonization (Enclosure (E)) and of the potential usefulness of low-temperature tar as a petroleum substitute. However, the maximum tar yield was only about 10 per cent by weight of the coal, and many Japanese low-grade coals yielded only 6-8 per cent. Furthermore, there was no ready market for the semi-coke, the weight of which was 65 per cent or more of the weight of the coal. Coal hydrogenation, on the other hand, offered the possibility of developing a commercial process for complete conversion of coal to oil.

Coal hydrogenation has probably been studied more thoroughly in Japan, at least on laboratory scale, than in any other country in the world, except Germany. There are records of nearly two hundred hydrogenation assay tests, including ninety tests on coals from Manchuria and China (Enclosure (B)22), and more than one hundred tests on coals from Japan proper (Enclosure (E)).

The Petroleum Section of NavTechJap interviewed research personnel and inspected coal hydrogenation equipment at the First Naval Fuel Depot, OFUNA, and at the Imperial Fuel Research Institute, KAWAGUCHI. Both organizations have done work on laboratory and semi-plant scale.

No industrial research laboratories investigating this subject were inspected. One such laboratory, under Japanese control, known to exist, is the South Manchurian Railway's Central Research Laboratory at DAIREN. In this laboratory much of the exploratory and development work was done which culminated in erection of the coal hydrogenation plant at FUSHUN, Manchuria.

The exact position of Japanese Universities in coal hydrogenation research is not known. The Meiji College of Technology near WAKAMATSU, Kyushu, is said to have facilities for this type of work. The Imperial University at

KYOTO has been active in Fischer-Tropsch investigations, but did no work on hydrogenation. The Imperial University at TOKYO is known to have supported fuel research, but the nature of this work has not been ascertained.

2. Coal Hydrogenation Work of the Japanese Navy

a. Laboratory work. The Japanese Navy's interest in coal hydrogenation was motivated by the desire and need to establish a dependable source of liquid fuels for the fleet. Therefore, consideration was given to all coals within, or controlled by, Japan. Assays were made in the Tokuyama laboratories on both Japanese and continental-Asiatic coals. However, in view of the direct co-operation between the Navy and the South Manchurian Railway Co., much of the Navy's earlier laboratory work was concentrated on developing a liquefaction process based on Fushun (Oyama coal (Enclosure (F)). Autoclave studies on the effect of catalyst (Enclosure (B)5), reaction temperature (B)6), hydrogen pressure (Enclosure (B)7), time of contact (Enclosure (B)8), viscosity of vehicle (Enclosure (B)4), and to some extent, the size of coal particles (Enclosure (B)3), comprised the nucleus of the early coal hydrogenation work.

The most important results of these experiments were:

(1) Zinc chloride was found to be the most effective catalyst, although later, (Enclosure (B)18), a mixture of ferric oxide, sulfur, and stannous hydroxide was chosen as the standard catalyst.

(2) Reaction temperatures near 420°C were found to be the highest practicable without encountering excessive coke and gas formation.

(3) At pressures below 200 atmospheres, excessive coke formation occurred and liquefaction was incomplete.

(4) Vehicle viscosity was without effect on the hydrogenation reactions.

(5) About one hour minimum contact time under conditions described in (1), (2), and (3) was required for complete liquefaction.

Physical properties of coal pastes made with Fushun coal, were also measured to assist in the design of plant equipment (Enclosure (B)13).

Relatively few records were found relating to work on the fundamental aspects of coal hydrogenation. Work of this nature which was done, comprised studies on the hydrogenation of simple compounds (Enclosures (B)1, (B)2, (B)14), the effectiveness of relatively pure compounds when used as vehicles (Enclosure (B)12), the behavior of coal substance and humus (Enclosure (B)10), and mechanism studies (Enclosure (B)16). Although results and conclusions of this work are of general scientific interest, they contributed little to the practical aspects of process development.

One of the most valuable contributions of this laboratory to the general fund of knowledge concerning coal hydrogenation was an extensive survey of the properties of Chinese and Manchurian coals (Enclosure (B)22). Fifty coals from North China and forty from Manchuria were assayed. Only a few experiments were reported on coals from Japan proper, Korea, and Formosa (Enclosure (B)11).

General conclusions were:

(1) The coals of North China (mostly caking varieties) were found to be more suitable for high-temperature coking than for hydrogenation.

(2) Most coals of Manchuria hydrogenated readily. Similarly those tested from Japan, Korea, and Formosa were suitable for hydrogenation.

A list of titles of reports in Japanese relating to coal hydrogenation work at the Navy's research laboratories will be found in Appendix C. These documents have been forwarded through ATIS to the Washington Document Center.

3. Semi-Plant Operation. Erection of a semi-commercial scale plant, the first in Japan, began in 1930 at TOKUYAMA. Construction was completed and preliminary operation began about 1932. The plant comprised a single converter liquid-phase system, with a throughput of about 7 tons of paste (3-3.5 tons of coal) per day. An electric hydrogen preheater was enclosed in the converter (Enclosure (B)17, Figure 1) otherwise the hydrogenation system was conventional. Equipment for stripping volatile liquid hydrocarbons from the converter exit gases was provided, in order that hydrogen recirculation could be effected. Process hydrogen was furnished by electrolysis of water in a Knowles generator, with a capacity of 200 m^3 per hour. Heavy oil, containing the ash and unliquefied constituents of the coal, was withdrawn through a manually controlled valve. Attempts to maintain continuous discharge with this system proved troublesome. Solids were separated from the heavy oil by centrifuging.

No written records were available for pilot plant operation between 1932 and 1938, but Japanese personnel estimated that during this period, the unit was actually on stream about one-third of the time.

Enclosure (B)17 summarizes data obtained in 1938-39 during a five-day run on Oyama coal and a one day run on Naibuchi coal from SAKHALIN. It was admitted that difficulties were experienced in these runs in the separation of solids from heavy oil by centrifuging, and in the non-uniform distribution of hydrogen and paste in the reactor. It was also stated that erosion of the heavy oil discharge mechanism was severe, and that the lack of flow control instrumentation made it difficult to maintain uniform operating conditions.

Results of the hydrogenation test on Oyama coal are of particular interest because of its relationship to the full scale operation at the South Manchurian Railway Co. plant at FUSHUN. Oyama coal is mined at FUSHUN and has been described (Enclosure (F)) as "a very high quality brown coal approaching bituminous". An analysis of the coal used in this test is given in Table II.

4. Coal Hydrogenation at the Imperial Fuel Research Institute. Both laboratory and semi-plant-scale hydrogenation of coal were studied by this organization from about 1931 to 1940. The purpose of the work was to carry to full demonstration scale, a process for liquefaction of Japanese coals. This work was done without direct co-operation with the Navy or any industrial group.

In all, over a hundred coals (Enclosure (E)) were hydrogenated in small autoclave tests showing, in general, that practically all Japanese coals are suitable for hydrogenation. Three of the more suitable coals were further studied in a small semi-commercial plant having a throughput capacity of 3 to 5 tons paste (1.5 to 2.5 tons of coal) per day. This plant comprised a double converter liquid-phase system (Enclosure (E),

Figure 2). It possessed simplified design features intended to insure maximum operability rather than to serve as a means for studying engineering problems connected with economical operation of a high-pressure plant. For this reason, its operation, although reported to be reasonably successful, contributed little to the development of commercial hydrogenation in Japan. It did, however, furnish information of general interest on the behaviour of Japanese coals upon hydrogenation.

5. Industrial-Scale Coal Hydrogenation

a. The South Manchurian Railway Co. Plant at FUSHUN, Manchuria. The construction of this plant was undertaken in 1936 (Enclosure (F)), about 10 years after experimentation on coal hydrogenation began on an extensive scale at the Navy's Research Laboratory at TOKUYAMA and the South Manchurian Railway's Central Research Laboratory at DAIREN.

Construction was completed and preliminary operation began in 1939. As a matter of interest, the reactors were made in Japan, and it was stated that there was no cooperation with foreign engineers in designing any of the equipment. Originally, the plant comprised a liquid-phase single converter system of essentially conventional design, at least with respect to material flow. Late in 1939, a second liquid-phase reactor was added, and early in 1940, a vapor-phase reaction system was installed. Between this time and July 1942, operation alternated between liquid-phase coal hydrogenation and vapor-phase treatment of fractions from low-temperature tar or from coal hydrogenation. From 1942 until the end of the war, at the direction of the Japanese Navy, the plant was completely converted to hydrocracking of gas oil and kerosene for production of gasoline.

For coal hydrogenation, operating conditions were 200 atmospheres and 430°C in the liquid-phase step, with a throughput of 4 tons of paste per hour. Ratio of coal to vehicle was 2 to 3 by weight. In the vapor-phase step, the input was 40 kl per day, at 200 atmospheres pressure and temperatures of 430°C and 440°C in the first and second stages respectively. The yield of gasoline obtained by combining liquid and vapor-phase operation was about 35% of the weight of coal charged.

It was not possible to visit this plant and no original operating records were located. T. MIYAMA, Technical Director of the plant from 1937 to 1942, advised that no particular mechanical operating difficulties had been encountered. N. SHONO, Assistant Technical Director of TEIKOKU NENRYO, stated that operating difficulties had been encountered, but he could give no specific information. Dr. H. FUJIMOTO, of the First Naval Fuel Depot at OFUNA, recalled that production schedules were irregular between 1939 and 1942, but that at the end of this period, a reasonably successful process had been evolved.

The nominal throughput was about 10,000 tons of Oyama coal per year, according to MIYAMA. He also stated that the approximate total oil output of the plant from 1939 to the present was 15,000 tons, most of which was heavy oil from liquid-phase hydrogenation of coal.

Both MIYAMA and SHONO maintained that, although the Fushun plant was large enough to be considered of industrial scale, it had always been considered an experimental venture rather than a production unit. However, it seems probable, that under the severe stress of Japan's need for oil during the war, it would have operated continuously at rated capacity if the coal hydrogenation process had been successful.

b. The Plant at Agochi, Korea. Information secured on this installation was meager. Interrogation of N. SHONO of TEIKOKU NENRYO revealed that it was installed about the same time as the Fushun plant and the design capacity was about 20,000 tons of coal per year. Dr. K. MITSUI of the Navy's First Fuel Depot at OFUNA, recalled the nominal production as 10,000 kl of heavy oil per year by liquid-phase hydrogenation of Agochi brown coal.

Information obtained on the operation of this plant indicated that it was not able to function as a coal hydrogenation unit, and that during the war, it was finally converted to methanol synthesis. SHONO stated that the plant contained 2 converters, 160 centimeters in diameter and 13 meters long, and that, when operated as a coal hydrogenation unit, there was severe overheating in the reaction zone, resulting in excessive coking. He also recalled that the converter walls were said to be too thin to withstand the design operating pressure (200-250 atmospheres).

All evidence indicated that the Fushun and Agochi works were the only commercial-scale coal-hydrogenation plants installed in the Japanese Empire. Their failure to maintain operation, together with the fact that no other plants were built, is interpreted to mean that Japan did not have a perfected process. Since these plants could not be inspected, in view of the military situation prevailing in Manchuria and Korea at the time of this investigation, the actual progress made in the development of these plants has not been ascertained.

In securing the information for this report, it has been revealed that Japan, in her acute need for oil, plunged into industrial coal hydrogenation without acquiring an adequate background of experience with the intermediate-scale equipment. It has also been revealed that materials, particularly heat-resistant alloy steels, were not available for the construction of suitable equipment, and that manufacturing facilities did not exist for fabricating reaction vessels of proper size.

B. HYDROGENATION OF TAR

1. Research at the First Naval Fuel Depot, OFUNA. As a war measure, the utilization of high and low-temperature tar as raw material for aviation gasoline production was considered an attractive possibility by the Japanese Navy. High-pressure vapor-phase hydrogenation or "hydrocracking" of tar fractions over fixed catalysts was the method chosen for investigation. In this process, the molecular weight of the hydrocarbons in the charge stock is reduced, and the phenols are destroyed.

At the Navy's laboratories, both autoclave and small continuous plant experiments were conducted, which resulted in the development of a tentative process (NavTechJap Report "Japanese Fuels and Lubricants, Article 2 - Naval Research on Aviation Gasoline," Index No. X-38(N)-2, Enclosure (B) 16, Parts I and II). The throughput of the continuous unit was 4 to 5 liters of liquid per hour and the amount of catalyst, 8 to 10 liters.

During this investigation, the field of single component catalysts was rather thoroughly covered. Molybdenum tri-sulfide, either alone, or mixed with acid clay was found to be the most favorable catalyst. It induced the highest hydrogen absorption with the lowest gas loss and best yields of gasoline.

The process was operated in two stages without inter-stage product condensation. Typical results obtained on processing high and low-temperature tars are presented in Table IV.

2. Commercial Developments. Eight oil-hydrocracking plants were reported to have been installed in the Japanese Empire. Three of these plants, were installed specifically for the processing of low-temperature tar, and the remaining five for processing petroleum kerosene and gas oil. In addition, the coal hydrogenation plants at FUSHUN and AGOCHI were both operated at times as hydrocracking plants. A tabulation of known hydrocracking plants is given in NavTechJap Report "Japanese Fuels and Lubricants, Article 2," Index No. X-38(N)-2. The low-temperature tar-hydrocracking plants were the TEIKOKU NENRYO plant at UBE, the TOHO KAGAKU plant at NAGOYA, and the NIPPON YUKA plant at KAWASAKI. Of these, the Nagoya plant was converted to the hydrocracking of petroleum oils and the Ube plant was not completed prior to the end of the war. No data were available on the Kawasaki plant.

Part III
FISCHER-TROPSCH SYNTHESIS

A. GENERAL REMARKS

Japan has maintained interest in the Fischer-Tropsch synthesis since shortly after the announcement of its discovery in 1926. Like direct coal hydrogenation, this process offers the possibility of essentially complete conversion of coal to liquid fuel. Fischer-Tropsch research work in Japan was pioneered by Prof. KITA, of the Kyoto Imperial University. It was later undertaken by the Imperial Fuel Research Institute, the Tokyo Imperial University, and by others, notably, the Mitsui Bussan Co., which in 1936, obtained licensing rights to the Ruhrchemie patents in Japan.

Just prior to the war, the Navy conducted a few laboratory experiments at the First Naval Fuel Depot at OFUNA. During the war, technologists at the Army Fuel Research Institute at FUCHU carried on pilot plant experiments on the use of an iron catalyst which was developed in KITA'S laboratories at KYOTO.

Since Japan has no resources of the expensive cobalt, much emphasis in Japanese research has been placed on substituting iron or nickel. Although none of this effort has been more than moderately successful, an iron catalyst developed at KYOTO has been used in a Fischer-Tropsch plant at TAKIKAWA, Hokkaido. This plant and two others, one at OMUTA (Miike Works) and the other at AMAGASAKI, were the only Fischer-Tropsch units reported to have been completed and operated in Japan. Two more plants were under construction in Manchuria.

The Petroleum Section of NavTechJap has inspected equipment and interviewed personnel at the Miike plant, the Kyoto Imperial University, the First Naval Fuel Depot at OFUNA, and the Imperial Fuel Research Institute at KAWAGUCHI. Information was also obtained from personnel of TEIKOKU NENRYO and the Nippon Jinzo Sekiyu Co., who managed the plants at MIIKE, AMAGASAKI and TAKIKAWA.

B. LABORATORY RESEARCH

1. Research at the First Naval Fuel Depot, OFUNA. Little work was done on the Fischer-Tropsch Process at the First Naval Fuel Depot. Two reports were obtained relating to studies on iron-oxide catalysts (Enclosures (B)20 and (B)21) and one concerning the reduction of cobalt catalysts (Enclosure (B)19). The work on reduction of the cobalt catalyst is of interest, since it concerns the behavior of fixed catalysts of the type employed in Germany.

2. Research at the Imperial Fuel Research Institute. Experimental work on both laboratory and semi-commercial plant scale was carried on at this institution from 1933 until 1940, with the intention of developing a complete full-scale process (Enclosure (E)). This work was abandoned in 1940 when the Miike plant began operation. Because of the high cost and difficulty of obtaining cobalt, studies on the substitution of nickel were

intensively conducted. Yields above 100 grams total liquid product per cubic meter of synthesis gas were obtained in laboratory tests, but the life of the best catalysts was apparently limited to about a month. In the semi-commercial plant, only a few days activity could be obtained. Iron catalysts were not investigated.

The Institute's largest scale of operation was an intermediate pressure plant with a catalyst charge capacity of about 3/4 cubic meter (Enclosure (E)). It was designed to produce about 200 kg/day of total liquid product from 100 cubic meters per hour of synthesis gas at a gauge pressure of five atmospheres. The system comprised a single-pass down-flow cylindrical converter, with a product recovery system consisting of air and water-cooled condensers and a pressure-type oil scrubber. Converter temperature control was effected by an intricate system of vertical tubes placed inside the converter shell, through which, water was circulated in a closed system containing an external condenser. The catalyst was packed in the interstices between the tubes.

Actual synthesis gas throughput and oil production in this plant never exceeded 30% of design capacity. One of the best runs yielded about 66kg of crude liquid product in 30 m^3/hr, using a catalyst whose active constituent was a mixture of 80% nickel and 20% cobalt. This yield corresponded to 85 grams per cubic meter of pure synthesis gas. The poor performance of this plant was attributed to poor catalyst activity and inadequate temperature control of the converter.

3. Research at Kyoto Imperial University. The work at KYOTO is undoubtedly Japan's most important contribution to the field of the Fischer-Tropsch synthesis. Experiments began in 1927 under Prof. G. KITA, with no objects in the beginning other than to study the scientific aspects of the problem (Enclosure (D)).

In 1937, work was started on iron catalysts for use at normal atmospheric pressure and it was continued through the war, the objective being to develop a substitute for cobalt. From 1937 to 1941, atmospheric pressure experiments were made in a semi-commercial pilot plant, whose throughput was 100 cubic meters of synthesis gas per hour. At the request of the Japanese Army, this plant was transferred to the Army Fuel Research Institute at FUCHU in 1942.

Although extensive work has been done at KYOTO to develop an iron catalyst for the atmospheric pressure synthesis, no catalysts yet discovered have proved equal to the conventional cobalt type. On the other hand, operation at intermediate pressures (10-15 atmospheres) was found to have a favorable influence on the performance of iron catalysts. Under these conditions, one of KITA'S best preparations produced about 120 gm/m^3 in laboratory tests (refer to Table IV, Enclosure (D)). A catalyst of this type was manufactured at KYOTO for full-scale tests at TAKIKAWA. KITA and his associates declared that six months' life would be expected from this catalyst.

4. Research at the Army Fuel Research Institute. A brief inspection of the Fuchu laboratory was made by the Petroleum Section of NavTechJap on 12 January 1946. It was ascertained that tests had been made there with a pilot plant, formerly at KYOTO, of 100 m^3/hr gas throughput capacity using a natural iron ore catalyst at normal pressure. The yield was reported to be 73 gm/m^3, obtained at an operating temperature of 250°C.

This catalyst was discovered by Prof. MATSUBARA of the Tokyo Imperial University (Enclosure (D)). Prof. KITA and his associates at KYOTO also contributed their time and laboratory facilities for developmental studies on this catalyst prior to the trial in the Fuchu pilot plant. The catalyst consists mainly of a natural iron ore, sometimes designated ochre of "yellow mud", obtained from NIWASAKA, Fukushima Prefecture, and also occurring elsewhere in Japan. X-ray studies of this material indicated it to have the crystal structure of alpha ($Fe_2O_3.H_2O$).

C. PLANT DEVELOPMENT

According to information obtained, only five Fischer-Tropsch plant installations were ever placed under construction in the Japanese Empire. Three were completed and put on stream, namely, the Miike and Amagasaki Works in HONSHU, and the Takikawa plant in HOKKAIDO. Two others in Manchuria, one at CHIELIN and the other at CHINCHU, were under construction at the end of the war.

The Miike Works was the only Fischer plant visited. Some information on the other installations was supplied by Mr. SOGABE of the Nippon Jinzo Sekiyu Co., and Mr. N. SHONO of TEIKOKU NENRYO. The Amagasaki plant had 24 double-tube Ruhrchemie-type converters and utilized a cobalt catalyst at atmospheric pressure. The Takikawa plant had 36 double-tube Ruhrchemie converters, 32 single-tube Ruhrchemie converters, and 4 of a Japanese design, in which internal cooling tubes, carrying circulated water, were arranged in a cylindrical converter shell. All operations at TAKIKAWA were at 10 atmospheres pressure, and both iron and cobalt catalysts were employed. Both the precipitated iron catalyst developed by Prof. KITA, and the natural iron catalyst of Prof. MATSUBARA have been utilized in this plant.

These installations, as shown in Table I, failed to produce in accordance with design figures. It is significant, however, that the Takikawa plant did manage to maintain production using Japan's only contribution to the Fischer-Tropsch process, namely the iron catalyst.

The Miike plant utilized the atmospheric pressure synthesis as licensed by Mitsui Bussan Co. from Ruhrchemie in 1936. Construction on the plant began in November, 1936, and oil production started in May, 1940. Most of the equipment was furnished by the Koppers Co. of Germany (Enclosure (G)).

The catalyst was licensed as part of the Ruhrchemie contract and consisted of cobalt, thoria, magnesia and kieselguhr, in the respective weight proportions 21.2 : 1.2 : 2.4 : 75.2. About 4.5 metric tons of catalyst, containing one ton of cobalt, was charged to each converter. The converters were the well known "fin and tube" type, with water at about 15kg/cm^2 static pressure circulating by thermo-siphon action through the tubes and an external cooling system. The catalyst was packed between the fins, outside the tubes.

The plant was operated as a two-stage system, comprising 30 converters in the first stage and 18 in the second, with total product recovery between stages. Eight additional converters were held in reserve or were "off-stream". The system was designed to operate at a gas throughput of 1,000 m^3/hr per converter, corresponding to an N.T.P. space velocity of about 75. The actual throughput was about 750 m^3/hr.

The synthesis was effected at 180-200°C, using a synthesis gas of nominal composition $2H_2$: 1 CO, made by blending water gas with re-formed coke oven gas. The design yield was 116 grams per cubic meter of inlet gas, whereas the actual yield was 70-85 gm.

The plant produced gasol (liquified propane and butane), motor gasoline, diesel fuel, and several grades of paraffin wax. A plant to manufacture lubricating oil by $AlCl_3$ polymerization of paraffin was under construction at the end of the war. Design capacity of the synthesis plant was 30,000 metric tons of crude product per year, but actual production during the peak year (1943) was only 16,000 tons. Low production was said to be due primarily to:

(a) Low production of synthesis gas, caused by generator difficulties. The coke from Miike coal, used in gas generation, has a low melting point ash, and a high sulfur content, necessitating a low operating temperature. This, in turn, resulted in production of a gas high in inerts, and also a substantial reduction of the gas yield per ton of coke.

(b) Poor catalyst activity.

(c) Leakage of the water tubes in the converter.

(d) Variation of synthesis gas composition.

The synthesis gas generating system consisted of 5 Koppers water-gas generators and a re-forming plant, also designed and constructed by Koppers. The latter comprised two sets of Cowpers stoves and auxiliary equipment. For de-sulfurizing the gases, the Klonne system was employed, comprising separate units for removing inorganic and organic sulfur. This system employed Luxmasse sodium-carbonate mixtures as the de-sulfurizing agent. The purified gas contained about 0.004 gm of total sulfur per cubic meter.

The catalyst life was about 120 days, requiring five activations, at intervals of 20 days. The plant contained complete facilities for the manufacture of new catalysts, and the recovery of cobalt and thorium from spent catalysts. Facilities were also provided for reducing new catalysts outside the converters, and storing the reduced product until required for plant service.

As previously stated, the Miike plant began operation in 1940. Steady production was maintained, but at a rate far below design capacity, until the gas generator system was damaged by bombing in August, 1945. Even at reduced production rate, however, this plant was Japan's most successful Fischer-Tropsch plant, as is shown by the production figures of Table I.

Properties of crude products from the Miike and Takikawa plants are presented in Table V, and those of finished products from Miike in Table VI. This information was obtained from TEIKOKU NENRYO in TOKYO. These data should be compared with the values in Table III, Enclosure (G). The high olefin content of the Takikawa product, (Table V), is characteristic of the Fischer-Tropsch process when using an iron catalyst. The low-octane and high-cetane values of the Miike products (Table VI) are typical of the Fischer-Tropsch process employing the conventional Ruhrchemie cobalt catalyst.

Part IV
COAL CARBONIZATION

A. GENERAL REMARKS

The study of low-temperature carbonization of coal in Japan began as early as 1921, being a part of the general program at the Imperial Fuel Research Institute for investigating the economical utilization of Japanese coals (Enclosure (E)). The Institute has maintained a leading position in the endeavor to establish a successful carbonization industry as part of Japan's normal economy. The objective of this research has changed from time to time. Early work emphasized the possibility of utilizing the semi-coke from low-temperature carbonization as a domestic fuel, but this product has never been accepted by the Japanese people, who prefer charcoal. In central and southern Japan, charcoal is used almost exclusively in the rural districts, and in most towns of less than 50,000 population. Mr. Y. BAN, present Director of the Institute, states that even in the larger cities, a large proportion of the domestic fuel consumed is charcoal. For example, it is estimated that 40% of the homes in TOKYO use no other fuel.

The tar from low-temperature carbonization is a valuable raw material. As one of its industrial possibilities, it is an attractive substitute for petroleum as a source of gasoline and fuel oil. Japan, having limited natural petroleum resources, has been acutely aware of this possibility for many years. As an outcome of the war, one of her most important sources of oil has been lost, namely, the lean shales of FUSHUN. This circumstance will undoubtedly stimulate further research on carbonization of native coals in the immediate future.

No attempt was made to study Japan's low-temperature carbonization industry and research in a comprehensive manner, but in the course of pursuing field activities, direct contact was made with a number of industrial installations and research institutions related to this field. Japanese technical personnel associated therewith have been interrogated and, in addition, some technical and statistical information has been obtained regarding carbonization installations in areas not visited. The information so obtained forms the basis for this report.

B. COAL CARBONIZATION RESEARCH

1. Research Activities of the Imperial Fuel Research Institute. The utilization of the low-rank non-caking bituminous coals and brown coals, with which Japan is plentifully supplied, has always constituted one of the country's more important problems.

At the Institute, low-temperature carbonization has always been considered an attractive and logical approach to the problem of utilization of such coals, and a continuous program of research has been carried on along this line (Enclosure (E)).

The tar is the most valuable product obtained from coal carbonization, but is produced only in yields of six to ten per cent, by weight, of coal charged, whereas, the semi-coke usually amounts to sixty-five per cent or more of the charge. Tar alone, therefore, cannot carry the cost of process. Table III of Enclosure (E) presents data on tar yields from typical Japanese coals.

The Institute has contributed much general information on the carbonization characteristics of Japanese coals, but no specific commercial process or equipment has evolved from this work. Its technologists are carrying out investigations on both laboratory and assay plant scale, the latter comprising a system of six externally-heated vertical retorts arranged in parallel, and having a total throughput of six tons of coal per day (Enclosure (E), Figures 4 and 5). This system was designed at the Institute and has been in operation, with some modifications, since 1921.

Since the end of the war, interest has revived at the Institute in promoting the use of low-temperature carbonization semi-coke as a domestic fuel, and in particular, the "coalite" obtained from brown coal. If a satisfactory product can be obtained, and commercial exploitation realized, the tar may become an important source of liquid fuels for Japan's peace-time economy. Already it has been determined that "coalite" from brown coal has satisfactory ignition and combustion properties and can be produced at about one half the cost of charcoal. However, all samples as yet prepared burn with a slight, but objectionable odor, which would prevent their ready acceptance.

2. Carbonization Research at the Army Fuel Research Institute. The Army Fuel Research Institute, at FUCHU, investigated the performance of a simplified low-temperature carbonization retort, internally heated, suitable for installation at mine sites. The project was strictly a wartime measure, intended to increase Japan's supply of low-temperature tar for use in liquid fuel production.

To economize on steel, brick was employed for constructing the experimental unit, except for critical supporting members. The charge to this retort was 300kg, and the time of carbonization about 10 hours. It was reported that this equipment was adaptable either to caking or non-caking charge stocks. Results were said to be favorable to the extent that large-scale expansion was contempleted.

Tar yields from several coals tested were as follows:

Ubari coal	10-12%	(on weight of charge)
Minami-Nayoshi	10-14%	(on weight of charge)
Toban Takahagi	6%	(on weight of charge)
Takasaki Peat	3.5	(on weight of charge)

3. Carbonization Research at the Naval Research Laboratory, TOKUYAMA. The Naval Research Laboratory at TOKUYAMA installed Thyssen and Davidson retorting systems in 1925. Carbonization work was carried on until about 1932, when it was abandoned. The results of some of this work have been obtained in the form of printed documents not yet translated, except for titles. A list of these documents, which were forwarded via ATIS to the Washington Document Center is contained in Enclosure (C).

C. INDUSTRIAL COAL CARBONIZATION

1. General Remarks. Because the tar produced could not carry the cost of the process, and no dependable market had been found for the semi-coke, industrial coal carbonization did not comprise an important phase of Japan's peace-time economy. However, under the stimulus of government subsidies, this industry expanded rapidly in recent years, the object being to increase the available supply of tar for use as a source of motor gasoline and heavy fuel oil.

Motor grade gasoline can be obtained from the tar by simple distillation, and it was planned to produce aviation grades by hydrocracking suitable middle and heavy fractions (refer to Part II, Section B, this report). Although the hydrocracking program materialized only to a limited extent, the manufacture of liquid fuels by simple distillation of low-temperature tar constituted a far greater share of Japan's war production than high-pressure coal hydrogenation and the Fischer-Tropsch synthesis combined (Table I).

From information obtained, it appears that growth of the coal carbonization industry began about 1934, with the building of the Chisso Plant at UBE. From that time until the present, at least 12 plants have gone into operation throughout the Japanese Empire, and 3 more were under construction at the end of the war, according to information obtained from Mr. N. SHONO, of TEIKOKU NENRYO. Miscellaneous technical information concerning these plants is presented in Table VII.

The Lurgi system is preferred in Japan. According to Mr. BAN, of the Imperial Fuel Research Institute, no Japanese carbonization system has been successful. The Tokyo Gas Co. type plants, installed at the Nagoya and Yokohama works (Table VII), were the only references found as to the commercial use of Japanese equipment. The retort of this system, according to Mr. SHONO, comprises a horizontal rotating steel drum, externally heated. It is provided with a rotating internal scraping device to prevent accumulation of partially carbonized coal on the walls. Six retorts constitute a production unit. The design throughput of each retort is 2.5 metric tons of coal per day. Excessive damage from overheating was suffered, both in the retort vessel and the scraping device, and the plants were abandoned about 1943. The coals charged to these plants possessed some caking properties, which, according to Mr. SHONO, contributed to the operating difficulties experienced.

The Ube, Kawasaki, Wakamatsu, Agochi, and Nagoya plants were originally built to supply tar for hydrocracking. Gasoline manufacture by this method was never actually realized, commercially, to a significant extent, therefore, the liquid fuel production figures for these plants (Table I) represent processing of low-temperature tar by conventional distillation methods.

No information other than production figures was obtained concerning the plants at AGOCHI, CHIELIN, KAWASAKI, NAIBUCHI, NAIHORO, HIRAGISHI, TAKIKAWA, MURORAN, EIAN and the Chisso works at UBE. These data were obtained through TEIKOKU NENRYO.

2. The Wakamatsu Plant. Both the Wakamatsu and Ube plants were inspected. The carbonization plant at WAKAMATSU was based on the Lurgi patents (Enclosure (H)). German engineers assisted in the construction and acceptance tests of the first units, which were completed in 1941, and production of gasoline, fuel oil and semi-coke began immediately. The original plan included installation of a research pilot plant for hydrocracking tar oils, and reaction vessels were ordered from the Krupp Corp. in Germany. Deliveries on these vessels and other equipment required were never made, however.

This plant was one of Japan's most important producers of liquid fuels from coal, according to information obtained, (Refer to Table I). Expansion of its carbonization and refining facilities continued, and steady production was maintained until the installation was disabled by a fire-bomb raid in August, 1945. It was stated that the tar yield actually attained was about 90% of the figure predicted by the Fischer-Hempel assay test, namely, about ten per cent, by weight, of the coal. The coal charged was a non-caking or weakly-caking bituminous variety from the nearby Orio district. Personnel interviewed stated that no operating difficulties were encountered, but that actual retort throughput varied somewhat with the properties of the coal charged.

3. The Ube Plant. The Ube plant was also an important producer of liquid fuels during the war, as shown by the production figures of Table I. At the time this plant was founded, in 1939, it was planned to install facilities for an annual production of 40,000 kl of gasoline. This output was to be obtained from Ube brown coal, by combining low-temperature carbonization with hydrocracking of the light tar oil. Synthetic ammonia and methanol were also to be manufactured (Enclosure (J)).

Construction of the plant began in 1941. The hydrocracking plant, which was never completed, was designed on the basis of the Navy's research at the First Naval Fuel Depot. (Refer to Part II, this report, and to NavTechJap report "Japanese Fuels and Lubricants, Article 2," Index No. X-38(N)-2, Enclosure (B)16, Parts I and II). Two Koppers carbonization units, each having a throughput capacity of 300 metric tons of coal per day were completed in February, 1942, and operation began at once. These units maintained production until the plant was severely damaged in bombing raids of July and August, 1945. Of the ten 300-ton Lurgi retorts originally planned, four were completed and in operation, and the remaining six were under construction when the plant was disabled by bomb damage.

Table I
LOCATION AND OUTPUT OF JAPANESE SYNTHETIC OIL PLANTS

Company	Location	Design Capacity	Actual Fuel Output*-(kl)				
			1941	1942	1943	1944	1945
Coal Hydrogenation:							
1. Manshu Jinzo Sekiyu Co., Fushun Works	FUSHUN, Manchuria	2.5 T/hr Paste charge	-	770	-	690	-
2. Chosen Jinzo Sekiyu Co., Agochi Works	AGOCHI, Korea	5 T/hr Paste charge	-	-	-	-	-
Total Coal-Hydrogenation Oil			-	770	-	690	-
Fischer-Tropsch:							
1. Nippon Jinzo Sekiyu Co., Miike Works	OMUTA, Kyushu	30,000 T/yr. oil output	7,200	9,290	13,870	11,070	1,720
2. Nippon Jinzo Sekiyu Co., Amagasaki Works	AMAGASAKI, Honshu	30,000 T/yr.	-	-	200	130	-
3. Nippon Jinzo Sekiyu Co., Takikawa Works	TAKIKAWA, Hokkaido	50,000 T/yr.	-	1,550	1,600	6,610	2,480
4. Manshu Jinzo Sekiyu Co., Chielin Works	CHIELIN, Manchuria	1,000 kl/yr.	under construction				
5. Manshu Gosei Nenryo Co., Chinchu Works	CHINCHU, Manchuria	40,000 kl/yr.	under construction				
Total Fischer-Tropsch Oil			7,200	10,840	15,670	17,810	4,200

Table I. LOCATION AND OUTPUT OF JAPANESE SYNTHETIC OIL PLANTS. (Cont.)

Company	Location	Design Capacity	Actual Fuel Output*-(kl)				
			1941	1942	1943	1944	1945
Low Temperature Carbonization:							
1. Nissan Ekitai Nenryo Co., Wakamatsu Works	WAKAMATSU, Kyushu	4 Lurgi Units 4 x 300 T/day Coal	8,760	9,620	16,850	21,570	6,550
2. Teikoku Nenryo Kogyo Co., Ube Works	UBE, Honshu	2 Koppers Units 4 Lurgi Units 6 x 300 T/day Coal		10,400	19,250	18,390	4,840
3. Ube Kosan Co., Chisso Works	UBE, Honshu	2 Koppers Units 2 x 300 T/day Coal	11,530	11,850	9,470	10,820	1,990
4. Toho Kagaku Kogyo Co., Nagoya Works	NAGOYA, Honshu	Toho Units	550	1,400	1,040	300	-
5. Nippon Yuka Kogyo Co., Kawasaki Works	KAWASAKI, Honshu	Knowles Ovens 30x7.5 T/day	320	2,170	4,700		-
6. Tokyo Gas Kagaku Co., Yokohama Works	YOKOHAMA, Honshu	-	310	790	430		-
7. Nippon Seitetsu Co., Wanishi Works	WANISHI, Hokkaido	Rotary-kiln 4 x 100 T/day	3,120	2,870	3,020	2,530	250
8. Nippon Jinzo Sekiyu Takikawa Works	TAKIKAWA, Hokkaido	Knowles Ovens 15x12 T/day	under construction				
9. Nippon Yuka Kogyo Co., Sorachi Works	SORACHI, Hokkaido	Knowles Ovens 120x12 T/day	under construction				
10. Teikoku Nenryo Kogyo Co., Naibuchi Works	NAIBUCHI, Sakhalin	Lurgi Units 2x300 T/day 2x200 T/day	-	-	3,560	16,770	8,330

Table I. LOCATION AND OUTPUT OF JAPANESE SYNTHETIC OIL PLANTS. (Cont.)

Company	Location	Design Capacity	Actual Fuel Output* (kl)				
			1941	1942	1943	1944	1945
11. Teikoku Nenryo Kogyo Co., Naihoro Works	NAIHORO, Sakhalin	Lurgi Units 4 x 200 T/day	14,000	15,330	17,920	12,140	2,950
12. Nippon Chisso Kogyo Co., Eian Works	EIAN, Korea			4,620	3,760	930	
13. Chosen Jinzo Sekiyu Co., Agochi Works	AGOCHI, Korea	Lurgi Units 6 x 150 T/day	6,260	6,090	10,470	11,920	240
14. Manshu Jinzo Sekiyu Co., Chielin Works	CHIELIN, Manchuria	Lurgi Units 4 x 150 T/day		under	construction		
Total Low-Temperature Oil			44,850	65,140	90,470	95,360	25,150
Total Actual Oil From Coal			52,050	76,750	106,140	113,860	29,350
Shale Oil:							
Minami Manshu Tetsudo Co., Fushun Works	FUSHUN, Manchuria		137,780	163,280	160,140	83,150	16,530

* Oil output includes only gasoline, kerosene, diesel oil and fuel oil. It does not include items such as pitch, wax, lubricating oils, cresols, "gasol", etc.

Table II
ANALYSIS OF OYAMA COAL

Proximate				Heating Value	Ultimate				
H_2O	Ash	Volatile Matter	Fixed C	Cal/gr	C	H	O	S	N
5.5	7.0	41.1	46.4	7,200	73.7	5.7	12.0	0.5	1.2

Table III
RESULTS OF HYDROGENATION OF OYAMA COAL

Catalyst	$ZnCl_2$ (amount used not specified)
Operating temperature	415°C
Average pressure	200 kg/cm^2
Fresh hydrogen input	185 m^3/hr (N.T.P.)
Rate of hydrogen recirculation	1,000 m^3/hr (N.T.P.)
Paste input	282 kg/hr
Ratio (vehicle/coal)	3/2
H_2 consumption (wt% of coal)	7.97
Wt% of coal liquified	77.9
Yield of oil, wt% of total oil:	
Oil boiling below 180°C	3
Middle oil, boiling 180-280°C	40
Heavy oil, boiling above 280°C	53

Table IV
HYDROGENATION OF HIGH AND LOW-TEMPERATURE TARS

	Creosote Oil from High-Temp. Tar.	Middle Oil from Low-Temp. Tar.
Catalyst	MoS_3	MoS_3
Reaction Temp. - 1st stage, °C	420	350
Reaction Temp. - 2nd stage, °C	470	430
Reaction Pressure, atm.	200	200
Space Velocity (liquid)	0.5 - 0.8	0.5
Aviation Gasoline:		
Yield, % by volume	Ca 25	Ca 50
Octane No., Clear	79	74
Octane No., 0.1% T.E.L.	92	88.5

Table V
PROPERTIES OF CRUDE FISCHER-TROPSCH PRODUCTS FROM MIIKE AND TAKIKAWA PLANTS

		Crude Condensed Product		Light Product Adsorbed on Charcoal	
Plant		MIIKE	TAKIKAWA	MIIKE	TAKIKAWA
Catalyst		Co	Fe	Co	Fe
Operating Pressure, atm.		1	10	1	10
I.B.P.		131°C	125°C	39°C	35°C
Vol. distilled:	5%	155	162	48	50
	10%	184	177	53	55
	20%	200	200	62	64
	30%	214	229	71	71
	40%	227	253	80	79
	50%	240	276	92	86
	60%	257	309	103	92
	70%	284	347	115	105
	80%	315	360	139	115
	90%	337	-	158	132
	97%	348	-	173	-
E.P.		373	-	195	152
Paraffins		93-96%	88.1%	88-90%	63.1%
Olefins		4- 7%	11.9%	10-12%	36.9%
Iodine Value		-	13	-	92.9
Sp. Gr.		0.768	0.761	0.693	0.681

Table VI
PROPERTIES OF PRODUCTS FROM MIIKE PLANT

Product		Motor Gasoline	Gas Oil B 1	Gas Oil B 2
Sp. Gr.		0.7081	0.770	0.780
I.B.P.		35°C	143°C	163°C
Vol. distilled	5%	40	171	192
	10%	53	193	216
	20%	62	215	226
	30%	71	225	235
	40%	81	234	246
	50%	92	242	260
	60%	103	252	280
	70%	116	275	322
	80%	129	292	341
	90%	143	301	356
	95%	154	320	362
E.P.		183	-	-
Octane No. (C.F.R. Motor Method)		40	-	-
Vapor Pressure, kg/cm^2		0.6	-	-
Cetane No.		-	75	-
Flash Point		-	56°C	87°C
Freezing Point		-	-4°C	-1°C

Table VII
MISCELLANEOUS INFORMATION ON JAPANESE LOW-TEMPERATURE CARBONIZATION PLANTS

Name of Instal-lation	Location	Owning Or Controlling Agency	Date Operation Began	Type Carboni-zation Unit Used	No. of Units	Nominal Unit Coal Cap. Metric Tons Per Day	Actual Total Coal Cap. Metric Tons Per Day	Name Of Coal Processed	Classifi-cation Of Coal Pro-cessed	Proximate Analysis of Coal						Approx. Tar Yield Wt. (%) of Coal
										H20	Vol. Matter	Fixed C	Ash	S	Heating Value Cal/gm	
Agochi Works	AGOCHI Korea	Chosen Jinzo Sekiyu Co.Ltd.	Some Const. At End Of War	Lurgi	6	150	750	Agochi	Brown Coal	10.95	36.98	35.41	16.66	0.35	5112	- -
Chielin Works	CHIELIN Manchuria	Manshu Jinzo Sekiyu Co.Ltd.	Under Construc-tion	Lurgi	4	150	- -	Fushin	1(1)	8.92	37.79	47.51	5.78	0.51	6433	- -
Chisso Works	UBE Honshu	Ube Kosan Co. Ltd.	Sept. 1934	Koppers Continuous Vertical	2	300	550	Ube (Itsudan)	Brown Coal	8.58	38.28	32.96	20.67	- -	5298	8
Kawasaki Works	KAWASAKI Honshu	Nippon Yuka Kogyo Co.Ltd.	Dec. 1939	Knowles	30	75	6000T Coal/Yr	Yubari	1	1.45	42.42	45.63	10.50	0.21	7579	- -
							50000T Pitch/Yr	Sunagawa	1	1.68	38.18	51.46	8.68	0.61	7260	
Naibuchi Works	NAIBUCHI Saghalien	Teikoku Nenryo Kogyo Co.Ltd.	Apr. 1943 Some Const. At End Of War	Lurgi	2 2	300 200	700-800	Naibuchi	- -	9.00	39.80	44.90	6.30	- -	6169	10
Naihoro Works	NAIHORO Saghalien	Teikoku Nenryo Kogyo Co.Ltd.	Aug. 1937	Lurgi	4	200	600	Naihoro	- -	12.59	43.08	39.48	4.85	- -	6461	10
Nagoya Works	NAGOYA Honshu	Toho Kagaku Kogyo Co.Ltd.	July 1940	Tokyo Gas Type	Not Known	Not Known	100	Yubari		See	Kawasaki		Works			- -
								Niisakutan (Karafuto)	- -	- -	- -	- -	- -	- -	- -	
Sorachi Works	HIRAGISHI Hokkaido	Nippon Yuka Kogyo Co.Ltd.	Under Construc-tion	Knowles	120	12	- -	Yubari		See	Kawasaki		Works			
								Mojiri	2	2.10	38.49	51.85	7.6	0.51	7480	
								Sunagawa		See	Kawasaki		Works			
Takikawa Works	TAKIKAWA Hokkaido	Nippon Jinzo Sekiyu Co.Ltd.	Under Construc-tion	Knowles	15	12		No	Information							- -
Ube Works	UBE Honshu	Teikoku Nenryo Kogyo Co. Ltd.	Feb. 1942	Lurgi Koppers Cont. Vertical	10 Planned 4 Completed 2	300 300	Lurgi 750 Koppers 550	Ube	Brown Coal	See	Chisso		Works			8
Wanishi Works	MURORAN Hokkaido	Nippon Seitetsu Co. Ltd.	1937	Rotary Kiln Type	4	100	300	Kakuda	1	3.06	39.55	46.63	10.73	0.43	6704	- -
Wakamatsu Works	WAKAMATSU Kyushu	Nissan Ekitai Nenryo Co.Ltd	Apr.1941	Lurgi	4	300	750	Takamatsu Otsuji Nakazaru	1 or 2 1 or 2 2	4.38 5.26 4.61	35.24 34.12 36.88	37.58 40.66 33.12	22.8 14.96 25.39	0.75 0.18 0.42	5581 6210 5497	10
Yokohama Works	YOKOHAMA Honshu	Tokyo Gas Kagaku Kogyo Co. Ltd.	Mar.1940	Tokyo Gas Type	20	15	100	Yubari		See	Kawasaki		Works			- -
Kian Works	KIAN Korea	Nippon Chisso Kogyo Co.Ltd.	- -	- -	- -	- -	No	Information								

Note (1)
1 = Bituminous Coal Weakly Caking.
2 = Bituminous Coal Non-Caking.

ENCLOSURE (A)

ENCLOSURE (A)

SUMMARY OF RESEARCH ON THE CONVERSION OF COAL TO OIL AT THE FIRST NAVAL FUEL DEPOT, OFUNA

by

CHEM. ENG. COMDR. DR. K. MITSUI

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

December 1945

ENCLOSURE (A)

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (A)

I. INTRODUCTION

The production of oil by low-temperature carbonization of coal had been studied in Japan since 1925. However, since this process gives only 10 wt.% yield of oil which contains 30 wt.% of tar acids, the Japanese Navy initiated studies on increasing the yield of oil, reducing coke formation and de-oxygenating this oil, particularly for use as bunker fuel.

In the meantime, the original Bergius process had been considered as applicable under Japanese conditions, and tests on Japanese coals (Shinbara and Oyama coal) were made with an autoclave and continuous pilot plant at Rheinau, Germany in 1926. The Japanese Naval Fuel Depot decided to study this process particularly for conversion of coal to oil, since it gives a range of products (gasoline, tar acids, boiler fuel, and pitch), whereas the Fischer-Tropsch synthesis gives only motor gasoline. Enclosures (B)11 and (B)20.

A number of research studies concerning the above processes were conducted at the Japanese Naval Fuel Depot at TOKUYAMA. Autoclave studies on the hydrogenation of coal were started early in 1925. In 1930, it was decided to build a large semi-commercial scale pilot plant to treat 7 tons of paste (oil/coal = 6/4 or 5/5) per day. Studies in this plant at TOKUYAMA were made from 1932 to 1939, and in 1940 the plant was transferred to the First Naval Fuel Depot at OFUNA. It was the first large semi-commercial plant for hydrogenation of coal constructed in Japan. This plant was also used for studying the hydrocracking of tars and oils.

In this work, many obstacles, such as non-uniform distribution of paste in the reaction chamber, corrosion of metals, and separation of produced oil free from unreacted coal and ash, were surmounted.

II. HYDROGENATION OF COAL

A. General

At first the reactions of chemically pure substances were studied, including phenol, benzene, naphthalene, anthracene, coal substance and humus, which were distributed in low and high-temperature tars and coal hydrogenation oils.

Simple hydrogenation progressed only in the presence of a favorable catalyst, solvent, and high pressure hydrogen, but in practical operations, the reaction was always followed by hydrocracking. Enclosures (B)1, (B)2, (B)10, (B)14, and (B)16. Hence, it was essential to explore the conditions of reaction under which cracking and hydrogenation proceeded simultaneously.

A large number of catalysts and solvents were studied to increase the yield of oil by decreasing the formation of gas and coke. Enclosures (B)5, (B)9, (B)12, (B)13, (B)14, (B)15, and (B)18.

B. Reaction Conditions

Reaction temperature, pressure, and time are important factors in the conversion of coals, tars, and oils. These factors vary widely according to the activity of catalyst.

In general, the smaller the ratio of charge stock to hydrogen and the higher the reaction temperature, the greater the coke and gas formation. At hydrogen pressures below 200 kg/cm², the hydrogenation of coal was not only incomplete, but a part of the hydrogenated product was converted to coke and gas. For continuous operation, a 200 kg/cm^2 hydrogen pressure and a 400-410°C reaction temperature were found to be favorable conditions for coal hydrogenation. Enclosures (B)6, (B)7, and (B)17.

The effect of time at the reaction temperature was also investigated in the autoclave tests, and it was found that most of the changes, (reduction of benzene insoluble substance, increase of total oil, benzene soluble substance, and low boiling oil), took place during the first hour. The reaction proceeded more slowly during the second hour, the hydrogen concentration decreased, and the formation of coke began to take place. For continuous operation, the most favorable space velocity was 1.5-1.0. Enclosures (B)8, (B)10, and (B)13.

C. Catalyst Studies

At the beginning of this work, very little authoritative work had been done on the effect of catalyst. Initially Fe_2O_3 was studied as a catalyst for the hydrogenation of coal. Enclosure (B)5.

In the course of these experiments, it was found that coal treated with 1% of a $ZnCl_2$ solution gave good results. Since then, a number of experiments with the $ZnCl_2$ catalyst were made. Enclosures (B)10, and (B)18.

A $ZnCl_2$ catalyst was understood to promote both dehydration and hydrocracking, and consequently it is favorable for the hydrogenation of coal and tar. In the autoclave test, the most suitable conditions for this catalyst were proved to be 200 kg/cm^2 of hydrogen pressure, a 400°C reaction temperature and 1 hour of reaction time. When this catalyst was employed in the commercial plant, however, troubles were encountered due to corrosion of metallic surfaces and the formation of NH_4Cl.

Stannic oxide was a good catalyst, but stannous chloride was much superior. Enclosure (B)18.

Sulphur was found to exert great influence on the catalytic activity of some substances. It was thought advisable to ensure the presence of a certain amount of free hydrogen sulphide since Varga stated that hydrogen sulphide, in the presence of MoS_3 or WS_3, promoted the hydrogenation reaction. (Brennstoff-Chemie 9, 277 (1928)). The catalytic activity of iron, especially, was enhanced by addition of sulphur. At the present time, the commercial catalyst used for hydrogenation of coal is a mixture of ferric oxide and sulphur or a mixture of ferric oxide, stannic oxide, and sulphur.

The catalyst used commercially for hydrocracking of tars and oils is MoS_3 or a mixture of MoO_3, Ni_2O_3, and acid clay.

D. Material Balance

Typical yields for hydrogenation of Oyama coal, using Fe_2O_3 and sulphur catalyst are given in Table I(A). Enclosure (B)17.

E. Secondary Hydrogenation

Typical yields for secondary hydrogenation of oil from Oyama coal, and also for hydrocracking of high and low-temperature tars using MoO_3, Ni_2O_3 and acid clay catalyst, are given in Table II(A). (See Article 2 of this series, Enclosure (B)16.)

F. Aviation Gasoline Properties

The properties of hydrocracked aviation gasoline made from various kind of charge stock are given in Table III(A). (A standard natural straight run aviation gasoline is also included as a reference.) Enclosure (B)15.

Hydrocracked aviation gasolines prepared from coal and tars are nearly the same as natural straight run gasoline, but the oil prepared from high-temperature coal tar is rich in aromatic content.

G. Commercial Applications

The preceeding experiments showed that commercial development was possible only with government assistance. Then the Chosen Nitrogen Fertilizer Company (AGOCHI, Korea) and the South Manchurian Railway Company (FUSHUN, Manchuria) designed and constructed the large-scale coal hydrogenation plants based on the Naval Fuel Depot's process. These two plants were the only commercial coal hydrogenation plants installed in the Japanese Empire. Enclosures (B)21, (B)22, and (B)23.

For the production of aviation gasoline from tars and oils, three large-scale commercial hydrocracking plants were constructed at the Second and Third Naval Fuel Depots (YOKKAICHI and TOKUYAMA) and Toho Chemical Industries Company (NAGOYA), and the construction of five more plants was undertaken. (NAIBUCHI in Saghalin, UBE and YAHATA in Honshu, KITSURIN and SHIHEIGAI in Manchuria); but they were not completed at the close of the war.

III. FISCHER-TROPSCH SYNTHESIS

This process was licensed from Germany by Mitsui-Bussan Company and construction of a 30,000 kl/year plant at MIIKE, Kyushu was started in 1938. Operating difficulties were encountered, however, and successful operations were not obtained until about 1942. The First Naval Fuel Depot started studies on the catalysts for this process in June 1940, but stopped in October 1943, after the process had been successfully operated at MIIKE. Enclosures (B)19, (B)20, and (B)21.

Table I(A)
MATERIAL BALANCE SHEET FOR THE PRIMARY HYDROGENATION OF COAL

Reaction Conditions				
Reaction Temp. (°C)	410	410	420	420
Reaction Press. (kg/cm^2)	200	200	200	200
Space Velocity of Paste	0.88	1.21	1.32	1.65
Yield of Products (wt.% of paste)				
Water	10.4	13.6	9.5	9.1
Light Oil (below 300°C)*	23.8	18.1	17.9	19.4
Heavy Oil (above 300°C)**	52.6	53.2	58.0	55.5
Solid Residue	8.2	10.8	8.5	8.1
Gas and Loss	5.0	4.3	6.1	7.0

* Charge stock for secondary hydrogenation of coal.
** Recycle oil for preparation of paste.

ENCLOSURE (A)

Table II(A)
TYPICAL YIELDS

Charge Stocks	Oyama Coal Hydrogen Oil	Ube Low-Temp. Tar	Showa High-Temp. Tar
Density (25°C)	0.951	0.974	0.977
50 Vol. % Point (°C)	230	255	254
Aniline Point (°C)	23.5		26.5
Reaction Conditions			
Reaction Temp. (°C)	400	400	430
Reaction Press. (kg/cm^2	200	200	200
Space Velocity	0.5	0.5	0.5
Yield of Products (wt.% of c.s.)			
Total Oil	95.2	92.2	99.0
Aviation Gasoline	23.4	50.1	18.6
H_2 Consumption	4.1	4.6	6.2

Table III(A)
PROPERTIES OF HYDROCRACKED AVIATION GASOLINE

Charge Stock	Oyama Coal	Ube Low Temp. Tar	Showa High Temp. Tar	Yabase* Str. Run
Density (20/4°C)	0.727	0.756	0.776	0.743
Vapor Press. (kg/cm^2)	0.53	0.54	0.56	0.24
Components (Vol. %)				
Aromatics	19.0	25.6	31.2	8.0
Naphthenes	42.4	49.6	62.2	35.0
Paraffins	37.6	23.3	11.0	56.4
Octane Value				
Clear	73.7	73.5	79.0	65.7
With 0.1 wt.% Lead	90.8	88.8	91.9	86.0

* Prepared from Yabase crude oil in AKITA Prefecture.

RESTRICTED

ENCLOSURE (B)

ENCLOSURE (B) 1

THE THERMAL CRACKING OF PHENOL UNDER HIGH PRESSURE HYDROGEN

Reference NavTechJap Document No. ND 26-0008.6 ATIS No. 4579

by

NAVAL ENGINEER
T. OGAWA

Research Period: 1928-1929

Translation Prepared by Chem. Eng. Lt. Cmdr. K. MITSUI
and Reviewed with him by the U. S. Naval Technical Mission to Japan.

December 1945

ENCLOSURE (B)1

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (3)1

I

SUMMARY

Phenol was heated to 450-500°C under high pressure of hydrogen, and a 20-60% yield of benzene was obtained.

The conversion of phenol to benzene was proved to be a simple dehydration reaction which was prompted by increasing temperature and reaction time.

I. INTRODUCTION

This investigation of the thermal cracking of phenol, in the presence of high pressure hydrogen, was related to the utilization of high and low-temperature tars as paste oils in the hydrogenation of coal, particularly to determine the necessity for specifications on tarry acids and asphaltenes contained in such tars.

Up to this time, many studies had been made on the thermal cracking or hydrogenation of phenol in the presence of various catalysts, but little work had been done on the conversion in the presence of high pressure hydrogen in the absence of catalysts.

Therefore this investigation was particularly concerned with conversion of phenol under the latter conditions.

The key research personnel working on the project were:

Naval Eng.	T. OGAWA
Naval Assist. Eng.	I. TAKAHASHI

II. DETAILED DESCRIPTION

A. Preparation of Sample

Commercial phenol was heated 2-3 hours with lead oxide, and distilled to yield a pure material with boiling point, 180°C, and melting point, 41°C.

In these experiments, 100 grams of the sample were put into a 2 liter rotating-type autoclave, and the air was displaced by hydrogen. Hydrogen pressure was increased to 100 atmospheres and the autoclave was heated to the desired reaction temperature.

B. Experiment I

No change of pressure was observed after the sample was heated 2 hours at a temperature of 475°C, and according to the analysis, nothing but hydrogen was found in the gas in the autoclave after the reaction.

The total liquid product (96.2gm) was fractionated into the following cuts:

Water	3.0 gm
75-83°C Fraction	7.6 gm
160-185°C Fraction	79.0 gm

Only a trace of residue over 200°C was obtained. No crystalline materials were present in this residue. The 75-83°C cut was redistilled, and the physical properties of each fraction determined, with the following results shown in Table I(B)1.

Fraction 2 (in Table I(B)1) was treated with a 50-50 mixed acid (H_2SO_4 and HNO_3). Examination of the physical constants of the nitrated product showed that it was practically pure nitrobenzene. It was, therefore, concluded that Fraction 2 was chiefly composed of benzene.

Fraction 1 was investigated by the same method and it was found that it consisted largely of benzene and a small amount of lower boiling compounds.

A large part of the 160-185°C reaction product was composed of crystals with 40°C mp, insoluble in NaOH solution, and which was proved to be phenol by the color reaction with $FeCl_3$.

C. <u>Experiment II</u>

When the autoclave was heated three hours at 500°C, the pressure decreased slightly, the difference of the pressure before and after reaction amounting to 10 atmospheres (S.T.P.).

The gas remaining in the autoclave after reaction contained 95.7% hydrogen and 4.3% (n=1.2) saturated hydrocarbons. From these results, the quantity of hydrogen converted into reaction product was calculated to be 1.2 mol percent of the original H_2, and that, converted into gaseous hydrocarbons was 0.45 mol percent. The liquid product (84 gm) was fractionated as follows:

50-160°C Fraction	39.3 gm
160-190°C Fraction	34.9 gm
Residue	0.4 gm
Water	8.2 gm

The 50-160°C fraction was redistilled and the specific gravity and the refractive index of each cut was measured as shown in Table II(B)1.

By physical constants, it was concluded that fraction 1 (in Table II(B)1) was chiefly composed of benzene, but, to make sure, 2cc of this cut were treated with 10% fuming sulphuric acid and a residue of 0.85cc was obtained. The physical properties of this residue, d^{15}_{4} of 0.754 and N^{15}_{D} of 1.414, were similar to cyclopentane or methyl-cyclopentane.

Fraction 2 was confirmed to be largely benzene by converting it to nitrobenzene.

The 160-190°C fraction was also treated by the methods of the previous experiment and it was found to be mainly unchanged phenol.

D. <u>Experiment III</u>

The autoclave was heated for five hours at 500°C, and the decrease of pressure amounted to 14 atmospheres. The gas remaining in the autoclave after the reaction, consisted of 94.0% hydrogen and 6.0% (n=1.2) saturated hydrocarbons. From these results, the quantity of converted hydrogen into reaction products was calculated to be 1.8 mol percent of original hydrogen, and that, converted into gaseous hydrocarbons was 0.6 mol percent. The liquid product (86 gm) was fractionated into the following cuts:

65-85°C Fraction	43.9 gm
85-179°C Fraction	1.5 gm
179-195°C Fraction	26.6 gm
Residue	Trace
Water	9.8

The 65-85°C fraction was redistilled and the specific gravity and refractive index of each fraction were measured as shown in Table III(B)1.

Fraction 1 (1.5cc) was treated with fuming sulphuric acid and 0.9cc of residue was obtained with d_4^{15} of 0.764 and N_D^{15} of 1.417. By comparison with previous results, it was concluded that fraction 2 was mainly benzene. Similarly, it was concluded that the 179-195°C fraction was phenol.

III. CONCLUSIONS

The results of these experiments are summarized in Table IV(B)1.

When phenol was heated two hours at 475°C with high pressure hydrogen, 20% was dissociated. Since no compounds such as diphenyl, diphenyl-ether were found in the reaction products, the reaction may be carried out according to the following equation:

$$C_6H_5OH + H_2 \longrightarrow C_6H_6 + H_2O$$

This dehydration proceeded three times as fast at 500°C, and gaseous saturated hydrocarbons were produced although the quantity was small.

The yield of benzene was higher when the time of reaction was longer, and it is clear from the analysis of the reaction products that benzene was chiefly obtained by the above reaction.

The thermal conversion of phenol to benzene under the normal pressure has been explained as due to phenol being first changed to ether, and then dissociating to phenol and benzene. But in this case, under high pressure of hydrogen, the reaction mechanism was probably only a simple dehydration reaction.

In the experiment carried out at 100 atmospheres of hydrogen pressure, and 500°C, a small amount of compounds with properties corresponding to cyclohexane and methyl cyclopentane, was obtained. This result showed that cracking and hydrogenation of the benzene ring occurred under high pressure and temperature conditions. The production of methane in the reaction also proved evidence that the before-mentioned reaction took place.

Table I(B)1
PHYSICAL PROPERTIES OF 75°C-83°C FRACTION

Fraction	B.P.(°C)	Yield(gm)	Sp. Gravity(25°/4°C)	Refractive Index(n_D^{25})
1	76-79	2.0	0.8427	1.4713
2	79-81	4.5	0.8504	1.4892
3	Residue	0.5	-	-

ENCLOSURE (B)1

Table II(B)1
PHYSICAL PROPERTIES OF 50°C-160°C FRACTION

Fraction	B.P.(°C)	Yield (gm)	Specific Gravity	Refractive Index(n_D^{15})
1	58-75	2.0	0.8117 (15°/4°C)	1.4596
2	75-85	30.7	0.8556 (25°/4°C)	1.4860
3	85-180	0.4	-	-

Table III(B)1
PHYSICAL PROPERTIES OF 65°C-85°C FRACTION

Fraction	B.P.(°C)	Yield(gm)	Specific Gravity	Refractive Index
1	65-75	1.6	0.7984 (15°/4°C)	1.4450 (n_D^{15})
2	75-85	40.0	0.8640 (25°/4°C)	1.4902 (n_D^{25})

Table IV(B)1
THERMOCRACKING OF PHENOL

Experiment Condition*				React. Prod. (mol/mol phenol)				
Exp. No.	Temp. (°C)	Time (hr)	Pressure Drop (atmospheres)	H_2 Absorption (mol %)	CH_4	H_2O	C_6H_6	C_6H_5OH
1	475	2	-	-	-	0.15	0.1	0.8
2	500	3	10	1.2	0.5	0.4	0.4	0.4
3	500	5	14	1.8	0.6	0.6	0.5	0.3

*For all experiments, 100 gm samples and an initial pressure of 100 atmospheres were used.

ENCLOSURE (B) 2

ON THE THERMAL CHANGE OF AROMATIC COMPOUNDS IN THE PRESENCE OF HIGH PRESSURE HYDROGEN

Reference NavTechJap Document No. ND 26-0008.7, ATIS No. 4579

by

NAVAL ENG. S. YAMAGUCHI

Research Period: 1928-1929

Prepared for and Reviewed with Author by
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ENCLOSURE (B)2

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)2

SUMMARY

Naphthalene, anthracene, phenol, a-naphthol and b-naphthol were heated at 450-500°C in the presence of a small amount of calcium chloride and hydrogen pressure of 70-80 atmospheres at 0°C. The chemical composition and physical properties of the reaction products were examined with the following results:

(1) Naphthalene: When naphthalene was heated at 500°C for 5 hours in the presence of calcium-chloride with hydrogen pressure of 80 atmospheres at 0°C, 60% of it was cracked, and the liquid reaction product consisted of benzene, and its homologues, and the gaseous reaction product consisted of methane (30 parts) and ethane (70 parts).

(2) Anthracene: This substance was cracked under the same conditions and was converted into 16% of gaseous hydrocarbons containing methane and ethane, and 74% of liquid hydrocarbons, containing 47% naphthalene and its derivatives, 27% benzene and its homologues, and 10% dianthracene.

(3) Phenol: At 500°C, phenol was decomposed into 30% benzene, 11% water and a small amount of di-phenyl, di-phenyl-ether and diphenol. The gaseous substances consisted of methane and ethane.

(4) Naphthol: When a-naphthol was heated at 450°C with a hydrogen pressure of 80 atmospheres at 0°C, most of it was liquefied. The products consisted of benzene homologues, naphthalene, tetralin, unreacted naphthol, and water.

b-Naphthol was cracked under the same conditions and its liquid product was very similar to that from a-naphthol.

I. INTRODUCTION

It is known that aromatic compounds are converted into lower aromatic compounds by cracking in the presence of hydrogen and a nickel catalyst. It was considered that further investigations along these lines would be of importance from the standpoint of developing a theory for production of gasoline from heavy oily substances, such as coal-tars or petroleum.

In earlier work on the cracking of aromatic compounds, the catalysts used were limited to reduced metals or metallic oxides. Calcium chloride was used in the present study, because it was known to be an excellent catalyst for catalytic cracking of petroleum oils.

Key research personnel working on project were: Chem. Eng. S. YAMAGUCHI and Chem. Eng. Assist. G. FUJII.

II. DETAILED DESCRIPTION

The naphthalene, anthracene, phenol, and a-, b-naphthol used in these experiments were proved to be fairly pure, on the basis of their physical constants, as shown in Table I(B)2.

In these experiments, a weighed sample was introduced into an autoclave, and after replacing the air by hydrogen, the pressure of the hydrogen was raised to the required value. The autoclave was electrically heated to the required temperature and was mechanically shaken during the reaction period. Changes of temperature and pressure during the reaction were recorded every ten minutes. After the reaction the apparatus was cooled, the volume of gas remaining was measured, and the chemical composition and physical properties of the reaction products were examined carefully.

A. Naphthalene

When naphthalene (100gm) was heated for 6 hours with 10% of calcium chloride at 500°C with initial hydrogen pressure of 71 atm. at 0°C, a fall of 11 atm. was observed (see Figure 1(B)2).

The gas in the autoclave was composed of 85.9% of H_2, 10.3% of C_2H_6, 4.6% of CH_4, and 0.2% of C_nH_{2n}.

The reaction product (67gm) in the autoclave consisted of liquid and solid substances, which were separated by filtration.

The solid amounted to 10gm and was found to be naphthalene, for, after purification by recrystallization from alcohol, it melted at 81°C, and the picrate at 151°C.

The liquid product (65gm) was distilled over metallic sodium at 759.5mm and separated into six fractions with the physical constants as shown in Table II(B)2.

Fractions 1 and 2, on the basis of their physical constants, appeared to be benzene and toluene respectively. The composition of the former was confirmed by converting it to nitrobenzene and then reducing it to aniline, and the latter by oxidation with potassium permanganate to benzoic acid (m.p. 121°C).

Fraction 3 and 4 were supposed, from their physical constants, to be a mixture of o-Xylene and ethyl benzene.

Fraction 5, consisting of naphthalene, Xylene, and ethyl benzene, was treated with picric acid in alcoholic solution to separate naphthalene.

The picrates, separated from volatile hydrocarbons by distillation under reduced pressure, amounted to 4.8gm, from which pure naphthalene was isolated with a yield of 1.2 gm.

The mixture of hydrocarbons separated from naphthalene weighed 3.6gm, and with its boiling point 124-145°C, refractive index $n_D^{25} = 1.4981$, and density $d_4^{25} = 0.8695$, the ratio of Xylene to ethyl benzene was estimated at 7:3.

Fraction 3 was composed of naphthalene as shown by the physical properties and also by the properties of the picrate.

B. Anthracene

Anthracene (100gm) was heated at 500°C for 6 hours with 10gm of calcium chloride and hydrogen pressure of 84 atm. at 0°C. The drop in pressure was 17.6 atm. at 0°C. (Refer to Figure 2(B)2).

The gaseous product was composed of 89.1% of H_2, 3.2% of CH_4, 7.6% of C_2H_6 and 0.1% of C_nH_{2n}. (Refer to Figure 2(B)2).

ENCLOSURE (B)2

From the reaction products, 10gm of solid and 74gm of liquid ($d_4^{25} = 0.984$, $n_D^{25} = 1.584$) were isolated.

The liquid reaction products (70gm) were fractionated at 758.8mm over metallic sodium as shown in Table III(B)2.

The fractions 1 and 2 were identified from their physical and chemical properties as benzene and toluene respectively.

The fractions 3 and 4 were also assumed to be mixtures of Xylene and ethyl benzene on the basis of their physical constants. Fractions 5 and 6, contained 14.9gm of crystals which had a m.p. of 78°C, and were confirmed to be naphthalene from the melting point and combustion analysis of the substance purified by crystallization from alcohol.

Found:	C, 93.62%;	H, 6.29%
Calc. for $C_{10}H_8$:	93.75%	6.25%

The liquid portion (7gm) remaining was supposed to contain alkyl-naphthalenes, and from it a-methyl naphthalene was isolated, by crystallization from hot alcoholic solution, in the form of a yellow crystalline picrate melting at 116-116.5°C in yield of 3.7gm.

Fractions 7 and 8, both were viscous liquids containing some solid substances, and were assumed to be mixtures of alkyl naphthalenes. The isolation of pure substances from the liquids by the formation of picrates was tried, but only red picrate melting at 161-172°C was isolated.

Lastly, there was a solid residue which was practically insoluble in alcohol, ether and benzene, and showed a melting point of 242-243°C. After purification by crystallization from ether solution.

These properties agreed with those of dianthracene prepared by Graebe and Lieberman, and by Ordendorff aud Cameron.

Combustion analysis gave the following results:

Found:	C, 93.85%;	H, 5.41%
Calc. for $C_{14}H_{10}$:	94.38%	5.61%

C. Phenol

Phenol (100gm) was heated at 500°C for 5 hours with 10gm of calcium chloride and hydrogen pressure of 75 atm. at 0°C. The fall in pressure was 12 atm. at 0°C (Refer to Figure 3(B)2).

The gaseous product was composed of 91.4% of H_2, 7.5% of C_nH_{2n+2}, 0.4% of C_nH_{2n}, 0.7% of CO and 0.2% of CO_2.

From the reaction products 77.5gm of liquid ($n_D^{25} = 1.532$, $d_4^{25} = 0.952$) and 10.7gm of water were isolated.

The liquid reaction product was subjected to fractional distillation as shown in Table IV(B)2.

Fractions 1, 2 and 3 were identified as benzene from their physical constants; and fractions 5 and 6 were assumed to be unreacted phenol and various kinds of di-phenols.

D. Naphthols

1. a-naphthol. When a-naphthol was heated at 450°C with 10% of calcium chloride and hydrogen pressure of 80 atm. at 0°C, a pressure drop of 19 atm. was observed. (Figure 4(B)2).

The compound was decomposed into 1-2% gas, 91% oily substance, and the balance, water.

The gas in the autoclave was composed of 97.8% of H_2, 1.0% of C_nH_{2n+2}, 0.4% of C_nH_{2n}, 0.3% of CO and 0.4% of CO_2.

The oily substance ($d_4^{25} = 1.021$, $n_D^{25}=1.594$) was treated with 10% of NaOH solution and separated into acidic and neutral fractions. The former was found to be unreacted naphthol, for, after purification by recrystallization from alcohol, it melted at 97°C. The latter substance, 72gm ($n_D^{25}=1.585$, $d_4^{25}=1.016$), was distilled under atmospheric and reduced pressures and separated into six fractions with physical constants as shown in Table V(B)2.

Fraction 1 was believed, from its physical constants, to be a benzene derivative. The crystals in fractions 2 and 3 (m.p. 81°C and m.p. of its picrate is 151°C) were assumed to be naphthalene.

The liquid substance in fraction 2 (12gm) was treated with picric acid (9gm) in alcoholic solution in order to separate naphthalene. The picrate, separated from the volatile hydrocarbons by distillation under reduced pressure, amounted to 7.5gm, and with its boiling point 196-202°C, refractive index $n_D^{25}=1.5363$, density $d_4^{25}=0.9650$ and combustion analysis (C = 91.04%, H = 8.94%, Calc. for $C_{10}H_{12}$ being C = 90.91%, H = 9.09%), this was confirmed to be tetralin. The residual portion (4gm) of yellowish crystals separated from tetralin was presumed to be naphthalene.

The crystals separated from fractions 4 and 5 by recrystallization (m.p. 181.5-182°C) were found to be b,b-dinaphthyl, for, its picrate melted at 184.2-184.6°C and combustion analysis was:

Actual:	C, 94.09%	H, 6.00%
Calc. for $C_{20}H_{14}$:	94.50%	5.50%

The solution from which b,b-naphthyl had been separated was assumed to be a mixture of di-naphthyl, di-naphthyl-ether and di-tetra-hydro-naphthyl-ether from its distillation (125-130oC at 2mm) and combustion anaylsis, C=88.1%, H=7.1% and O=4.8%.

2. b-Naphthol. The cracking of b-naphthol was performed under the same conditions and the compounds was decomposed into 2.5% gaseous hydrocarbons (H_2 = 94.9%, C_nH_{2n+2} = 4.2%, CO = 1.4%) and the balance, liquid hydrocarbons, (Refer to Figure 5(B)2).

The latter was examined similarly to the a-naphthol case, and analytical results are as follows:

ENCLOSURE (B)2

III. CONCLUSIONS

By comparison of these results with previous work, it is evident that the thermal conversion of aromatic compounds in the presence of high pressure hydrogen was accelerated by the presence of calcium chloride, and the rate of conversion into lower hydrocarbons was about the same as when metallic or metallic oxide catalysts are used.

Table I(B)2
PHYSICAL CONSTANTS OF COMPOUNDS USED

	B.P.(°C)	M.P.(°C)
Naphthalene	214-218(761mm)	81
Anthracene		216
Phenol	179-180(764mm)	41
α-naphthol		97.5
β-naphthol		106

Table II(B)2
PHYSICAL CONSTANTS OF FRACTIONS

Fraction	B.P. (°C)	Yield (gm)	n^{25}_{D}	d^{25}_{D}	Remarks
1	75-90	4.5	1.497	0.869	Benzene
2	90-120	13.1	1.496	0.867	Toluene
3	120-140	10.1	1.495	0.865	Ethyl-Benzene
4	140-155	3.0	1.499	0.871	O-Xylene
5	155-200	4.8	1.531	0.916	
6	200-220	26.5	Solid		

ENCLOSURE (B)2

Table III(B)2
FRACTIONATION OF REACITON PRODUCTS

Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}	Remarks
1	75-90	6.0	1.490	0.858	Benzene
2	90-120	13.5	1.495	0.862	Toluene
3	120-140	1.5	1.497	0.866	Ethyl-Benzene
4	140-200	3.2	1.528	0.895	o-Xylene
5	200-220	8.7	Liquid with naphthalene crystals		
6	220-240	13.5			
7	240-270	13.5			
8	270-325	5.0	Resin with crystals		
9	Residue	5.1			

Table IV(B)2
FRACTIONATION OF PHENOL REACTION PRODUCT

Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}
1	70-79.5	10.8	1.484	0.852
2	79.5-80	19.5	1.494	0.869
3	80-81	1.0	1.496	0.870
4	81-175			
5	175-182	41.0	Crystals	
6	(120-154) at 2mm	2.1	Resinous matter	
7	Residue	3.1		

Table V(B)2
FRACTIONATION OF a-NAPHTHOL REACTION PRODUCT

Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}
1	180-200	2.1	1.5306	0.9305
2	200-220	50.0	1.5607	0.9821
3	(120) at 2.5mm	0.5	Crystal	
4	(120-200) at 2.5mm	6.5	Resin with crystals	
5	(200-240) at 2.5mm	7.5		
6	Residue	5.4		

Table VI(B)2
FRACTIONATION OF b-NAPHTHOL REACTION PRODUCT

Acidic Substance: 19.5% (mostly unreacted ß-naphthol)		
Fraction	B.P. (758mm) (°C)	Yield (gm)
1	270-277	2.5
2	277-280	14.5
3	280	2.5

	Neutral substance: 69.5% of b-naphthol				
Fraction	B.P. (°C)	Yield (gm)	n_D^{25}	d_4^{25}	Remarks
1	132-190	0.5	1.5260		Benzene-derivative
2	190-208	27.5	1.5517	0.9731	Naphthalene 28 + Tetralin 72
3	208-215	15.3	White crystal		Naphthalene
4	(60-120) 2.5mm	3.6			
5	(120-200) 2.5mm	5.4	Resin with Crystals		Crystal, ß,ß-Dinaphtyl
6	(200-240) 2.5mm	13.8			Resinous matter*
7	Residue	3.4			

* Mixture of ß,ß-Dinaphthyl, tetra-hydro-dinaphthyl ether and dinaphthyl ether.

ENCLOSURE (B)2

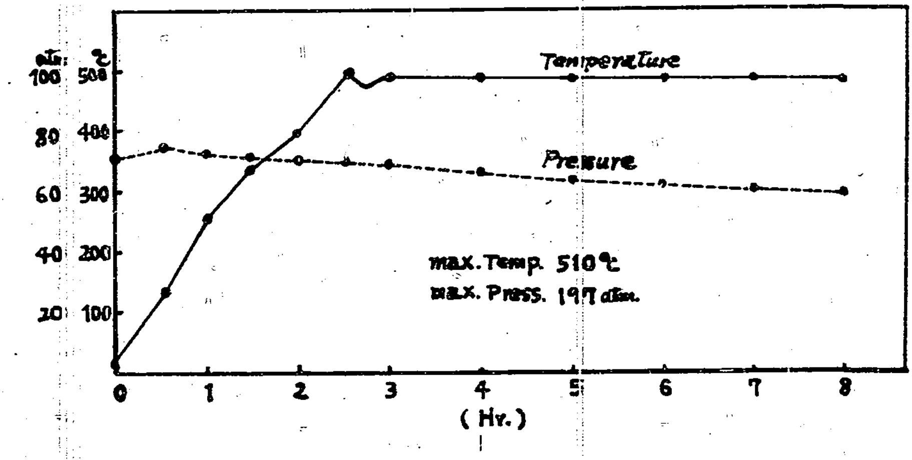

Figure 1(B)2
NAPHTHALENE

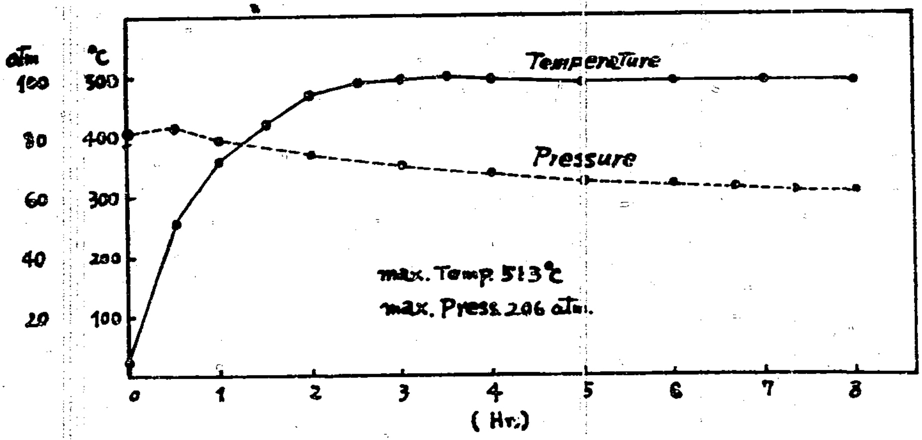

Figure 2(B)2
ANTHRACENE

ENCLOSURE (B)2

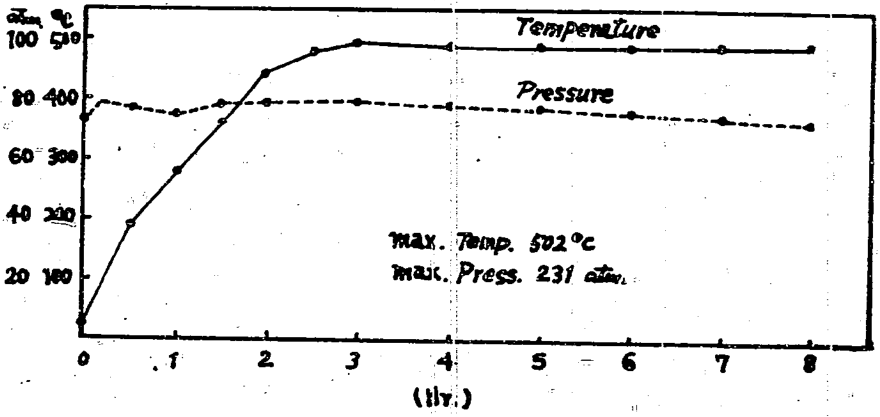

Figure 3(B)2
PHENOL

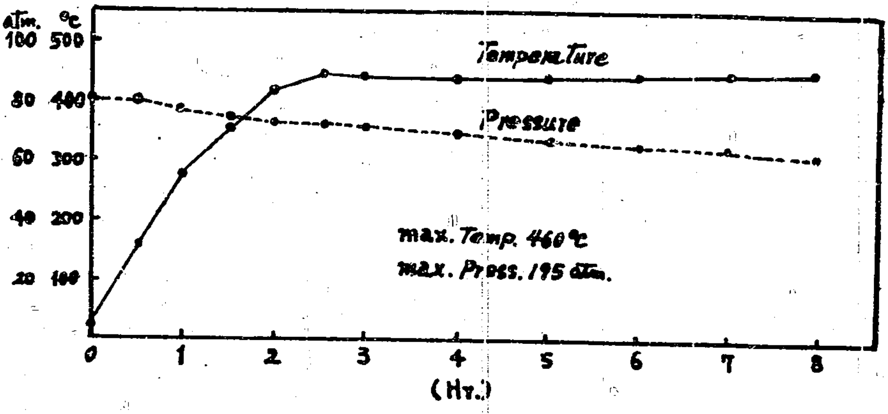

Figure 4(B)2
α-NAPHTHOL

ENCLOSURE (B)2

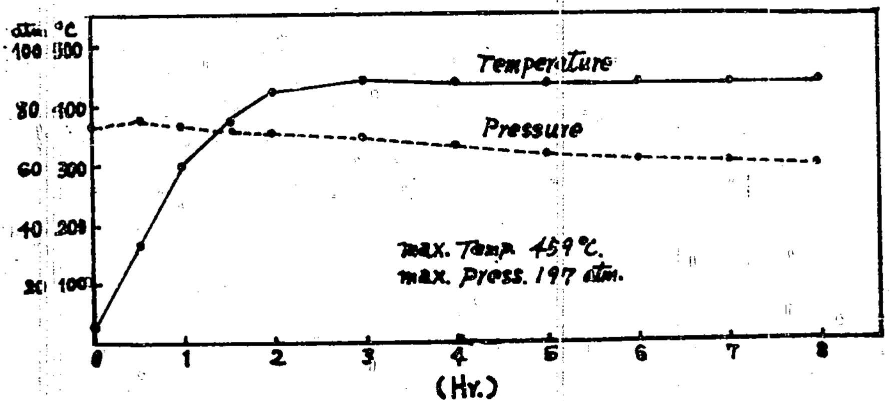

Figure 5(B)2
b-NAPHTHOL

ENCLOSURE (B) 3

EFFECT OF SIZE OF COAL ON COAL HYDROGENATION

Reference NavTechJap Document No. ND 26-0008.11 ATIS No. 4579

by

NAVAL ENGINEER
T. OGAWA

Research Period:
March 1938 - August 1929

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

December 1945

ENCLOSURE (B)3

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)3

SUMMARY

To determine the influence exerted by the size of the coal on coal hydrogenation, Fushun coal was crushed to two size ranges, below 20 mesh and below 60 mesh, and tested on an autoclave scale. It was established that the size of the coal charge had no influence on the quantity or quality of the oil produced.

I. DETAILED DESCRIPTION

A. Test Apparatus and Procedures

The apparatus used in these experiments was a rotating type autoclave (refer to Figure 1(B)3). It was made from Mo-Ni-Cr steel and its volume was 2.4 lit.

Twenty steel balls (dia. 20mm and weight 27 gms) were put into the autoclave to assist in agitation. After introducing the oil sample and balls, air was displaced by hydrogen and the pressure was then raised to the required amount. The temperature and pressure of the autoclave were measured every five minutes. When the reaction period was over, the gas fire was turned off, but rotation was continued until the temperature dropped to 150°C. The autoclave was allowed to stand for one day, and the pressure and temperature were recorded before releasing the hydrogen. After the gas had been released, the products were removed, put into a flask, and called "Crude oil 'A'".

The residue sticking to the autoclave and balls was washed with about 100gms of benzene, and the solution was called "Crude oil 'B'".

Gas samples were analyzed by Hempel's method. Gas volumes were corrected to standard conditions (0°C, 1/atm).

Crude oil "A" was distilled in a column with an ice-cooled condenser. The oil was cut at 180°C, and the volume and weight of the oil and water measured. The solid residue was washed with benzene until the benzene was colorless. The residue was weighed and the benzene solution was added to the benzene soluble part of crude oil "B".

The water content of Crude oil "B" was determined by Deanstark's distillation method. The residue was separated by filtration and washed with benzene. The benzene soluble part of crude oil "B" was added to the benzene soluble part from crude oil "A", and the insoluble part from crude oil "B" was added to the insoluble part from crude oil "A".

The benzene and a small amount of light oil boiling below 180°C were removed by distillation and discarded. The product boiling below 180°C was blended with the oil obtained from crude oil "A".

The benzene insoluble residues obtained from crude oil "A" and "B" were dried at 80°C and reduced pressure to remove benzene, and then cooled and weighed. A portion of this residue was used for determination of benzene solubles by Soxhlet's extraction apparatus, and another portion was used for determination of ash content.

B. Properties of Feed Stocks

Properties of the Fushun coal used in these experiments are given below:

ENCLOSURE (B)3

Proximate Analysis (wt %)

Water	5.5
Volatile matter	41.1
Fixed Carbon	46.4
Ash	7.0
Lichter's coefficient	6.0

Elementary Analysis (wt %)

Carbon	79.3
Hydrogen	6.2
Oxygen	12.9
Nitrogen	1.3
Sulphur	0.3

Sieve Test (wt %)

	below 20 mesh	below 60 mesh
20-60 mesh	74	-
60-120 mesh	17	41
120-200 mesh	4	39
Below 200 mesh and less	5	20

The paste oil was low-temperature tar oil made in a Davidson Retort operating on Shinbara coal, (30% of oil had been removed by topping).

Ferric oxide, commercial grade, was used as catalyst. Hydrogen of 99% purity was secured from the Hodogaya Chem. Co.

These items were mixed in the following proportions:

Coal	100gms
Tar	50gms
Ferric oxide	5gms
Hydrogen	19gms(100 atm at 0°C)

C. Experimental Results

Experimental results are summarized in Table I(B)3.

III. CONCLUSIONS

It was concluded that the size of coal charged, within the range investigated, had no influence on the yields or properties of products from coal hydrogenation on autoclave scale.

ENCLOSURE (B)3

Table I(B)3
EXPERIMENTAL RESULTS

		Run Number				
		1	12	15	25	9
Experimental Conditions	Size of Coal (mesh)	<60	<20	<20	<20	<60
	Reaction Temperature (°C)	500	500	480	450-470	460-480
	Initial Pressure (kg/cm^2)	100	100	101	98	97
	Pressure Drop (kg/cm^2)	27	26	11	18	10
	Preheating Time (hr-min)	2-10	1-50	2-55	2-10	1-55
	Reaction Time (hr-min)	2-50	3-0	1-0	1-0	1-0
Yield of Products(gm)	Gas	56.9	55.1	41.8	28.7	46.1
	Water	12.5	14.0	11.0	13.7	10.0
	Oil	62.4	65.2	75.1	78.7	79.5
	Residue	25.3	20.5	23.9	25.6	28.6
	Total	153.1	154.8	151.8	146.7	164.2
Gas Analysis(gm)	CO_2	0.6	0.6	1.3	0.6	5.5
	C_nH_{2n}	1.6	1.6	-	-	1.6
	O_2	-	-	-	-	-
	CO	2.7	2.3	2.3	2.0	4.5
	H_2	10.5	10.5	12.5	13.9	16.5
	C_nH_{2n+2}	41.3	40.1	25.7	12.7	18.0
	N_2	-	-	-	-	-
	Total	56.9	55.1	41.8	28.7	46.1
	No. of C of Sat. Hydrocarbon	1.8	1.5	1.5	1.0	1.4
Yield of Crude Oil(gm)	Crude Oil "A"	72.5	78.0	83.0	111.5	57.0
	Crude Oil "B"	28.7	21.7	27.0	6.5	61.1
	Total	101.2	99.7	110.0	118.0	118.1
Yield of Water(gm)	Crude Oil "A"	12.5	14.0	11.0	11.0	10.0
	Crude Oil "B"	-	-	-	2.7	-
	Total	12.5	14.0	11.0	13.7	10.0
Fractional Distillation (gm)	Below 180°C	17.9	18.4	7.8	8.9	6.7
	180-230°C	9.8	8.4	8.5	8.5	6.5
	230-280°C	8.9	10.2	17.3	14.4	14.3
	280-360°C	12.6	12.4	19.9	21.2	22.4
	Pitch and Loss	12.5	15.3	21.0	25.3	27.7
	Total	61.7	64.7	74.5	78.3	77.6
Yield of Residue(gm)	Crude Oil "A"					
	Crude Oil "B"					
	Total	27.0	21.0	24.5	26.0	30.5
Analysis of Residue(gm)	Soluble in Benzene	0.7	0.5	0.6	0.4	1.9
	Organic Residue	16.8	11.1	12.0	13.7	18.2
	Ash	9.5	9.4	11.9	11.9	10.4
	Total	27.0	21.0	24.5	26.0	30.5

ENCLOSURE (B)3

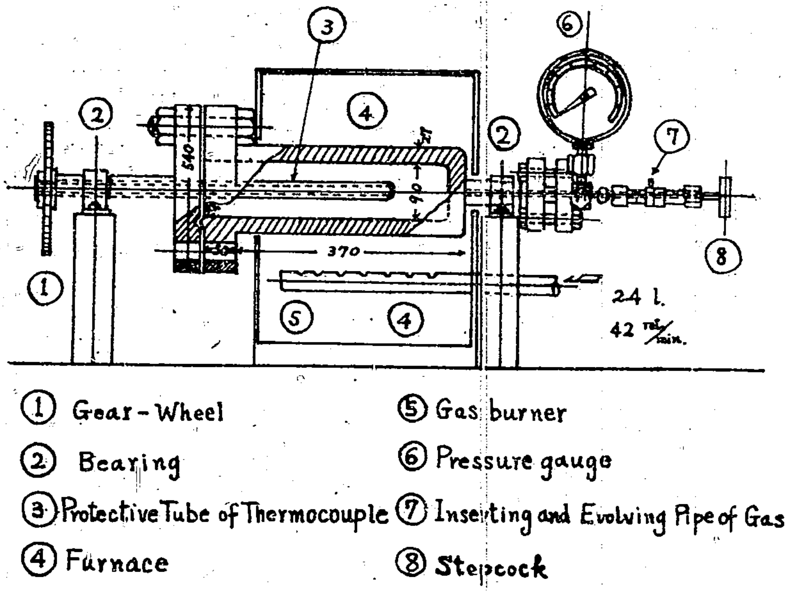

Figure 1(B)3
ROTATING TYPE AUTOCLAVE

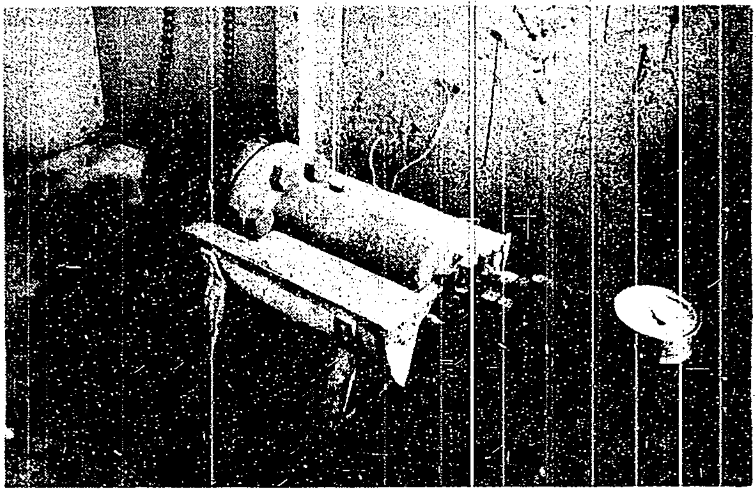

Figure 2(B)3
AUTOCLAVE USED IN THE COAL-HYDROGENATION EXPERIMENT

ENCLOSURE (B) 4

EFFECT OF VISCOSITY OF PASTE OIL ON COAL HYDROGENATION

by

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NAVAL ASS'T. ENG. I. TAKAHASHI

Research Period: March, 1938 - August, 1929

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

December 1945

ENCLOSURE (B)4

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)4

SUMMARY

Autoclave studies were made to determine the effect of the viscosity of paste oil on the hydrogenation of Fushun coal.

The results of these experiments indicated that variation in viscosity of the paste oil had no appreciable effect on the hydrogenation.

I. DETAILED DESCRIPTION

Experiments were conducted in an autoclave. A detailed description of the test procedures is given in report No.3 of "Studies on the Hydrogenation of Coal". Fushun coal, sieved to 60 mesh or below, was used. The paste oils were obtained from the low-temperature carbonization of Shinbara coal in a Davideson type retort.

Two runs were made, one using total tar and one using heavy tar made by topping 30% of the light oil from the total tar.

Properties of these oil are given in Table I(B)4.

The autoclave charge was composed as follows:

Coal	100/grams	
Tar	50/grams	
Fe_2O_3	5/grams	(commercial grade)
Hydrogen	19/grams	(100 atm. at S.C.) (99.5% purity)

Experimental results are summarized in Table II(B)4 and Table III(B)4.

II. CONCLUSIONS

It is concluded from these tests that the variations in boiling range, viscosity, etc., of the two paste oil fractions, had no significant effect on the yield or quality of the products from hydrogenation of Fushun coal.

ENCLOSURE (B)4

Table I(B)4
PROPERTIES OF PASTE OILS

	Crude Tar	Heavy Tar
Specific Gravity (20°C)	0.99	1.02
Flash Point (°C)	63	121
Viscosity Rd. No.1 at 30°C (sec)	93	1180
Viscosity at 40°C (sec)	64	358
Acidity (Vol.%)	38	36
Industrial Analyses (wt.%)		
Water	1.5	-
Dirt	0.5	0.5
Light Oil (230°C)	27	6
Heavy Oil (230-360°C)	49	61
Pitch	22	32
Ultimate Analyses (wt.%)		
Carbon	83.9	85.4
Hydrogen	9.3	9.5
Oxygen	6.0	4.2
Nitrogen	0.6	0.7
Sulphur	0.2	0.2
Cal. Value	9.700	9.760

ENCLOSURE (B)4

Table II (B)4
TEST CONDITIONS AND PRODUCTS

	Run Number			
	5		9	
Reaction Condition				
Paste Oil	Crude Tar		Heavy Tar	
React. Temp. (°C)	480		480	
Initial Pressure (atm)	102		97	
Pressure Drop (atm)	19		10	
React. Time (hr-min)	1-0		1-0	
Yield of Products				
Gas	39.6		46.1	
Water	12.1		10.0	
Oil	83.3		79.5	
Residue	24.8		28.6	
Total	159.8		164.2	
Gas Analyses	Vol.%	(gm)	Vol.%	(gm)
CO_2	0.2	0.8	1.2	5.5
C_nH_{2n}	0	0	0.6	1.6
O_2	1.0	-	0.6	-
CO	2.0	4.8	1.4	4.5
H_2	86.5	14.6	84.0	16.5
C_nH_{2n+2}	7.7	19.4	8.3	18.0
N_2	2.6	-	3.9	-
Carbon Number of S.H.C.	2.0	-	1.4	-

ENCLOSURE (B)4

Table III(B)4
YIELD AND PROPERTIES OF OIL PRODUCED

	Run Number					
	5			9		
Yield of Produced Oil (gm)						
Crude Oil "A"	94.0			57.0		
Crude Oil "B"	26.2			61.1		
Total Oil	120.2			118.1		
Yield of Water from Crude Oil "A" (gm)	12.1			10.0		
Properties of Produced Oil	Yield (gm)	d^{20}_{20}	(vol.%) Tar acid	Yield	d^{20}_{20}	(vol.%) Tar acid
-180°C	14.4	0.844	13.0	6.7	0.744	8.0
180-230°C	8.5	0.942	35.0	6.5	0.928	31.0
230-280°C	16.1	0.950	-	14.3	0.963	32.0
280-360°C	18.6	0.977	26.0	22.4	1.044	16.0
Pitch	25.0	1.160	-	27.7	1.117	-
Total	82.6	-	-	77.6	-	-
Yield of Residue (gm)						
Soluble in Benzene	0.7			1.9		
Organic Residue	13.6			18.2		
Ash	11.2			10.4		
Total	25.5			30.5		

ENCLOSURE (B) 5

EFFECT OF FERRIC OXIDE
ON COAL HYDROGENATION

by

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Research Period: March, 1928 - Oct., 1929

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

December 1945

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)5

SUMMARY

Autoclave experiments were made to determine the effect of ferric oxide as a catalyst in the high-pressure hydrogenation of coal. The results indicated that the yield of oil was increased, and the solid residue decreased when ferric oxide was used.

I. DETAILED DESCRIPTION

The test apparatus and procedure were the same as described in Enclosure (B)3.

Fushun coal, sized below 20 mesh, and heavy oil made by topping 30% of the light oil from the low-temperature tar from Shinbara coal, were used as charge stocks.

Ferric oxide, commercial grade, was used as a catalyst, and hydrogen of 99% purity was employed.

These materials were mixed inthe following proportions.

Coal	100grams
Tar	50grams
Ferric oxide	5grams
Hydrogen	19grams (100atm at 0°C).

Experimental results are summarized in the tables below.

Some water should be produced by the reduction of Fe_2O_3, but the difference is not apparent from this table. It is not understood why this is so.

Although some difference of yield was caused by the reaction temperature, in general, when Fe_2O_3 was used, the yield of oil product was greater.

II. CONCLUSIONS

When Fe_2O_3 was used in the high-pressure hydrogenation of coal, the consumption of hydrogen, the volume of saturated hydrocarbons in the produced gas and the yield of oil were greater than when Fe_2O_3 was not present.

When no Fe_2O_3 was used, solid substances often stuck to the inside of the autoclave and a large percentage of organic residue was contained in the solid residue.

It was concluded that Fe_2O_3 had a favorable effect on the hydrogenation of coal.

ENCLOSURE (B)5

Table I(B)5
REACTION CONDITIONS AND YIELDS OF PRODUCTS

Run Number	28	27	61	65	62	66	64	13
React.conditions:								
Catalyst	Fe_2O_3	None	Fe_2O_3	Fe_2O_3	None	None	Fe_2O_3	Fe_2O_3
React.Temp.(°C)	430-450			450-455			470-480	
Initial Press. (atm)	99	98	101	100	100	100	100	100
Pressure Drop. (atm)	17	12	19	20	10	12	21	14
Preheating Time (hr)	1-0	1-30	1-45	1-40	1-40	1-40	1-45	1-50
Reaction Time (hr)	2-0	2-10	1-0	1-0	1-0	1-0	1-0	1-0
Yield of Products (gm):								
Gas	35.2	22.8	35.5	35.2	30.6	29.4	38.1	39.4
Water	15.0	10.0	14.0	14.8	15.4	10.3	16.3	13.0
Oil	76.0	71.6	88.9	80.5	67.8	67.3	68.9	62.0
Residue	22.4	40.5	29.8	30.0	51.8	47.3	37.0	36.7
Total	148.6	144.9	168.0	160.5	165.6	154.6	160.3	151.1

Table II(B)5
GAS ANALYSES (VOL %)

Run Number	28	27	61	65	62	66	64	13
Co_2	0.4	0.4	0.5	0.3	0.5	0.2	0.2	0.8
$C_n H_{2n}$			0.1		0.1		0.1	0.4
O_2	1.6	1.6	0.3	0.2	0.5	0.3	0.2	1.0
CO	0.8	0.4	0.6	0.5	0.6	0.3	0.6	0.8
H_2	82.5	89.7	85.5	84.4	88.5	89.2	82.4	84.7
C_nH_{2n+2}	9.8	2.9	12.5	11.2	7.9	5.5	14.9	7.7
N_2	4.9	5.0	0.5	3.3	1.9	4.6	0.8	4.6
n	1.4		1.2	1.4	1.0	1.5	1.3	1.8

ENCLOSURE (B)5

Table III(B)5
YIELDS OF CRUDE OIL AND WATER.

Run Number	28	27	61	65	62	66	64	13
Yield of Crude Oil (gm)								
Crude Oil "A"	117.5	65.0	84.0	105.0	53.0	40.0	108.0 14.2	59.0
Crude Oil "B"	*	57.1	48.5	20.3	82.0	85.2	*	52.7
Total	*	122.1	132.5	125.3	135.0	125.2	122.2	111.7
Yield of Water (gm)								
Crude Oil "A"	13.0	10.0	11.5	13.5	13.0	5.5	14.5	13.0
Crude Oil "B"	2.0	Trace	2.5	1.3	2.4	4.8	1.8	
Total	15.0	10.0	14.0	14.8	15.4	10.3	16.3	13.0

*Part of sample lost.

Table IV(B)5
DISTILLATION OF TOTAL OIL (gm)

Run Number	28	27	61	65	62	66	64	13
-180°C	11.0	6.8	8.9	11.5	6.5	3.6	12.3	5.7
180-230°C	6.5	3.7	80.0	69.0	59.0	64.0	56.1	5.6
230-280°C	15.7	13.4						14.1
280-360°C	17.2	22.5						16.6
Pitch	23.7	25.0					*	17.2
Total	74.1	71.4	88.9	80.5	65.5	67.6	68.4	59.2

*Part of sample lost in distillation

ENCLOSURE (B)5

Table V(B)5
YIELD OF RESIDUE AND ITS PROPERTIES

Run Number	28	27	61	65	62	66	64	13
Yield of Residue (gm)								
Crude Oil "A"	19.0	11.2	8.8	18.0	8.1	3.4	18.3	39.5
Crude Oil "B"	5.3	29.5	20.8	12.0	44.4	43.9	19.2	
Total	24.3	40.7	29.6	30.0	52.5	47.3	37.5	39.5
Properties of Residue, (gm)								
Soluble in Benzene	1.9	0.2			0.7		0.5	2.8
Organic Residue	11.0	32.4	17.5	17.8	43.4	39.0	21.9	29.6
Ash	11.4	8.1	12.1	12.2	8.4	8.3	15.1	7.1
Total	24.3	40.7	29.6	30.0	52.5	47.3	37.5	39.5

ENCLOSURE (B) 6

EFFECT OF REACTION TEMPERATURE ON THE HYDROGENATION OF COAL

Reference NavTechJap Document No. ND 26-0008.12 ATIS No. 4579

by

NAVAL ENG. T. OGAWA
NAVAL ASST. ENG. I. TAKAHASHI

Research Period: 1928-1929

Prepared for and Reviewed with Authors by
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ENCLOSURE (B)6

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)6

SUMMARY

These experiments were carried out to investigate the effect of temperature on the properties and yields of liquid products prepared by high-pressure hydrogenation, and to determine the most suitable range of temperature for the reaction. FUSHUN coal was used in these experiments and the following results were obtained.

(1) Paste oil, when reacted in the presence of Fe_2O_3 and high-pressure hydrogen, showed a considerable conversion and the extent of this conversion varied according to the reaction temperature.

(2) The most effective temperature range was between 420°C and 480°C. The reaction was incomplete below these temperatures, and large amounts of coke-like substances were formed above these temperatures.

(3) The maximum yield of liquid product when FUSHUN coal (moisture content 5.5%) was used, was 53%, (61% on a moisture and ash-free coal basis) under the above-mentioned conditions.

(4) The maximum yield of liquid product was obtained at a reaction temperature of 420°C. Increase of temperature beyond this resulted in secondary decomposition reactions reflected by decrease in yield.

I. DETAILED DESCRIPTION

A. Tests on Coal and Paste Oil

The apparatus and procedure used were the same as described in report No. 3 on "Studies on the Hydrogenation of Coal." (See Figure 1(B)6). The following materials were charged to the autoclave:

Coal: FUSHUN coal pulverized to below 20 mesh and maintained at constant moisture content.
Paste Oil: Low-temperature tar produced from SHINBARD coal by Davidson retort, from which light oil (30% of total) had been topped.
Ferric Oxide and Hydrogen: Fe_2O_3 was a commercial grade, and hydrogen was of 99% purity.

In the first series of experiments the above materials were used in the following proportions:

Coal	100 grams	
Tar	50 grams	
Fe_2O_3	5 grams	
Hydrogen	100 atm.	(Initial pressure at 0°C corresponding to about 19 grams by weight)

Experimental results are summarized in Tables I(B)6 through IV(B)6.

B. Tests on Paste Oil Only

In the next series of experiments, tests were made on the hydrogenation of paste oil only. The charge stocks were mixed in the following proportions:

Tar	100 grams	
Fe_2O_3	10 grams	
Hydrogen	100 atm.	(Initial pressure at 0°C corresponding about 19 grams by weight)

The experimental results are summarized in Tables V(B)6 through VII(B)6.

II. CONCLUSIONS

A. It was shown that at a reaction temperature of 390°C the appearance of the crude oil product did not differ from the original oil, evolution of gas was very low, and much coal remained unreacted. The coal, however, was changed to benzene soluble state during the reaction.

B. At 420°C, dehydration of the coal was almost completed. No increase or decrease of produced water occurred above this temperature.

C. The oil yield reached a maximum at 420°C, amounting to 61.4% of ash- and moisture-free coal after correcting for the conversion of the paste oil.

D. Above 420°C, the viscosity of the crude oil decreased, while the oil yield decreased and gas production increased.

E. At 500°C, the crude oil product had very low viscosity and organic residues with increasing content of benzene insolubles began to separate, while the yield diminished to 38.2% of moisture-and ash-free coal.

F. The experimental data showed that secondary decomposition of liquid and solids took place at the higher reaction temperatures.

ENCLOSURE (B)6

Table I(B)6
REACTION CONDITIONS AND YIELD OF PRODUCTS

Run Number	34	26	71	63	15	72
Reaction Conditions						
Reaction Temp. (°C)	390	420	440	460	480	500
Initial Press. (atm.)	103	100	102	102	101	100
Pressure Drop (atm.)	9	16	24	25	25	21
Time of Preheating (hr-min)	2-10	2-05	1-50	1-50	1-55	1-40
Time of Reaction (hr-min)	1-0	1-0	1-0	1-0	1-0	1-0
Yield of Products (gm)						
Gas	24.4	29.0	33.2	33.9	41.8	40.6
Water	14.3	17.1	14.7	17.5	11.0	16.5
Oil	76.0	98.6	89.1	84.0	75.1	73.9
Solid Residue	60.0	27.5	25.2	25.0	23.9	20.0
Total	174.7	172.2	162.2	160.4	151.8	151.0

Table II(B)6

GAS ANALYSES (VOLUME %)

Run Number	34	26	71	63	15	72
CO_2	0.6	0.4	0.3	0.2	0.4	0.3
C_nH_{2n}	0.1	0.2	0.1			0.1
CO	0.1	0.6	0.7	0.4	1.1	0.7
H_2	98.5	92.6	86.6	85.1	83.6	82.4
C_nH_{2n+2}	0.7	6.2	12.3	14.3	14.9	16.5
Total	100.0	100.0	100.0	100.0	100.0	100.0
No. of C,		1.3	1.2	1.2	1.5	1.3

ENCLOSURE (B)6

Table III(B)6
YIELD AND DISTILLATION OF CRUDE OIL (gm)

Run Number	34	26	71	63	15	72
Yield of Crude Oil						
Crude Oil "A"	154.0	120.0	116.0	119.0	83.0	93.0
Crude Oil "B"		3.7	13.0	7.5	27.0	17.4
Total	154.0	123.7	129.0	126.5	110.0	110.4
Distillation Test						
-180°C		10.0	11.6	12.8	7.8	14.1
180-230°C		6.5	6.8	5.9	8.5	7.5
230-280°C	76.0	15.4	17.7	17.0	17.3	15.1
280-360°C		25.0	21.5	22.1	19.9	17.7
Pitch		38.0	31.5	26.0	21.0	19.0
Total	76.0	94.9	89.1	83.8	74.5	73.4

Table IV(B)6
YIELD OF SOLID RESIDUE (gm)

Run Number	34	26	71	63	15	72
Soluble in Benzene		3.7		0.2	0.6	0.5
Organic Residue	46.7	14.3	13.5	12.9	12.0	12.1
Ash	13.3	13.2	11.7	12.1	11.9	7.9
Total	60.0	31.2	25.2	25.2	24.5	20.5

ENCLOSURE (B)6

Table V(B)6
REACTION CONDITIONS AND YIELD OF PRODUCTS

Run Number	24	29	23	14	74
Reaction Conditions					
Reaction Temp. (°C)	420	440	460	480	500
Initial Press. (atm.)	102	101	100	100	101
Pressure Drop (atm.)	6	5	7	10	14
Time of Preheating (hr-min)	2-15	2-10	2-15	2-55	2-30
Time of Reaction (hr-min)	1-0	1-0	1-0	1-0	1-0
Yield of Products (gm)					
Gas	21.8	23.4	25.3	38.1	33.0
Water	5.1	2.5	3.2	1.0	2.1
Oil	89.8	90.3	88.2	86.8	80.9
Solid Residue	10.2	6.7	7.5	1.0*	1.5*
Total	126.9	122.9	123.2	121.9	117.5

*Runs Number 14 and 74, 5 grams of Fe_2O_3

ENCLOSURE (B)6

Table VI(B)6
GAS ANALYSES (VOLUME %)

Run Number	24	29	23	14	74
CO_2		0.1		0.6	0.2
C_nH_{2n}		0.1	0.4	1.1	0.1
CO	0.2	0.5	0.4	0.4	0.4
H_2	97.7	97.5	95.4	90.7	88.3
C_nH_{2n+2}	2.1	1.8	3.8	7.2	11.0
Total	100.0	100.0	100.0	100.0	100.0
No. of C.			1.0	1.6	1.0

Table VII(B)6
DISTILLATION TEST OF TOTAL OIL (gm)

Run Number	Raw Crude Tar	24	29	23	14	74
-180°C		2.5	5.6	5.4	11.5	11.8
180-230°C	5.8	3.2	7.5	8.8	10.0	11.7
230-280°C	19.7	24.0	25.0	25.0	24.0	24.5
280-360°C	41.2	35.0	32.2	31.3	27.0	20.8
Pitch	33.3	26.1	20.0	19.7	14.3	2.1
Total	100.0	89.8	90.3	88.2	86.8	80.9

ENCLOSURE (B) 7

EFFECT OF REACTION PRESSURE ON HYDROGENATION OF COAL

by

NAVAL CHEM. ENG. T. OGAWA

Research Period: 1929-1930

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

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LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)7

SUMMARY

The effect of hydrogen pressure on the hydrogenation of Fushun Oyama coal was studied, using low-temperature tar as Paste Oil and a ferric oxide catalyst. It was shown that at least 200 atmospheres of pressure was needed for the hydrogenation reaction to proceed smoothly. At pressures lower than 200 atmospheres the hydrogenation of coal was not only incomplete, but a part of the hydrogenated product was converted to coke and gas.

I. INTRODUCTION

The reaction pressure is an important factor in the hydrogenation of coal. Up to the time of this study, many experiments had been made on this subject, and it was concluded that, in general, the higher the pressure, the higher the yield of oil and the lower the solid residue.

In this study the hydrogenation of Fushun Oyama coal was investigated at different hydrogen pressures and with other reaction conditions constant (reaction temperature, 455°C, reaction time, 1 hour).

II. DETAILED DESCRIPTION

The test apparatus and procedure were the same as described in previous reports of this series. The following feed stocks were used:

Coal :	Fushun Oyama coal crushed to under 20 mesh size.
Tar :	Light oil fraction from Shinbara low-temperature tar obtained by Davidson Retort and 30% topped.
Catalyst :	Ferric oxide
H_2 :	Obtained from electrolysis of water, purity above 99.5%.

These materials were used in the following amounts: coal, 100 grams; tar, 40 grams; ferric oxide, 5 grams. The H_2 pressure was varied on each run as shown in Table I(B)7.

The reaction pressure was the only variable in these runs and other conditions were kept as constant as possible. Experimental conditions and results are as shown in Table II(B)7.

III. CONCLUSIONS

The higher the hydrogen pressure, the greater the yield of oil products and the smaller the coke formation. From the results of the gas analysis, it was found that decreasing hydrogen pressure resulted in more saturated hydrocarbon gases being formed and more of the hydrogen being converted into gas than into liquid and solid products, as shown by the following Table IV(B)7.

Thus, higher pressure of hydrogen resulted in more complete hydrogenation of coal, and reduced gas formation and secondary cracking of produced oil.

ENCLOSURE (B)7

Table I(B)7
HYDROGEN REACTION PRESSURES

	Run Number			
	76	47	307	308
Reaction Press. (atm.)	205	225	200	175
Weight of H_2 (gm.)	19.8	18.3	15.4	13.0
H_2/coal (wt. %)	19.8	18.3	15.4	13.0

Table II(B)7
COAL HYDROGENATION EXPERIMENTAL RESULTS

		Run Number			
		76	47	307	308
Reaction Conditions	Reaction Conditions (atm.)	250	225	200	175
	Reaction Temperature (°C)	455	455	455	455
	Initial Pressure (atm.)	101	93.5	79	66
	Pressure Drop (atm.)	19	17	17	16
	Reaction Time (hr.-min.)	1-0	1-0	1-0	1-0
	Preheating Time (hr.-min.)	2.15	1-55	2-45	2-55
Reaction Products (gm.)	Gas	33.6	36.6	35.7	34.3
	H_2O	17.4	16.9	16.8	15.8
	Oil	85.9	79.2	60.8	59.3
	Residue	24.9	27.4	40.0	41.3
Gas Analysis (vol.%)	CO_2	0.2	0.5	0.7	0.6
	C_nH_n	0.2	0.1	0.2	0.3
	CO	0.7	0.5	0.7	0.8
	H_2	88.8	88.3	70.8	80.6
	C_nH_{2n+2}	10.1	10.6	18.6	17.7
	n	1.3	1.7	1.3	1.5
Distillation of Oil (wt.%)	~180°C	12.4	12.8	18.7	15.5
	180~23°C	6.8	7.7	16.1	13.2
	230~360°C	42.0	42.1	40.8	44.2
	Pitch	38.8	37.4	24.4	26.1
Analysis of Solid Residue (gm.)	Benzene Soluble	0.2	0.1	5.4	5.6
	Organic Solid Residue	12.0	15.1	27.4	28.7
	Ash	12.9	12.3	12.6	12.4

Table III(B)7
ABSORPTION OF HYDROGEN

	Run Number			
	76	47	307	308
Reaction Pressure (atm.)	250	225	200	175
Hydrogen Adsorption Total (gm.)	5.5	5.1	5.8	4.3
Hydrogen in Hydrocarbon Gas (gm.)	3.7	4.3	5.1	4.9
H_2 in Absorbed in Liquid and Solid (gm.)	1.8	0.8	0.7	0.6

ENCLOSURE (B) 8

EFFECT OF REACTION TIME ON THE HYDROGENATION OF COAL

by

NAVAL ENGINEER
T. OGAWA

Research Period: 1929 - 1930

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

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ENCLOSURE (B)8

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)8

SUMMARY

Studies were made on the effect of varying reaction time on the hydrogenation of Oyama coal, holding reaction conditions constant at 455°C, hydrogen pressure at 100 atmospheres and using Fe_2O_3 as a catalyst. It was found that under these conditions, the optimum reaction time was 1 hour.

I. INTRODUCTION

In the hydrogenation of coal, reaction time is an important factor, particularly from the standpoint of commercial plant design. Although many reports had previously been made on this subject, accurate conclusions could not be drawn, since the experiments had not been made under comparable conditions. This study was limited to the investigation of the effect of reaction time only, holding other variables constant.

Key research personnel working on project were Naval Eng. T. OGAWA and Naval assist. Eng. I. TAKAHASHI.

II. DETAILED DESCRIPTION

The autoclave and test procedures were the same as described in report No. 3 of this series.

Samples were as follows, (same as in report No. 3):

Coal	:	Fushun Oyama coal, sized to under 20 mesh.
Tar	:	30% topped light oil fraction from Shinbara low-temperature tar made in a Davidson type retort.
Catalyst	:	Ferric oxide (commercial grade)
H_2	:	Prepared by electrolysis, purity above 99.5%.

These components were mixed in the following amounts: coal, 100 grams; tar, 40 grams; Fe_2O_3, 5 grams; and H_2, 19 grams.

Runs were made for reaction times of 0 minutes, 30 minutes, 1 hour, 3 hours, and 5 hours and the other reaction conditions were held as constant as possible. Results of the several runs are summarized in Table I(B)8.

III. CONCLUSIONS

From the preceding experiments, it was noted that a part of the coal was hydrogenated during the period of heating to reaction temperature, and the hydrogenation was well underway after 30 minutes. After one hour, the reaction was complete and the yield of liquid products reached a maximum. With increasing reaction time the yield of liquid decreased and the formation of gas increased due to secondary thermal cracking.

ENCLOSURE (B)8

Table I(B)8
EFFECT OF REACTION TIME

		Run Number				
		48	50	76	43	44
Reaction Conditions	React. Time (hr-min)	0-0	0-30	1-0	3-0	5-0
	React. Temp. (°C)	455	455	455	455	455
	Initial Pressure (atm.)	95	100	101	99	98
	Pressure Drop (atm.)	8	21	19	23	23
	Preheating Time (hr-min)	1-30	1-30	1-55	1-25	1-25
Reaction Products (gm)	Gas	29.3	33.5	33.6	33.8	40.5
	Water	13.7	17.8	17.4	17.4	17.5
	Oil	64.0	78.3	85.9	79.2	74.1
	Residue	52.8	29.1	24.9	22.1	25.0
Gas Analyses (gm)	CO_2	2.2	1.3	0.7	0.6	1.6
	C_nH_{2n}	0.5	0.5	0.5	0.3	0.4
	CO	0.8	1.3	1.6	1.3	2.3
	H_2	15.8	13.5	14.3	12.8	23.5
	C_nH_{2n+2}	10.0	16.9	16.5	18.8	12.7
		1.3	1.2	1.3	1.2	1.8
Distillation of Oil (gm)	--180°C		12.3	10.6	11.2	12.0
	180--230°C	3.7	5.8	5.8	6.4	7.2
	230--360°C			36.0	34.0	32.7
	Pitch	60.3	60.2	33.3	27.0	22.1
Analyses of Residue (gm)	Benzene Soluble			0.2		0.1
	Benzene Insoluble	40.1	15.2	12.0	9.5	12.4
	Ash	12.7	13.9	12.9	12.6	12.6

ENCLOSURE (B) 9

STUDIES ON THE HYDROGENATION OF LOW-TEMPERATURE TAR

Reference NavTechJap Document No. ND 26-0008.13 ATIS No. 4579

by

CHEM. ENG. T. OGAWA

Research Period: 1936 - 1937

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ENCLOSURE (B)9

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)9

SUMMARY

This investigation was made to determine properties of products, and the effect of different catalysts on the hydrogenation of low-temperature tar from FUSHUN coal. The low temperature tar was hydrogenated with and without catalysts, and the following significant results were obtained:

(1) When no catalyst was used, optimum conditions were established as follows:

Temperature	450°C
Pressure	250 atm.
Time	2 hr

In this case, many acidic, basic, and asphaltic substances included in the raw tar were not removed by hydrogenation.

(2) In the case of catalytic hydrogenation, several different catalysts were investigated and molybdenum sulphide was found to be the most effective. Asphaltene, and acidic and basic substances were catalytically reduced to neutral hydrocarbon oils by using MoO_3 or MoS_3.

I. INTRODUCTION

Low temperature carbonization oil cannot be used directly for motor fuel owing to the high content of acidic, basic and asphaltic substances.

These experiments were started in 1936, and continued until March 1937, to investigate the hydrogenation of low-temperature tar as a process for making satisfactory motor fuel.

II. DETAILED DESCRIPTION

A. Test Apparatus and Procedure

A rotating type autoclave of 2.4 liters capacity was used in these experiments.

300 grams of low-temperature tar were charged and, after displacing air by hydrogen, the pressure was increased to 100 kg/cm^2. About 2 hours was allowed for heating and the autoclave was held at the reaction temperature for 1 hour. After cooling, the products were removed and analyzed.

The gaseous product was analyzed by Hempel's method.

A part of the liquid product, including solid substances such as coke, ash and catalyst, was filtered, and the properties of the filtered oil were determined.

Benzene was added to the other portion of the liquid product, (including solid matter), and moisture and benzene-insoluble substances were determined.

B. Experimental Results

ENCLOSURE (B)9

1. The properties of the low-temperature tar used as feed stock are given below:

d_4^{40}	1.019
Benzene-insoluble (wt %)	2.3
Asphaltenes (wt %)	27.3
Distillation (wt %)	
-180°C	0.6
180-230°C	2.2
230-280°C	16.2
280-360°C	37.3
Above 360°C	43.2
Loss	0.5

2. Tests without a catalyst.

The effects of temperature and time on hydrogenation, in the absence of a catalyst, were investigated and the results are tabulated in Tables I(B)9 and II(B)9.

The hydrogen consumed and content of unsaturated hydrocarbons in the gas increased with increasing temperature, but the yield of liquid product decreased. The content of acidic substances remained practically constant above 425°C.

It was concluded that the optimum reaction conditions were as follows:

Temperature: ....450°C
Pressure: ....250 kg/cm^2 at reaction temperature
Time: .... 2 hours

3. Tests with catalysts.

The following catalysts were used and the experimental results are given in Tables III(B)9 and IV(B)9.

Catalysts:		
(1)	Fe_2O_3	Commercial grade
(2)	NiO	Nickel nitrate was ignited at 300°C
(3)	Al_2O_3	Freshly precipitated aluminum hydroxide was dried at 150°C.
(4)	MoO_3	Ammonium molybdate was ignited at 350°C.
(5)	MoS_3	The precipitate from the neutralization of ammonium-thio-molybdate solution with dil. H_2SO_4 was washed and dried at 150°C.
(6)	CoS	Freshly precipitated by H_2S and washed and dried at 115°C.
(7)	$AlCl_3$	Commercial grade
(8)	$ZnCl_2$	Commercial grade

In all cases, yield of the reaction product was almost constant. It was difficult to conclude that the amount of water formed was dependent on the acidic substances in the raw tar, since water might be produced by the reduction of the catalyst in some cases.

The properties of the liquid product were affected by the type of catalyst used. Acidic and basic substances were converted into neutral oils by using MoO_3 as a catalyst. The yield of light oil was better using MoS_3 than with NiO, CoS, $AlCl_3$ and $ZnCl_2$.

ENCLOSURE (B)9

III. CONCLUSIONS

1. When no catalyst was used, the optimum conditions for motor fuel production by hydrogenation of low-temperature tar were determined as: reaction temperature, 450°C; pressure, 250 kg/cm^2; and time, 2 hours.

Asphaltene content was lowered to 3-4%, but the content of acidic substances was not reduced in those experiments.

2. When a catalyst was used, the yield of liquid product was almost constant in all cases, but the properties of the liquid were affected by the catalyst used. MoO_3 or MoS_3 catalyst appeared to be the most suitable for production of high yields of light oil, in which all acidic, basic, and asphaltic compounds had been reduced to neutral oil.

Table I(B)9
EXPERIMENTAL CONDITIONS AND YIELD OF PRODUCTS. (NO CATALYST)

Run No.	Initial Press. (kg/cm^2)	Temp. (°C)	Time (hr)	Press. Drop (kg/cm^2)	H_2 Compound (gm)	Sat. HC'S in gas(gm)	Oil Yield (wt %)	Water (wt %)	Cakes (wt %)	Asphaltene (wt %)
1	100	400	2	7.0	1.1	4.3	89.9	7.2	0.4	17.4
2	100	425	2	10.0	1.8	5.9	89.6	8.1	0.5	14.8
3	100	450	1	9.0	2.0	8.4	83.5	6.1	1.5	18.4
4	100	450	2	15.0	2.1	10.9	83.2	6.1	1.0	3.4
5	50	450	2	4.0	2.1	13.5	63.5	5.7	37.0	14.2
6	100	475	1	20.0	4.2	22.7	60.7	7.3	5.8	3.4
7	100	500	1	22.0	4.4	23.7	58.2	7.1	4.0	4.2

Table II(B)9
PROPERTIES OF OIL PRODUCT. (NO CATALYST)

		Constituent				Distillation (vol. %)				
Run No.	sp. gr. (25/4)	acidic (vol. %)	basic (vol. %)	neutral (vol. %)	I. D.	below 180°C	180°C~230°C	230°C~280°C	280°C~360°C	above 360°C
1	1.0008	29	4	67	62	5.0	7.0	17.0	31.0	39.5
2	0.9858	22	2	76	61	6.4	12.3	22.7	17.7	35.5
3	0.9838	26	3	71	68	10.3	18.2	23.6	25.1	27.0
4	0.9468	23	3	74	52	16.7	18.3	23.9	25.1	19.5
5	0.9834	25	4	71	50	20.8	26.4	22.7	19.1	20.9
6	0.9710	24	5	71	50	26.1	26.7	20.0	17.7	16.3
7	0.9772	25	6	69	38	28.8	25.7	20.1	18.8	15.2

ENCLOSURE (B)9

Table III(B)9
EXPERIMENTAL CONDITIONS AND YIELD OF PRODUCT

Run No.	Initial Press. (kg/cm^2)	Temp. (°C)	Time (hr)	Press. Drop (kg/cm^2)	Catalyst	H_2 consumed (gm)	Sat. HC's in gas(gm)	Oil yield (wt. %)	Water (wt. %)	Cakes (wt. %)	Asphaltene (wt. %)
4	100	450	2	15	none	2.1	10.9	83.2	6.1	1.0	3.4
8	100	450	2	19	Fe_2O_3	2.9	9.4	82.8	6.6	5.3	0.5
9	100	450	2	29	NiO	3.2	6.5	84.5	9.0	4.5	trace
10	100	450	2	15	Al_2O_3	2.6	11.0	79.2	6.0	6.2	0.9
11	100	450	2	38	MoO_3	4.9	9.7	81.8	9.2	4.9	0.0
12	100	450	2	38	MoO_3	4.6	7.5	80.0	11.4	4.3	0.0
13	100	450	2	27	CoS	3.4	7.9	84.1	9.2	4.2	0.7
14	100	450	2	24	$AlCl_3$	3.2	9.3	82.2	4.2	11.9	0.4
15	100	450	2	22	$ZnCl_2$	2.8	7.9	83.4	5.4	7.5	0.2

Table IV(B)9
PROPERTIES OF OIL PRODUCT

		Constituent (vol. %)			Distillation Property (vol. %)					
Ex. No.	Sp. gr. (25/4)	acidic	basic	neutral	I. D.	below 180°C	180°C~230°C	230°C~280°C	280°C~360°C	360°C~
4	0.9468	23	3	76	52	13.0	17.1	23.4	25.3	20.6
8	0.9466	24	5	71	58	12.2	17.4	25.4	25.4	19.0
9	0.8944	16	2	82	38	16.6	19.5	23.1	26.9	12.5
10	0.9393	20	4	76	48	13.4	21.1	22.9	25.2	16.5
11	0.8547	0	0	100	43	29.5	18.0	21.9	22.3	6.7
12	0.8567	0	0	100	68	31.4	20.8	23.1	20.7	4.5
13	0.9174	18	3	79	58	15.3	19.8	23.3	27.4	12.8
14	0.9166	18	1	81	49	16.4	19.5	24.5	25.5	14.0
15	0.9123	18	3	79	47	15.0	18.2	20.8	27.9	16.8

ENCLOSURE (B) 10

THE COAL HYDROGENATION REACTION

by

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Research Period: 1938-1939

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

December 1945

ENCLOSURE (B)10

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)10

SUMMARY

To obtain oil of good quality from the hydrogenation of coal, the reaction must be carried on at a favorable low temperature since thermal cracking and polymerization occur at higher temperatures. This can be achieved by using a catalyst to activate the reactant (coal).

I. INTRODUCTION

In Japan, KOMATSU and SUMIMOTO*, had studies the hydrogenation of coal components, namely, resinous coal substance and unchanged vegetable substance. The most important component in coal is "coal substance" and studies on the hydrogenation of it are of particular interest.

This investigation was centered on the hydrogenation of coal substance from Fushun Oyama coal and of pure humus derived from cane sugar, using nickel oxide and zinc chloride as catalysts.

II. DETAILED DESCRIPTION

A. Raw Materials

1. Coal substance was prepared from Fushun Oyama coal according to the method described by Francis and Wheeler**. The yield and properties of coal substance were as follows:

Yield (wt.% of Oyama coal)	35.98%
Analysis (wt.% of coal substance)	
H_2O	4.50%
Organic substance	86.65%
Ash	9.85%
Elementary Analysis (wt.% of coal substance)	
C	62.81
H	4.49
N	4.89
S	0.55
O (difference)	27.25
C/H ratio	12.0

2. Humus, prepared from pure cane sugar by steaming under pressure, was a black brownish powder and its yield and properties were as follows:***

Yield (wt. of cane sugar)	12.20
Content of H_2O	6.75
Elementary Analysis (wt.% of humus)	
C	66.10
H	4.48
O (difference)	29.42
C/H ratio	12.0

3. Catalyst: $ZnCl_2$ (commercial grade)
Ni_2O_3 (Prepared from nitrate by precipitation method)

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* S. KOMATSU and M. SUMIMOTO: Bull. Chem. Soc. Japan 261 (1935).
** W. Francis and R. V. Wheeler: J. Chem. Soc. 2967 (1928).
*** C. TANAKA and S. KOMATSU: Sexagent of Prof. Y. OSAKA.

4. **Hydrogen:** Prepared by electrolysis of water.

B. Test Apparatus and Procedures

A shaking type autoclave of 600cc capacity was used in these experiments.

50 grams of coal substance or humus and 2.5 grams (5 wt.%) of catalyst were used as charge in these experiments. Initial hydrogen pressure was 100 kg/cm^2 (standard conditions) and the period at reaction temperature was one hour.

After the reaction period was completed, shaking was continued until temperature dropped to 100°C. After cooling overnight, the gas was released, the liquid reaction product was divided into three parts, and the amounts of water, benzene soluble (Bitumen), and benzene insoluble substance were determined.

III. EXPERIMENTAL RESULTS

A. Coal Substance

1. The absorption of hydrogen by coal substance, as shown in Figure 1(B)10 was very slow at 200-300°C. At 300-350°C the absorption rate increased, but at 350-400°C it decreased and above 400°C it increased again.

From this experiment, it appeared that hydrogen absorption up to 300°C was mainly due to saturation of double bonds and carbonyl radicals and also, that the rapid hydrogen absorption period from 300-350°C was due to saturation of benzene nuclei in polycyclics. It appeared that the $ZnCl_2$ catalyst was less active in promoting these reactions than Ni_2O_3. The distribution of oxygen radicals in coal has been reported by W. Fuchs as shown in Table I(B)10.

2. The relation between yield of product and reaction temperature is given in Figure 2(B)10. The composition of reaction gases is given in Table II(B)10.

It will be noted that the cracking of oxygen compounds, indicated by high production of CO_2 and CO, reached a maximum at 350°C. Formation of light hydrocarbon gases began at 400°C, probably the result of cracking of aromatic hydrocarbons. This phenomenon was confirmed by study of the bitumen content, which began to be produced at 330°C, reached 50% at 430°C and then began to decrease (refer to Figure 3(B)10). Benzene insoluble substances began to decrease suddenly at 330°C and finally dropped to 13% at 430°C (refer to Table III(B)10 and Figure 2(B)10).

From Table III(B)10 it is noted that hydrogen content increased gradually from 200°C to 350°C, and above 390°C began to decrease, whereas the carbon content varied inversely.

3. The most important problem in the hydrogenation of coal is to remove oxygen from the coal substance. Data on the conversion of oxygen into CO_2, CO and H_2O, obtained in this study and reported for the low-temperature carbonization of coal,**** are given in Table V(B)10. In the hydrogenation of coal substance, a maximum was reached at 350°C.

**** S. SUMIMOTO: The Report of the Naval Fuel Depot. 100(1945)

This phenomenon was quite different from the deoxidation reactions in low-temperature carbonization. The oxygen contents of bitumen and benzene insolubles produced from coal substance by catalytic hydrogenation are given in Table IV(B)10. The content is smaller in the case of $ZnCl_2$ than for Ni_2O_3 and in this respect $ZnCl_2$ is better than Ni_2O_3 as a catalyst for hydrogenation of coal substance.

B. Humus

1. The oxygen in humus was mainly contained in carbonyl, hydroxyl, and ether groups and accordingly, consumption of hydrogen was less than for coal substance, in which the oxygen was mainly in carbonyl form.

2. The deoxidation rate of coal substance was greater than that for humus up to 350°C, but at 390°C, was less (refer to Table V(B)10). This was due to high saturation of benzene nuclei in humus at 390°C and over.

3. Analyses of bitumen and benzene insoluble substance are given in Table VI(B)10.

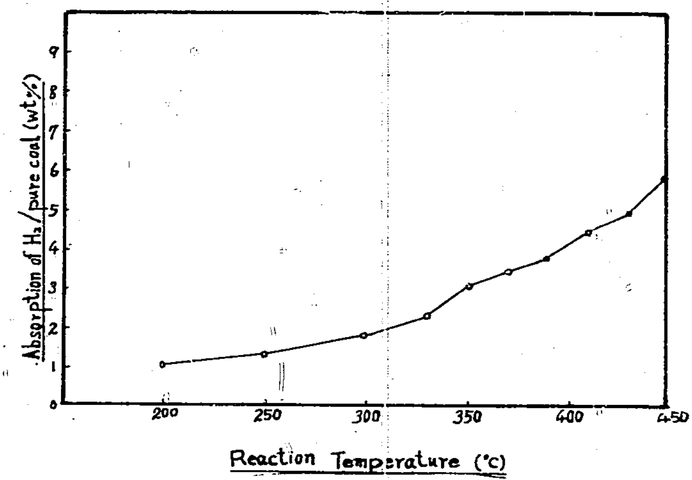

Figure 1(B)10

H_2 ABSORPTION CURVE OF COAL SUBSTANCE (Ni_2O_3)

ENCLOSURE (B)10

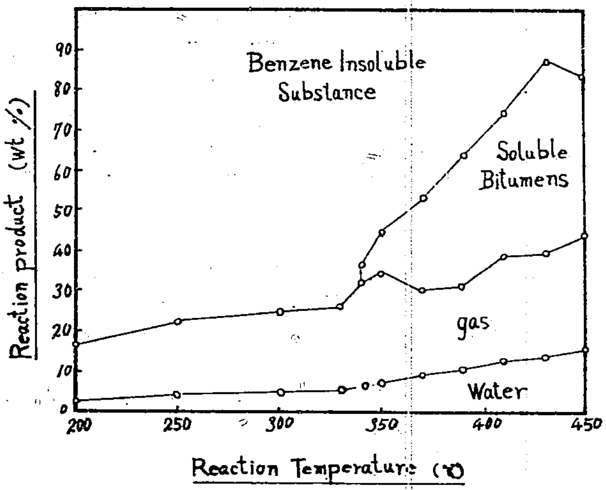

Figure 2(B)10

RELATION BETWEEN YIELD OF PRODUCTS AND TEMPERATURE (Ni_2O_3)

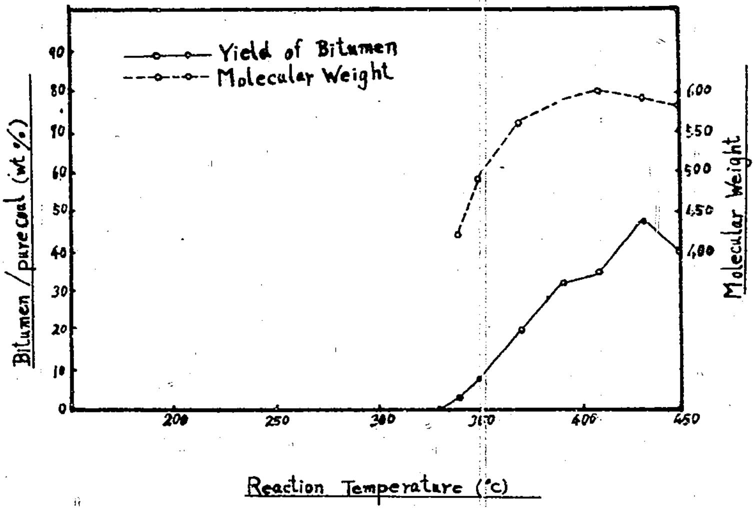

Figure 3(B)10

YIELD OF BITUMEN AND ITS MOLECULAR WEIGHT

(COAL SUBSTANCE) (Ni_2O_3)

ENCLOSURE (B)10

Table I(B)10
WT.% OF SUBSTANCE

Type of Oxygen Radical	In Humic Acid	In Brown Coal
Carboxyl group	4	1 - 10
Hydroxyl group	6	2 - 8
Methoxyl group	2	1 - 5
Carbonyl group	5	3 - 4

Table II(B)10
GAS YIELD FROM COAL SUBSTANCE*

Gas Component	Temperature (°C)									
	200	250	300	330	350	370	390	410	430	450
CO_2	2.76	4.83	5.41	5.76	8.67	5.55	4.84	5.77	4.70	3.61
C_nH_{2n}	0.34	0.40	0.53	0.51	0.18	0.22	0.21	0.25	0.24	0.22
CO	-	0.13	0.26	0.33	1.07	1.32	1.48	1.58	1.78	1.89
H_2	4.51	4.38	4.19	3.95	3.62	3.45	3.32	3.00	2.81	2.34
C_nH_{2n+2}	-	-	-	-	-	-	-	1.47	2.29	4.73
H_2	2.49	2.47	2.44	2.42	2.13	1.98	1.96	1.93	1.73	1.50
n	-	-	-	-	-	-	-	1.5	1.8	1.6
Total	10.10	12.21	12.83	12.97	15.67	12.52.	11.81	14.00	13.55	14.29

* Grams of Ni_2O_3.

ENCLOSURE (B)10

Table III(B)10
ANALYSIS OF BENZENE INSOLUBLE SUBSTANCE*

Reaction Temp.(°C)	Yield (wt.%)	Carbon (wt.%)	Hydrogen (wt.%)	Oxygen (wt.%)
200	84	68	3.2	22.6
330	74	77	4.9	11.7
350	56	80	5.4	11.8
390	37	80	5.2	9.7
430	13	88	5.1	7.6
450	18	90	4.6	6.2

* Ni_2O_3

Table IV(B)10
OXYGEN CONTENT IN HYDROGENATED COAL SUBSTANCE
WT.% OF MATERIAL

Catalyst	Ni_2O_3		$ZnCl_2$	
Material React. Temp(°C)	Bitumen	B.Insob.Sub.	Bitumen	B.Insob.Sub.
300	-	20.2	-	18.4
350	10.8	11.8	8.9	8.2
390	9.9	9.7	12.2	9.9
450	14.3	6.2	11.4	5.6

Table V(B)10
CONVERSION OF TOTAL OXYGEN INTO CO_2, CO and H_2O
(WT.%)

R. Temp.	(Ni$_2$O$_3$ Catalyst) Hydrogen of Humus				(Ni$_2$O$_3$ Catalyst) Hydrogen of C. Subst.				Low Temp. Carb.		
(°C)	CO_2	CO	H_2O	Sum	CO_2	CO	H_2O	Sum	CO_2	CO	Sum
200	9.2	2.3	4.3	15.9	17.1	-	9.5	26.6	-	-	-
250	10.4	2.3	9.1	21.8	26.9	0.7	13.3	40.8	-	-	-
300	18.5	2.1	14.5	35.0	33.5	1.3	15.2	50.0	2.1	0.7	2.8
350	29.7	2.4	34.1	66.2	53.7	5.2	22.8	81.7	4.7	2.3	7.0
390	38.3	7.3	44.4	90.0	30.0	7.1	36.1	73.3	6.1	3.8	9.9
450	31.4	5.9	60.7	98.0	22.4	9.2	52.0	83.6	7.0	6.9	13.9

Table VI(B)10
YIELD AND ANALYSIS OF BITUMEN AND BENZENE INSOLUBLE SUBSTANCE
(WT.% Ni$_2$O$_3$)

Reaction Temp.	Bitumen				Benzene Insol. Sub.			
(°C)	Yield	C	H	O	Yield	C	H	O
200	0	-	-	-	91.4	66	4.0	26.0
250	0	-	-	-	89.4	69	4.5	26.3
300	0	0	-	-	84.7	72	4.5	23.5
350	4.8	82	7.3	10.6	68.9	74	4.6	21.6
390	20.1	86	7.8	5.8	36.6	86	5.1	8.2
450	16.5	89	7.6	2.6	29.4	97	3.9	0

ENCLOSURE (B) 11

EXPERIMENTS ON VARIOUS COALS PRODUCED IN JAPAN

Reference NavTechJap Document No. ND 26-0008.17 ATIS No. 4579

by

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Research Period: 1936-1937

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

December 1945

ENCLOSURE (B)11

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)11

SUMMARY

High pressure hydrogenation tests were made on coals from NAIBUCHI (Saghalien), BIBAI and URYU (Hokkaido), IWAKI (Fukushima), KITOMO (Yamagata), MOKUSAN, ZUIHO, TANISHO and NANSHO (Formosa), and AGOCHI (Korea), and the results are presented below.

I. INTRODUCTION

In previous reports, the effect of changing reaction conditions on the hydrogenation of Oyama coal were investigated. In this report various kinds of coals were liquefied under the same conditions and the yields and qualities of the oils were compared with those of Oyama coal.

II. DETAILED DESCRIPTION

A rotating autoclave with a capacity of 2.4 liters was used. The charge to the autoclave consisted of 150 grams of coal (crushed finer than 60 mesh) together with 5 % by wt. of $ZnCl_2$ catalyst. The initial pressure of electrolytic hydrogen was 100 atmospheres. The autoclave was heated to the reaction temperature at a rate of 2.75°/min, and was maintained at that temperature for 1 hour.

Analyses of the coals used are given in Table I(B)11 and the experimental results are summarized in Table II(B)11.

III. CONCLUSIONS

1. **Naibuchi coals were liquefied much easier than Oyama coal and gasoline content of produced oils was good.**

2. **Bibai coals were liquefied easier then Oyama coal and the gasoline content of produced oils was also good.**

3. **In the case of Uryu coal, a higher reaction temperature was required than for Oyama coal and the produced oil was more viscous and had a lower content of gasoline.**

4. **Iwaki and Kitomo coals had high ash contents and required higher reaction temperatures.**

5. **In the case of Mokusan #3 mine coal and Zuiho coal, the reaction temperatures were lower and the yields of oil were higher than for Oyama. Although Taisho and Mokusan #1 mine coals required slightly higher temperatures, the rates of liquefaction and the qualities of the produced oils were good.**

Nansho coal was more difficult to liquefy than the others.

6. **The rate of liquefaction and the quality of the produced oil from Agochi coal were almost the same as for Oyama coal.**

ENCLOSURE (B)11

Table I(B)11
PROPERTIES OF COAL

Coal	Proximate Analysis(wt %)				Ultimate Analysis(wt %)				
	Moisture	Vol.Matter	F.Carbon	Ash	C	H	O	N	S
Ovama	5.5	41.1	46.0	7.0	79.0	6.2	13.0	1.3	0.5
Naibuchi #3	4.8	44.0	43.1	8.1	76.4	5.9	16.1	1.4	0.2
Naibuchi #5	4.6	43.9	38.5	13.0	77.5	6.1	14.8	1.4	0.2
Naibuchi #7	5.2	44.2	41.4	9.2	76.4	5.7	16.3	1.4	0.2
Naibuchi #8	5.0	45.8	42.0	7.2	77.6	5.9	15.0	1.3	0.2
Bibai, upper	4.0	39.6	46.0	10.4	79.6	6.0	12.5	1.6	0.3
Bibai, lower	2.8	41.8	48.9	6.5	80.8	5.8	11.7	1.4	0.3
Iwahi	6.3	37.2	29.5	28.0	71.2	5.6	17.5	1.0	4.7
Uryu	3.7	35.0	41.8	19.5	79.3	5.7	12.8	1.7	0.5
Kitomo	15.0	28.8	17.7	28.5	67.2	5.3	25.3	1.0	1.2
Mokusan #1	2.2	43.3	47.4	7.1	81.3	6.6	7.7	1.6	2.8
Mokusan #3	2.3	37.3	47.3	12.7	81.2	6.0	9.2	1.9	1.7
Taisho	2.3	38.3	49.6	9.8	82.5	5.7	8.4	1.7	1.7
Zuiho	4.1	42.0	45.0	8.9	80.0	6.7	9.8	1.9	1.6
Nansho-	6.7	21.3	73.9	4.0	89.4	5.2	1.7	2.0	1.7

Table II(B)11
RESULTS OF HYDROGENATION RUNS

Coal	R.Temp $(^{\circ}C)$	Initial P. (atm)	Final P. (atm)	Yield of Oil (wt% of charge)	Yield of 240°C Gasoline (wt% of charge)
Fushun Oyama	425	100	65	63.8	15.5
Naibuchi #3	425	100	65	69.2	15.8
Naibuchi #5	425	100	75	75.8	11.4
Naibuchi #7	425	100	70	73.0	13.8
Naibuchi #8	425	100	70	73.5	14.7
Bibai, upper	425	100	67	70.3	17.9
Bibai, lower	425	100	67	78.5	23.7
Iwaki	425	100	87	58.7	3.8
Uryu	425	100	76	78.9	10.2
Kitomo	425	100	94	58.3	5.4
Mokusan #1	425	100	71	65.1	15.5
Mokusan #3	425	100	71	66.0	18.6
Taisho	425	100	66	66.1	15.6
Zuiho	425	100	67	65.0	19.1
Nansho	425	100	66	46.7	9.4
Nansho	450	100	65	39.2	10.0
Agochi	425	100	71	69.4	19.7
Agochi	400	100	76	71.7	12.8
Agochi	375	100	76	71.0	8.8

ENCLOSURE (B) 12

STUDIES ON TAR FOR PASTE

by

COMDR. T. YOKATA

Research Period: 1934-1935

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

December 1945

ENCLOSURE (B)12

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)12

SUMMARY

Partially hydrogenated polycyclic compounds, such as tetralin, were tested and found to be suitable components for coal hydrogenation past oils.

I. INTRODUCTION

In experimental work, coal is usually hydrogenated in an autoclave by heating coal powder with a catalyst under high pressure of hydrogen. However, in industrial operations, a coal paste is employed in order to promote the hydrogenation action and to facilitate handling. The present experiments, therefore, were undertaken to test the relative effectiveness of several compounds as paste oils in coal hydrogenation.

II. DETAILED DESCRIPTION

The compounds used as paste oils in these experiments were tetralin, decalin, naphthalene, and cyclohexane.

These compounds, except naphthalene, were prepared from naphthalene and benzene by hydrogenation.

Oyama coal of the following properties was used:

Water	5.5 %
Ash	7.0 %
Volatile Matter	41.1 %
Fixed Carbon	46.4 %

C	73.2 %
H	5.7 %
O	12.0 %
N	1.2 %
S	0.78%

Water	5.5 %
Ash	7.0 %
Resin	3.4 %
Coal Substance	80.5 %
Vegetable Matter	3.6 %

A 625 cc autoclave was used in these experiments, and the following reaction conditions are listed below. $ZnCl_2$ was used as a catalyst (3-5 % by wt. of coal).

Exp. (I) 50 grams of the coal were heated at 480°C for 2 hours under 60 atmospheres of nitrogen.

Exp. (II) A mixture of 50 grams of the coal and 50 grams of the solvent was treated at 480°C for 2 hours under 60 atmospheres of nitrogen.

Exp. (III) A mixture of 50 grams of the coal and 50 grams of the solvent was heated at 480°C for 3 hours under 92 atmospheres of hydrogen.

Exp. (IV) 50 grams of tetralin were heated at 480°C for 2 hours under 60 atmospheres of hydrogen.

After cooling the reaction vessel, the volume and composition of the gas, and the solubility of the reaction product in benzene was determined. The results of the experiments are shown in Table I(B)12.

The benzene soluble substance in the hydrogenated coal, when tetralin was used as a solvent, was distilled under 3.3mm of pressure to 300°C. The residual pitch had the following analysis:

C	90.4 %
H	6.7 %
S	0.1 %
N	2.0 %
O (by diff.)	0.8 %
Ash	1.3 %
Volatile Matter	59.9 %
Fixed Carbon	38.2 %

50 grams of the pitch were hydrogenated in an autoclave at 450°C for 3 hours under 92 atmospheres hydrogen with and without a catalyst. The reaction products were treated in the same manner as in the previous experiments, and the results are shown in Table II(B)12.

The pitch in the coal hydrogenation products was easily hydrogenated without catalyst.

III. CONCLUSIONS

Under the experimental conditions, coal was appreciably soluble in tetralin, and its solubility decreased in order of decalin, cyclohexane and naphthalene. When coal was hydrogenated with these compounds, under high temperature and high pressure of hydrogen, the yield of hydrogenated liquid from the coal paralleled the solubility in these solvents. The presence of partially hydrogenated polycylic compounds, such as tetralin, in paste oil would have a beneficial effect on the hydrogenation of coal.

ENCLOSURE (B)12

Table I(B)12
AUTOCLAVE TESTS OF VARIOUS PASTE OIL COMPONENTS

Exp. No.	Solvent	Pressure Increase (atm)	Gas Used	Produced Gas Composition				Benzene Solubility. (Wt.% of original Oil)
				CO_2+CO	H_2	C_nH_{2n+2}	N_2	
I	None	7	N_2	3.6	0.6	8.0	87.8	
	Naphthalene	8	N	3.2	1.9	0.3	94.6	22
	Tetralin	12	N	2.0	0.1	0.9	94.1	48
II	Decalin	17	N	2.0	1.3	34.6	61.8	31
	Cyclohexane	21	N	2.4	1.9	31.3	64.4	24
								Liquefied* wt. %
III	Naphthalene	-40	H_2	5.7	61.2	32.1		64.2
	Tetralin	-29	H	2.1	74.5	20.7		83.3
	Decalin	-48	H	3.0	55.0	39.6		73.5
	Cyclohexane	-36	H	1.5	73.1	19.2		67.2
IV	Tetralin (alone)	-13	H		83.3	16.7		

$$\text{*Liquefied Wt. \%} = \frac{\text{Pure coal}-(\text{benzene insoluble} + \text{gas from pure coal})}{\text{Pure Coal}}$$

Table II(B)12
HYDROGENATION OF PITCH

Catalyst	Pressure Drop. (atm)	Gas Composition			Benzene Insoluble (gm)	Liquefied (wt. %)
		CO_2+CO	H_2	C_nH_{2n+2}		
None	31	0.6	75.9	18.7	5.5	75.8
Ni	34	0.5	71.0	26.6	3.0	75.5
Fe_2O_3	33	0.4	78.0	18.8	7.0	73.0

ENCLOSURE (B) 13

ON THE PHYSICAL PROPERTIES OF PASTES

Reference NavTechJap Document No. ND 26-0008.18, ATIS No. 4579

by

ENG. LT. COMDR. T. SUZUKI

NAVAL ENG. R. YUMEN

Research Period: 1938-1939

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

December 1945

ENCLOSURE (B)13

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)13

SUMMARY

To assist in the design and operation of Bergius coal hydrogenation plants, the viscosity, heat conductivity, heat propagating ratio, density, specific heat, and electrical conductivity of coal pastes and hydrogenated oil product were determined.

I. DETAILED DESCRIPTION

A. Description of Samples

Fushun-Oyama coal was crushed to 120 mesh and thoroughly mixed in a tube mill with heavy oil from hydrogenation of Oyama coal. The properties of the coal and the resulting paste are shown below.

Composition of Fushun-Oyama Coal

Water (wt %)	5.5
Volatile matter	41.4
Carbon	46.4
Ash	7.0

Composition of the Paste

Water (wt %) ...	3.3
Coal	41.8
Heavy oil	54.9

B. Description of Test Procedures and Results

1. Viscosities at atmospheric and 200 atmospheres of pressure were measured in a falling ball viscosimeter, made of 18-8 Cr-Ni steel, 24.90mm inner diameter, and one meter in length (refer to Figure 1(B)13). A steel ball (7.93mm in diameter) was released by means of handle "B", and the rate of fall was measured by an electrical indicator at "D". Viscosities of the paste and the heavy oil determined by this apparatus are shown in Figures 2(B)13 and 3(B)13.

The relation between the viscosity of the paste and its coal content is shown in Figure 4(B)13. In this case, a MacMichel's viscosimeter was used.

The device shown in Figure 5(B)13, was inserted within the apparatus shown in Figure 1(B)13, and viscosities at 200 atmospheres of pressure and high temperatures were measured.

In Figure 5(B)13, "B" is a cylinder 20mm in diameter and 88mm in depth, and "C" is a capillary (1.5mm in diameter and 100mm in length). An electromagnet is set outside of the tube and the iron cylinder "A", closing the opening to the capillary, can be lifted for a definite time. The viscosity was calculated from the quantity of the liquid that flowed through the capillary per unit time.

By this method, the viscosity of the paste, free from larger particles of solid matter which might plug the viscosimeter, was measured (refer to Table I(B)13).

2. Heat Conductivity. Heat conductivity was measured in the apparatus shown in Figure 6(B)13.

The temperature at the points "A" "B" and "C" were measured with copper-constanton thermocouples (0.1mm in diameter) which were attached by means of tin foil circles, 20mm in diameter. The thickness of the sample was measured with a micrometer. The results are shown in Table II(B)13.

3. Heat Propagating Ratio. The apparatus used for measuring the heat propagating ratio is shown in Figure 7(B)13. The paste was put in "A" and maintained at a constant temperature. Ice water was put in "C" (separated from "A" by copper plate "B"), and vigorously stirred.

Immediately the temperature of the paste at a distance of 1.75cm from the copper plate was measured.

The heat propagating ratio, **d**, was calculated using the following equation:

$$\theta = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4\alpha t}}} e^{-\gamma^2} d\gamma$$

where "θ" is the temperature of a point at a distance "X" within a solid which is infinite in the direction perpendicular to a plane held at a temperature of 0°C.

The temperature variance and the heat propagating ratio (α) in the case X = 1.75cm are shown in Table III(B)13.

The heat propagating ratio of the paste was found to be 0.000979 cm^2/sec at 15°C.

4. Density. The densities of the paste, produced oil, and Fushun-Oyama coal are shown in Table IV(B)13.

5. Specific Heat. The results of specific heat determination in an ice calorimeter are shown in Table V(B)13.

6. Electrical Conductivity. Two copper plates (3.4 x 5.7cm) were set parallel in the medium, and the electrical conductivity of paste was determined (refer to Figure 8(B)13).

ENCLOSURE (B)13

Table I(B)13
VISCOSITY OF THE PASTE IN THE REACTION CHAMBER

Temp.(°C)	Viscosity (Poise)	
	At Atm. Press.	At 200 Atm.
40	680	
50	155	
60	50	
80	9.1	
200	0.18	
300	0.043	0.075
350		0.043
400		0.028
450		0.018

Table II(B)13
HEAT CONDUCTIVITY AT 15°C

Sample	Paste	Paste 10% water	Paste 20% water	Heavy Oil	Produced Oil
Heat conductivity (Kcal./m hr.°C)	0.142	0.163	0.186	0.124	0.114

(See page 122 for Table III(B)13.)

Table IV(B)13
DENSITY

Samples	Paste	Produced Oil			Coal
		225	225-250	250-280	
Density d_4^{20}	1.15	0.8955	0.9373	0.9442	1.25

Table V(B)13
SPECIFIC HEAT

Sample	Paste	Produced Oil			Coal
		-225°C	225-250	250-280	
Sp. heat(cal/gm)	0.348	0.491	0.489	0.471	0.299

ENCLOSURE (B)13

Table III(B)13
HEAT PROPAGATING RATIO OF PASTE

Time past (sec)	Temp. at x = 17.5mm The initial temp. (21.7°C) is assumed	α which is calculated from equation (1) (cm^2/sec)
0	1.000	
60	1.000	
120		
160	0.997	0.00107
240	0.991	0.00092
300	0.977	0.00097
360	0.964	0.00097
420	0.948	0.00096
480	0.936	0.00093
540	0.913	0.00097
600	0.897	0.00096
660	0.880	0.00096
720	0.866	0.00095
780	0.847	0.00096
840	0.832	0.00095
900	0.816	0.00097
960	0.802	0.00096
1020	0.787	0.00097
1080	0.773	0.00098
1140	0.763	0.00096
1200	0.749	0.00097
1260	0.735	0.00098
1320	0.724	0.00098
1380	0.714	0.00097
1440	0.703	0.00097
1500	0.695	0.00097
1560	0.684	0.00097
1620	0.673	0.00098
1680	0.665	0.00098
1740	0.658	0.00098
1800	0.650	0.00098
1860	0.639	0.00099
1920	0.633	0.00098
1980	0.626	0.00097
2040	0.618	0.00098
2100	0.610	0.00098
2160	0.604	0.00098
2220	0.597	0.00099
2280	0.591	0.00098
2340	0.585	0.00099
2400	0.500	0.00098
2440	0.573	0.00098
2520	0.587	0.00099
2580	0.562	0.00099
2640	0.558	0.00098
2700	0.552	0.00099
2760	0.547	0.00099
2820	0.542	0.00098
2880	0.538	0.00098
2940	0.534	0.00098
3000	0.529	0.00098
3300	0.508	0.00098
3600	0.489	0.00098
3900	0.471	0.00099
4200	0.456	0.00099
4500	0.441	0.00099
4800	0.429	0.00100
5100	0.417	0.00100
5400	0.407	0.00099
5700	0.396	0.00100
6000	0.384	0.00102
		mean 0.000979

ENCLOSURE (B) 13

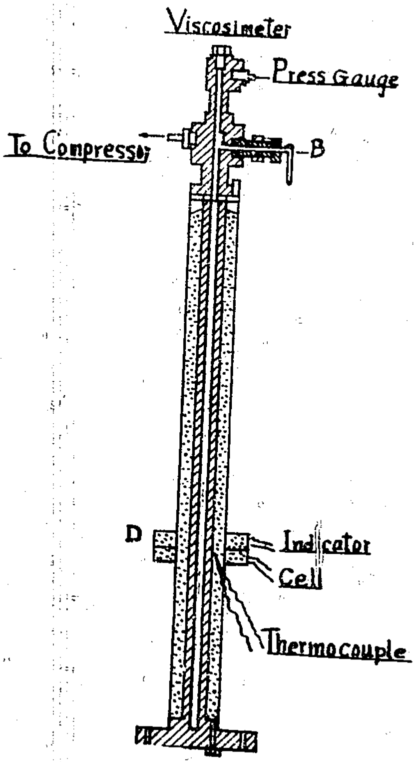


Figure 1 (B) 13
VISCOSIMETER

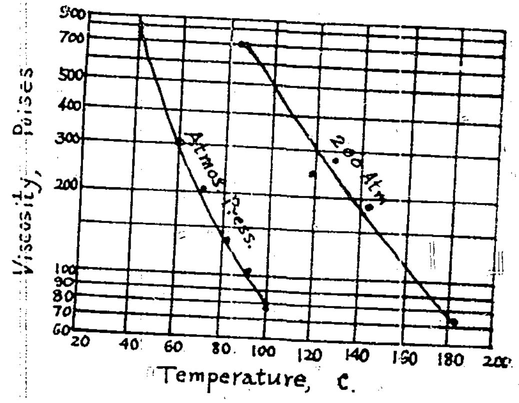


Figure 2 (B) 13
VISCOSITY OF PASTE

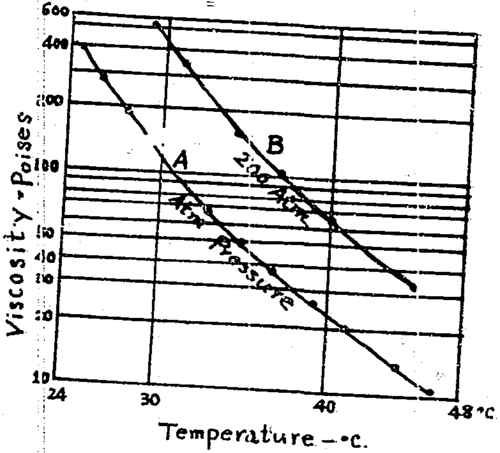


Figure 3 (B) 13
VISCOSITY OF LIQUEFIED HEAVY OIL

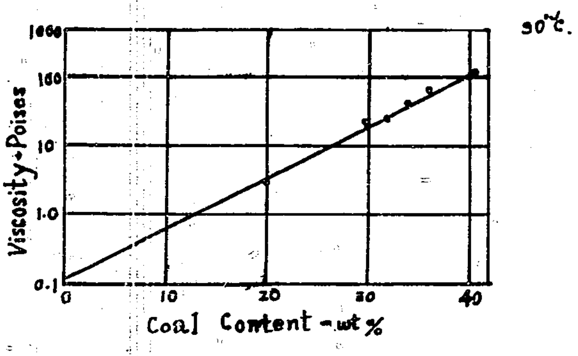
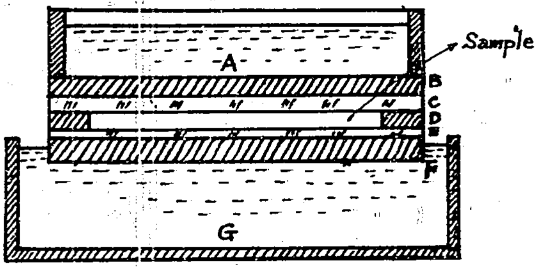


Figure 4(B)13
EFFECT OF COAL CONTENT ON PASTE VISCOSITY



A,G	Thermostats	
B,F	Copper Plate	200×200×10 mm.
C	Glass Plate	200×200×10 ″
E	Glass Plate	200×200×5 ″
D	Ebonite Frame	200×200×10 ″

Figure 6(B)13
APPARATUS FOR MEASURING HEAT CONDUCTIVITY

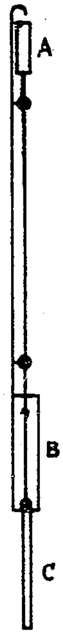


Figure 5(B)13
VISCOSIMETER FOR PASTE AND HEAVY OIL

ENCLOSURE (B)13

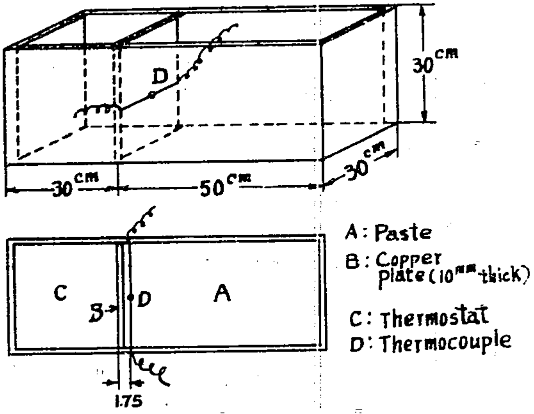


Figure 7(B)13
APPARATUS FOR MEASURING HEAT PROPAGATING RATIO

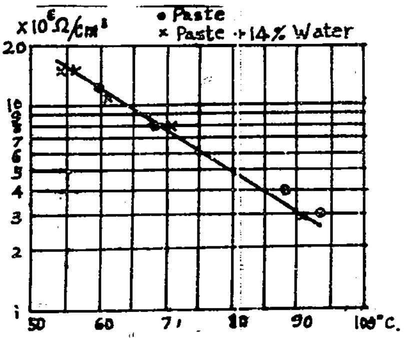


Figure 8(B)13
ELECTRICAL CONDUCTIVITY OF PASTE

ENCLOSURE (B) 14

STUDIES ON THE HYDROGENATION OF MIXTURES OF AROMATIC COMPOUNDS

Reference NavTechJap Document No. ND 26-0008.20 ATIS No. 4579

by
COMMANDER DR. T. SUZUKI

Research Period: 1940-1941

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

December 1945

ENCLOSURE (B)14

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (3)14

SUMMARY

The object of these studies was to investigate the catalytic hydrogenation of mixtures of aromatic compounds to obtain a better understanding of coal tar hydrogenation reactions. The following results were obtained:

(1) High pressure hydrogenation of anthracene over a nickel catalyst was accelerated by mixing with benzene, whereas, conversion of the latter was retarded.

(2) The effect of cyclo-hexane on the hydrogenation of anthracene was similar to that of benzene.

I. INTRODUCTION

These studies on the hydrogenation of mixtures of aromatic compounds, especially benzene and anthracene, which are two important components of coal tar, were made from January, 1940 to June, 1941.

II. DETAILED DESCRIPTION

A. Feed Stocks

1. Anthracene. An extra-pure commercial anthracene was treated with acid clay and recrystallized with alcohol and benzene. The melting point of the final product was 214-216°C.

2. Benzene. A fraction of an extra-pure commercial benzene, boiling at 79.5°C, was washed with 80% concentrated sulphuric acid and 10% concentrated caustic soda solution. The fraction of this refined distillate boiling from 80°C. to 80.3°C. was further washed with a solution of mercuric oxide and sulphuric acid, then with 10% caustic soda solution and distilled water, dried with calcium chloride, redistilled and dehydrated over metallic sodium. Properties were as follows:

Boiling point .... 80.2°C.

Density (20/4) 0.8793

Refractive index (n_D^{20}).......... 1.4986

3. Cyclo-hexane. The product of refined benzene, hydrogenated at 200°C. over a nickel catalyst, was washed with 98% concentrated sulphuric acid, 10% concentrated caustic soda solution, and distilled water, dried with calcium chloride, redistilled and dehydrated over metallic sodium. Properties were as follows:

Boiling point .... 80.5°C.

Density (20/4) 0.7780

Refractive index (n_D^{20})..... 1.4230

4. Hydrogen. Hydrogen gas was produced by electrolysis of water with a purity over 99.5%.

5. **Catalyst.** An extra-pure metallic nickel was dissolved in concentrated nitric acid and, after filtering off impurities, this solution was diluted and neutralized with ammonia. The precipitated nickel hydroxide was washed with distilled water, dried and powdered. This catalyst was oxydized and reduced at 280-290°C. before using.

B. **Apparatus.** A shaking type autoclave was used with the following characteristics:

Inner volume	625 c.c.
Material	Ni-Cr-steel.
Heating	Outside, electric.
Frequency of vibration	60-70/min.

C. Experimental Procedure

The autoclave, including the sample and catalyst, was pressured with hydrogen to the 100 atmospheres, and heated to the required temperature at a rate of 2°C/min.

After holding at the reaction temperature for one hour, heating was stopped, but the shaking was continued until the temperature fell below 200°C. After cooling for one day, the pressure and the temperature were measured and the gas was released. The liquid product was separated by distillation into a benzene-cyclohexane cut and an anthracene-hydroanthracene cut. The benzene yield was determined by the density and the refractive index of the first cut.

The latter cut was analyzed by recrystallization with alcohol and each compound was determined by appearance, melting point, properties of picrate and ultimate analysis.

D. Hydrogenation of Benzene

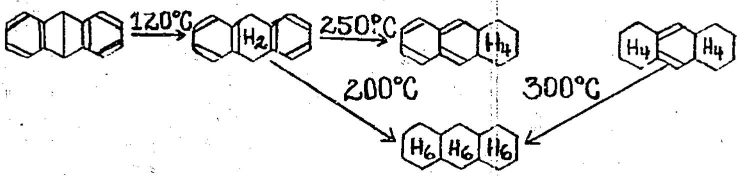
It is well known, that the reduction of benzene to cyclohexane in the presence of reduced nickel catalyst starts at 70°C. and is accelerated by increased temperature, up to 300°C. Over 300°C., cyclohexane is dehydrogenated again to benzene.

The author hydrogenated benzene at several temperatures under high pressure hydrogen in the presence of reduced nickel catalyst and obtained the yields summerized in Table I(B)14.

The content of saturated hydrocarbons in the produced gas was 2.5%. The change of reaction velocity with temperature, as indicated by change of pressure with time, dp/dt, was as shown in Table II(B)14. (Also refer to Figures 1(B)14 through 3(B)14.)

E. Hydrogenation of Anthracene

Dr. YOKOTA reported, that by hydrogenation of anthracene, the dihydrocompound was produced first, and this compound changed, on one hand, directly to the perhydro-compound and, on the other hand, the tetrahydrocompound, octahydro-compound, and finally to the perhydro-compound:



ENCLOSURE (B)14

The author hydrogenated anthracene in the presence of reduced nickel catalyst under high pressure and the results are summarized in Table III(B)14.

At 180-200°C a small amount of tetrahydro-compound was produced. Above 217°C, the melting temperature of this compound, the hydrogenation was accelerated and the tetrahydro-compound was hydrogenated to octa- or perhydro-compounds.

The maximum rates of pressure change were as shown in Table IV(B)14. (Also refer to Figures 2(B)14 and 3(B)14.)

F. Hydrogenation of a Mixture of Benzene and Anthracene

1. Hydrogenation of a mixture of 1 part benzene and 1 part anthracene.

At a temperature of 140°C, the reaction of a mixture of 1 part benzene and 1 part anthracene began at 70°C after 35 minutes, and dp/dt reached the maximum value of 1 kg/min after 1 hour (refer to Figure 1(B)14).

After this, only a slow reaction occurred. This showed, that for the first hour, only the hydrogenation of benzene took place and after one hour, anthracene was converted.

At a reaction temperature of 200°C, the maximum value of dp/dt, 0.7 kg/min, was reached after one hour. Afterwards, a slow reaction took place and the value of dp/dt was 0.3 kg/min after 1 hr. 45 min., and 0.6 kg/min after 2 hrs. 20 min. (refer to Figure 2(B)14). This indicated, that after 1 hr. 45 min., the hydrogenation of anthracene began.

At a reaction temperature of 260°C, the maximum point dp/dt at 1 hour was due to the hydrogenation of benzene and the maximum of 3.6 kg/min at 1 hr. 45 min. was due to hydrogenation of the anthracene.

The amount of cyclohexane produced by hydrogenation of benzene decreased from 7%, at 80°C, to 2%, at 140°C, and afterwards, increased to 34%, at 230°C. On the contrary, the hydrogenation of anthracene was much accelerated; the reaction began at 100°C, and 12.5% of tetrahydro-compounds was produced at 140°C, (the temperature giving minimum amount of cyclohexane), and at 180°C, half of the anthracene was converted. The conversion was much improved over the hydrogenation of anthracene alone, and the lowering of reaction temperature, equivalent to about 60°C, resulted from the addition of the benzene. It is interesting to note that the hydrogenation of benzene began at 200°C, at which temperature the conversion of anthracene was 95%. Refer to Tables V(B)14 and VI(B)14 and Figure 4(B)14.

It is concluded from these results that the following held true:

a. Benzene was first hydrogenated at temperatures below 100°C.

b. In the range of temperature from 100°C to 200°C, the hydrogenation of benzene was retarded, and the hydrogenation of anthracene was accelerated.

c. Over 200°C, benzene was freed from restraint of the anthracene and was converted to cyclohexane. At these temperatures, however, dehydrogenation of cyclohexane also took place and the benzene-cyclohexane equilibrium concentration ratio was about 1:1.

2. Hydrogenation of a mixture of 1 part of benzene and 2 parts anthracene:

The results of hydrogenation tests on a mixture of 1 part benzene and 2 parts anthracene are given in Table VII(B)14 and Figures 1(B)14 through 3(B)14. The hydrogenation of anthracene began at 140°C and its conversion was 50% at 200°C and 100% at 230°C. The conversion of benzene was higher than in the preceding experiment, amounting to 24% at 80°C, and it did not increase until the hydrogenation of anthracene was completed. This experiment also showed, that the hydrogenation of anthracene was accelerated by the presence of benzene and the hydrogenation of benzene took place after the former reaction was finished.

G. Hydrogenation of a Mixture of Anthracene and Cyclohexane

The author hydrogenated a mixture of equal parts of anthracene and cyclohexane at temperatures of 180°C, 200°C and 230°C. The results, summarized in Table VIII(B)14, showed that the hydrogenation of anthracene in this mixture was similar to its reaction in a mixture with benzene. No conversion of cyclohexane was observed.

From these results it was concluded, that the effects of benzene and cyclohexane on the hydrogenation of anthracene was similar.

III. CONCLUSIONS

The following conclusions were drawn with regard to the high-pressure hydrogenation of benzene and anthracene in the presence of a reduced nickel catalyst:

1. The hydrogenation of anthracene was accelerated by the existence of benzene, and the hydrogenation of the latter was retarded, taking place after the hydrogenation of anthracene was completed.

2. The effect of cyclohexane on the hydrogenation of anthracene was similar to that of benzene.

3. The results are of significance in connection with the hydrogenation of mixtures of aromatic compounds, such as coal-tar, and they give a suggestion as to methods for controlling reactions.

ENCLOSURE (B)14

Table I(B)14
HYDROGENATION OF BENZENE

Reaction temp.	Yield of cyclohexane
140°C	50 wt %
200°C	100 wt %
260°C	94 wt %

Table II(B)14
RELATIONSHIP BETWEEN REACTION RATE AND TIME (BENZENE)

Max. value of dp.dt.	Reaction temp.	Reaction time.
1.4 kg/min	140°C	1 hr. 20 min
3.1 kg/min	200°C	1 hr. 15 min
1.4 kg/min	260°C	1 hr. 50 min

Table III(B)14
HYDROGENATION OF ANTHRACENE

React. temp. (°C.)	Conversion (%)	Amount of hydrogenated product (% by wt.)			
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.
180°	5.1	0	5.1	0	0
200°	10.6	0	10.6	0	0
230°	100.	0	0	86.8	13.2
260°	100.	0	0	76.3	23.7

Table IV(B)14
RELATIONSHIP BETWEEN REACTION RATE AND TIME (ANTHRACENE)

Max. value of dp/dt.	React. temp.	Time of progress
0.3 kg/min	200°C	55 min.
1.4 kg/min	260°C	115 min

Table V(B)14
HYDROGENATION OF MIXTURE OF BENZENE AND ANTHRACENE (1:1)

Reaction Temp. (°C)	Conversion of Anthracene %	Yield of Products from Anthracene(%byWt)				Conversion of Benzene (% by Wt)
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.	
80	0	0	0	0	0	6.8
100	0.6	0	0.6	0	0	2.9
120	6.8	0	6.8	0	0	3.4
140	12.5	0	12.5	0	0	2.1
160	39.3	2.0	37.3	0	0	2.4
180	46.7	3.1	43.6	0	0	3.9
200	95.0	15.4	79.6	0	0	8.0
230	100	0	0	87.3	12.7	33.5
260	100	0	0	83.4	16.6	49.9
300	100	0	0	64.1	35.9	50.8

Table VI(B)14
PROPERTIES OF GAS PRODUCED BY HYDROGENATION OF MIXTURE OF BENZENE AND ANTHRACENE (1:1)

Reaction Temp.	Yield (%)		
(°C)	C_nH_{2n}	C_nH_{2n+2}	n
230	0.3	0	-
260	0.6	3.3	1.3
300	0.4	2.0	1.8

ENCLOSURE (B)14

Table VII(B)14
HYDROGENATION OF MIXTURE OF BENZENE AND ANTHRACENE (1:2)

Reaction Temp. (°C)	Conversion of Anthracene %	Yield of Products from Anthracene(%byWt				Conversion of Benzene (% by Wt)
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.	
80	0	0	0	0	0	24.0
100	0	0	0	0	0	30.6
120	0	0	0	0	0	24.3
140	0.4	0	0.4	0	0	23.8
160	6.0	0	6.0	0	0	26.5
180	7.7	2.5	5.2	0	0	28.9
200	52.9	14.9	38.0	0	0	32.9
230	100	8.8	64.2	22.8	4.2	50.4
260	100	0	0	78.0	22.0	86.7
300	100	0	0	62.7	37.3	86.4

Table VIII(B)14
HYDROGENATION OF A MIXTURE OF ANTHRACENE AND CYCLOHEXANE (1:1)*

Reaction Temp. (°C)	Conversion of Anthracene (%)	Yield of Products from Anthracene (% by wt)			
		Dihydro Compd.	Tetrahydro Compd.	Octahydro Compd.	Perhydro Compd.
160	32.8	0	32.8	0	0
200	100	3.8	87.1	9.1	0
230	100	0	0	82.6	97.4

*No conversion of cyclohexane

ENCLOSURE (B)14

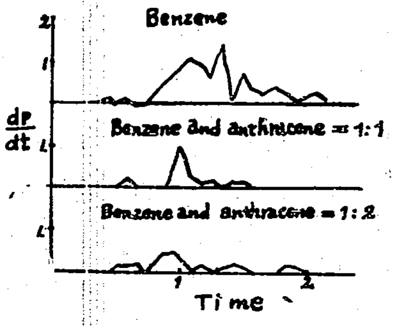


Figure 1(B)14
RELATION OF $\frac{dp}{dt}$ AND TIME IN THE HYDROGENATION AT 140°C

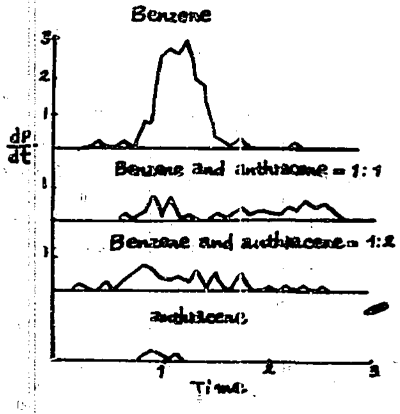


Figure 2(B)14
HYDROGENATION AT 200°C

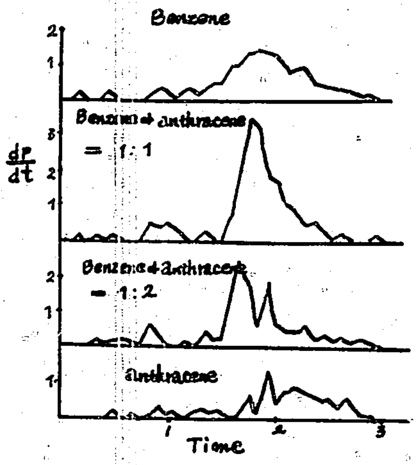


Figure 3(B)14
HYDROGENATION AT 260°C

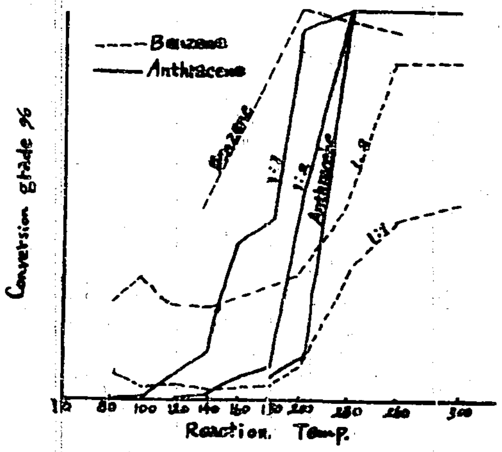


Figure 4(B)14
REACTION TEMPERATURE CONVERSION GRADE RELATION IN THE HYDROGENATION OF BENZENE, ANTHRACENE AND THEIR MIXTURE

ENCLOSURE (B) 15

STUDIES ON THE PROPERTIES OF TAR FROM COAL HYDROGENATION

by

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NAV. ENG. K. MITSUI

Research Period: 1949-1940

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

December 1945

ENCLOSURE (B)15

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)15

SUMMARY

The tar from the South Manchurian Railway Co. coal hydrogenation works at FUSHUN was investigated to determine the properties and composition of its light oil (boiling up to 220°C) and heavy oil (boiling 220-280°C).

The crude tar contained 20-30% of phenolic substances which were mostly in the fractions boiling from 165 to 245°C. The chemical constituents in the neutral oils from the light and heavy oils were as shown in Table I(B)15

Aviation gasolines were prepared by two methods from the neutral light oil; (1) by distillation and (2) by hydrogenation and distillation.

The properties of these two aviation gasolines were as shown in Table II(B)15.

The gasoline made by hydrogenation of the neutral oil was far superior to that obtained by straight distillation.

A number of pure hydrocarbons were identified in the crude tar, acidic fractions of the crude tar, and aviation gasoline from hydrogenated oil.

I. INTRODUCTION

The present investigation was made to determine (1) the quality of gasoline obtained by hydrogenation of coal, and (2) to obtain data on hydrocarbon composition which might be useful in improving the process.

The work was started in 1939 and completed in 1940. The key research personnel were Comdr. T. YOKOTA and Nav. Eng. K. MITSUI.

II. DETAILED DESCRIPTION

A. Crude Tar and Neutral Oil.

The crude hydrogenated tar was obtained from the South Manchurian Railway Co. plant at FUSHUN. At this plant, OYAMA coal was hydrogenated over an Fe_2O_3 catalyst at 410°C and 200 atmospheres. This tar had a deep brownish color, which gradually became darker on standing in air. Some solid matter was held in suspension. The crude tar and neutral oil obtained by dephenolating the crude tar with 10% caustic soda solution, were distilled and the results are given in Table III(B)15.

It can be seen from the table that the acidic oil is contained in the fractions boiling above 200°C.

B. Light and Heavy Oils From Crude Tar.

Light and heavy oil fractions, obtained by fractionation of the crude tar were analyzed for hydrocarbon composition by the usual methods, and the results are given in Table IV(B)15.

C. Neutral Oil From Crude Tar

Neutral oil from crude tar was dried with anhydrous sodium sulphate, distilled carefully, and the composition and property of each fraction determined. The results are given in Table V(B)15.

The lighter neutral oil fractions were rich in naphthenic compounds, whereas the heavier fractions were rich in aromatics.

Next, these fractions were studied to determine naphthenic and aromatic compounds present, and various compounds were isolated. The amount of these compounds present was not determined. The results are shown below.

Fraction	Compounds Isolated In Neutral Oil.
1	Benzene, Methyl-cyclopenthane.
2	Toluene, Cyclohexane, Methyl-cyclohexane.
3	o,m,p--Xylenes.
4	Mesitylene
5	Tetralin, Di-hydro-naphthalene.
6	Naphthalene, Hydro-naphthalene (?).
7	a,b--Methylnaphthalenes.
8	a,b--Methylnaphthalenes.
9	b,b'-Dimethylnaphthalene.
10	b,b'-Dimethylnaphthalene.

D. Acidic components in crude tar

Crude tar was fractionated into 21 cuts, and the phenolic content of each fraction was determined by treatment with 10% NaOH. The results are shown in Table VI(B)15.

The acidic components were mostly contained are in the fractions boiling from 165-245°C.

To confirm this, the caustic-soluble fraction obtained in the preparation of neutral oil was treated with 10% HCl to produce free acidic oil. The acidic oil was fractionated as follows:

Fraction	Vol. %
i.p. -215°C	21
215-225	33
225-235	19
235-245	12
245-255	8
255-265	4
265-275	4

The above fractions were each redistilled and the resulting cuts recombined to give close boiling range fractions. From ultimate analyses and molecular weight determinations, the components were identified as shown below.

Fraction	Constituent
195-200°C	o,m,p,-Cresols: C_7H_9O
200-205	
206-215	Xylenols: $C_8H_{11}O$
214-221	
221-228	
230-240	Phenols: $C_9H_{12}O$
240-245	Phenols: $C_{10}H_{13}O$
245-248	

E. Aviation Gasoline

1. An aviation gasoline was prepared from neutral light oil by distillation and final treatment with 10% caustic soda solution. The properties of the gasoline are given in Figure 1(B)15 and listed below.

Unsaturates	5.3
Aromatics	24.2
Naphthenes	39.3
Paraffins	31.2
Sulphur (wt %)	0.15
Octane no.	69
Clear with 0.1% lead	82

2. An aviation gasoline was also prepared from neutral gas oil (boiling range of 200-230°, d^{15}_{15} = 0.879), which was hydrogenated over Ni_2O_3, MoO_3 clay catalyst, (wt. ratio of 1:2:3), at 450°C under 270 atm. pressure of hydrogen and S. V. of about 2. The yield of hydrogenated oil was 88% by weight.

The hydrogenated oil (44-263°C) was fractionated and the results compared with the original gas oil sample (Table VII(B)15.

Aviation gasoline with properties shown below was prepared with a yield of 26% by fractionation of the hydrogenated oil.

Density (20/4 °C)	0.7348
Solid Point (°C)	-50
Vapor Press (kg/cm²)	0.427
Gummy Matter (mg/100cc)	4.6
Sulphuric Acid Absorption (%)	0.5
Content of C. (wt %)	86.04
Content of H. (wt %)	13.87
Content of S (wt %)	0.01
Engler Distillation (Vol. %)	
I.B.P.b	51.0°C
10%	64.5°C
20%	71.0°C

The hydrogenated aviation gasoline was fractionated into 8 cuts, and the octane number of each cut determined (Table VIII(B)15).

The hydrogenated aviation gasoline was closely fractionated in a podbialniak still, and the following compounds were isolated from each cut.

Fraction (°C)	Compound
I.P. - 30	n-Butane, iso-Pentane, n-Pentane.
45 - 50	n-Pentane, Cycloptane, Neohexane, 2-Methyl-pentane.
70 - 75	n-Hexane, Methyl-cyclo-pentane, Benzene, Cyclo-hexane.
75 - 81	2,2-Dimethyl-pentane, Benzene, Cyclohexane. 2,4-Dimethyl-pentane, 3,3-Dimethyl-pentane.
98 - 101	n-Heptane.
101 - 111	Toluene

III. CONCLUSIONS

Tar prepared by the hydrogenation of coal, was obtained in yield of 77 % on ash-free coal. It consisted of 26% acidic, 4% basic and unsaturated, and 67% neutral substances. The neutral part of the tar was composed of 31% paraffins, 15% naphthenes and 54% aromatic compounds. The acidic compounds were mostly contained in the crude light oil fraction.

The crude heavy oil, used for making paste with coal, which boiled from 220 to 280°C, was composed of 28% paraffins and 36% aromatics.

The aviation gasoline derived from the hydrogenated neutral light oil, showed an octane value of 90 with 0.1% lead.

Table I(B)15
COMPOSITION OF OILS

	Aromatics	Naphthenes	Paraffins
Light Neutral Oil	43	4	49
Heavy Neutral Oil	60		36

Table II(B)15
COMPOSITION AND OCTANE NUMBER OF THE GASOLINES

	Component			Octane Value	
	Aromatics	Naphthenes	Paraffins	Clear	0.1% Lead
Neutral Oil Distillation	24	39	31	69	82
Hydrogenated Neutral Oil	14	38	48	73.8	90.5

ENCLOSURE (B)15

Table III(B)15
DISTILLATION OF CRUDE TAR AND NEUTRAL OIL

Engler Distillation	Crude Tar (A)	Neutral Oil (B)	A -
~ 105°C		0.1 Vol.%	
105 ~ 115	0.4 Vol.%	0.2	0.2
115 ~ 125	0.6	0.2	0.4
125 ~ 135	0.7	0.5	0.2
135 ~ 145	0.8	0.7	0.1
145 ~ 155	1.1	1.0	0.1
155 ~ 165	1.4	1.5	-0.1
165 ~ 175	2.3	2.0	0.3
175 ~ 185	3.5	2.7	0.8
185 ~ 195	5.0	3.5	1.5
195 ~ 205	7.6	4.9	2.7
205 ~ 215	11.0	7.3	3.7
215 ~ 225	14.0	8.4	5.4
225 ~ 235	16.2	11.7	3.5
235 ~ 245	19.5	13.8	5.7
245 ~ 255	22.8	17.5	5.3
255 ~ 265	27.8	22.3	5.5
265 ~ 275	32.3	24.5	7.8
275 ~ 285	37.2	28.5	8.3
285 ~ 295		32.0	
295 ~ 300		35.0	

ENCLOSURE (B)15

Table IV(B)15
PROPERTIES OF CRUDE TAR FRACTIONS

	Light Oil	Heavy Oil
Boiling Range (°C)	below 220°C	220-280°C
Specific Gravity d^{15}_{15}	0.875	0.949
Acidic Substances (Vol.%)	26.0	27.0
Yield from Tar (Vol.%)	14	23
Base Unsat. (Vol.%)	7.5	10.3
Paraffins (VOl.%)	28.3	18.2
Naphthenes (Vol. %)	8.9	8.4
Aromatics (Vol. %)	29.3	36.1
Water (Vol. %)		0.3
Flashpoint (°C)		115
Viscosity (Red. 1) 40°C		12.6
Conradson's Carbon (wt. %)		0.73
Net Heat of Combustion (Cal/gr.)		10.269

Table V(B)15
PROPERTIES OF NEUTRAL OIL

Fraction	d^{20}_{4}	n^{25}_{D}	Composition			
			Unsats.	Arometics.	Naph.	Paraff.
75 - 85°C	0.745	1.414	15	8	55	22
95 - 105	759	425	14	15	45	26
115 - 125	781	432	13	25	29	29
135 - 145	808	454	8	35	18	38
155 - 165	815	461	6	43	10	40
175 - 185	840	474	4	48	7	41
195 - 205	865	490	4	53	1	42
215 - 225	876	495	3	56		40
235 - 245	896	510	3	59		48
255 - 265	918	523	5	60		35
275 - 285	927	528	4	60		34

ENCLOSURE (B)15

Table VI(B)15
PHENOLIC CONTENT OF CRUDE TAR FRACTIONS

Fraction	Yield (Vol.%)	Phenolic Content (Vol. %)
-75°C	2.3	
75-85	0.6	
85-95	0.8	
95-105	1.5	0.2
105-115	1.7	0.2
115-125	1.5	0.3
125-135	1.7	0.4
135-145	2.4	0.9
145-155	2.4	2.3
155-165	2.9	3.9
165-175	3.3	6.0
175-185	2.6	5.8
185-195	3.3	8.0
195-205	6.1	15.7
205-215	8.7	19.3
215-225	8.3	13.2
225-235	8.7	9.2
235-245	9.8	6.0
245-255	10.0	3.8
255-265	9.9	2.7
265-275	11.5	1.9

Table VII(B)15
COMPARISON OF CHARGE AND HYDROGENATED PRODUCT

Boiling Point (°C)	Neutral Gas Oil (Vol.%)	Hydrogenated Oil (%)
60		0.7
70		1.4
80		3.0
90		3.0
100		4.6
110		6.5
120		9.0
130		11.0
140		13.0
150		15.0
160		18.0
170		21.5
180		26.0
190	0.4	32.0
200	5.2	40.0
210	41.0	71.0
220	78.5	86.0
230	91.5	93.0
240	96.0	95.5
250	98.5	96.5
260		97.0

ENCLOSURE (B)15

Table VIII(B)15
OCTANE NUMBER OF HYDROGENATED AVIATION GASOLINE CUTS

Fraction (°C)	Octane Number	
	Clear	With 0.1% Lead
I.P.- 60	78.2	101.3
60- 70	72.4	92.1
70- 80	73.9	91.4
80- 90	73.1	89.6
90-100	69.2	86.3
100-110	72.1	87.7
110-120	68.8	85.4
120-130	63.5	81.5
30%	77.5	
40%	83.0	
50%	89.0	
60%	95.5	
70%	103.5	
80%	114.5	
90%	135.0	
Dry pt.	177.5	
Components (Vol.%)		
Unsaturates	1.0	
Aromatics	13.8	
Naphthenes	37.8	
Paraffines	47.7	
Octane Number	Clear	74
	0.1% Leaded	91

ENCLOSURE (B)15

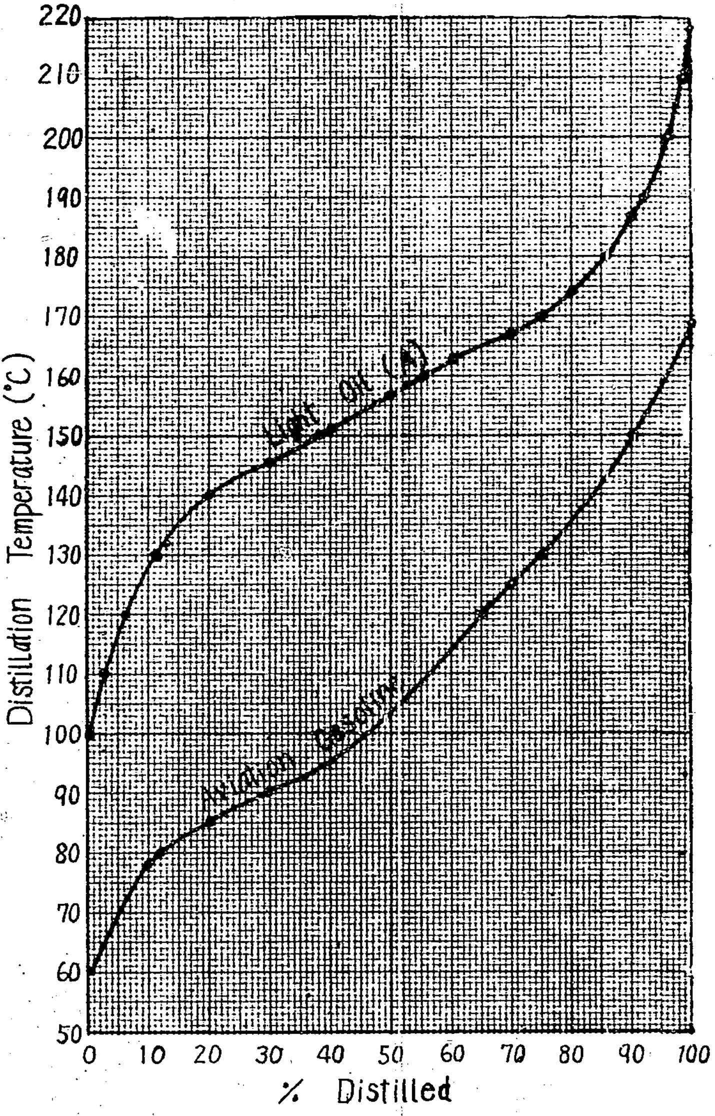

Figure 1(B)15
DISTILLATION CURVE OF GASOLINE

ENCLOSURE (B) 16

STUDIES ON THE HYDROGENATION OF COAL. THE MECHANISM OF COAL HYDROGENATION

Reference NavTechJap Document No. ND 26-0008.19, ATIS No. 4579

by

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Research Period: 1937-1938

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

December 1945

ENCLOSURE (B)16

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)16

SUMMARY

These experiments were made in a specially designed autoclave to study in more detail the chemical changes occuring during the hydrogenation of coal. On the basis of experimental results, conclusions are drawn as to the reaction mechanism.

I. DETAILED DESCRIPTION

A. Apparatus

The autoclave used for these experiments was an electrically-heated rotating type made of V 2 A-steel, with a capacity of 2.4 liters. Two thermocouples were used, one of which served to measure the inner temperature of the autoclave, and the other to measure the wall temperature of the autoclave as shown in Figure 1(B)16.

Both temperatures were measured on a recording pyrometer. Twenty steel balls, with a diameter of 20mm, were put in the autoclave to agitate the contents. The autoclave was rotated within an electric heater at the rate of 42 RPM.

B. Sample

Fushun Oyama coal, with the properties given below and in Table III(B)15 was used for these experiments. After crushing to below 60 mesh, it was stored in a constant humidifier (using $CaCl_2$ solution, 1.30 sp. gr.). 150 grams of coal were used in each experiment and 5% (by wt) of $ZnCl_2$ catalyst was added. The hydrogen was prepared by electrolysis.

Proximate Analysis of Coal (wt %)

Water	5.5	Ash	7.0
Volatile Matter......	41.1	Calorific value (cal/g)	7,200
Fixed Carbon	46.4		

C. Test Procedure

After the sample and steel balls were put in the autoclave, air was displaced and hydrogen was added to the desired pressure. The temperatures were recorded every minute by the pyrometer and the pressure was measured every five minutes. The heating rate of the autoclave was controlled to 2.75°C/min. When the inner temperature reached the desired level, heating was stopped and the upper half of the electric heater was removed. The rotation of the autoclave was continued until the outer temperature had dropped to 100°C. Accordingly, the outer temperature showed a smooth curve, but the inner temperature showed the change due to reaction heat. After cooling, the gas was released and the reaction products were taken out. The small amount of products remaining in the autoclave were washed out with benzene. The greater part of the liquid and solid products was topped at 180°C and the water and oil distilled over were measured. After cooling the distillation residue was separated into two portions; benzene soluble and insoluble. The benzene soluble portion, after distilling off benzene, was fractionated in an Engler flask. The portion insoluble in benzene was vacuum dried for several hours, until benzene was removed completely, and was weighed. The gas was analyzed by Hempel's method.

D. Experimental results

Each experiment was carried out using the same starting conditions and the same heating rate, but different maximum inner temperatures of 100°C, 200°C, 300°C, 325°C, 350°C, 360°C, 380°C. 425°C and 450°C. The experimental results are given in Table I(B)16 and Table II(B)16 and a typical temperature-pressure curve is shown by Figure 2(B)16.

Analyses of the solid matter remaining in the autoclave for experiments below 300°C are shown in Table III(B)16.

Results of analyses of the oil produced are given in Table IV(B)16.

A plot showing production of gas constituents is given by Figure 3(B)16.

C_nH_{2n+2} showed the greatest change, first appearing at 390°C and increasing rapidly. The waste gas at 450°C inner temperature was passed through active charcoal and the gaseous hydrocarbons absorbed were fractionated in a Podbielniak apparatus. The results are given below

Analysis of Light Hydrocarbons (vol %)
(450° Reaction Temperature)

C_1	58.9
C_2	18.0
C_3	15.1
C_4	8.0

The data in Tables III(B)16 and IV(B)16 were plotted in Figure 4(B)16.

As shown by Figure 4(B)16 if the main component of the sample coal is $C_nH_mO_x$, the substance having a composition of C=73.2, H=5.7, O=12.0 is changed by the hydrogenation and heat decomposition into unsaturated hydrocarbons having a composition C_nH_{2m-x}. Until about 340°C, the H/C in Figure 4(B)16 shows little change from the original coal, but between 340 and 390°C, the oil formation reactions began and continued to 450°C.

As shown on Figure 4(B)16 deoxygenation started at about 120°C, proceeded slowly until 340°C, become very rapid between 340 and 400°C, and then slowed down again. Figure 3(B)16 indicates that below 340°C the deoxygenation occurred by the elimination of CO_2. It is presumed that the CO_2 was produced when COOH groups in the resinous matter, and the uncharged vegetable matter in the coal were decomposed by heat. The formation of CO above 340°C indicated that deoxygenation next occured due to break down of ketones, aldehydes and cyclic bindings, and the molecular weight decreased rapidly due to collapse of the higher molecules. Further, the existence of the more stable oxygen bonds was indicated from the fact that the deoxygenation did not progress so rapidly at the higher temperature. It can be presumed, from the existence of the phenolic oil in the product, that the OH radical is most stable. The formation of CH_4 and slow increase of CO and CO_2 at higher temperature indicated the decomposition of the cyclic compounds, and the hydrogenation of CO and CO_2 to methane.

ENCLOSURE (B)16

II. CONCLUSIONS

1. From the preceding, it is concluded that the decomposition of COOH groups starts at about 120°C, as indicated by formation of CO_2. On the basis of water formation and the temperature gradients, it is known that the hydrogenation began at about 250°C. At this temperature, the coal powder began sticking to the wall of the autoclave, and indicating formation of a boundary oil film. deoxygenation become vigorous, a great deal of water was formed, and CO began to appear from 340-350°C due to the decomposition of ketones aldehydes and cyclic bound oxygen compounds.

At 390°C the H/C-ratio changed from that of coal to that of oil.

From the fact that the molecular weight decreased rapidly from above 2000 to about 500 at 390-400°C. it is concluded that the molecules collapsed due to deoxygenation of the polycyclic compounds. It is presumed that the sudden rise of temperature from about 375 to 390°C was the result of the violent evolution of heat due to the deoxygenation. Another rise from about 390 to 430°C was probably due to the heat of reaction from the cracking of hydroaromatic hydrocarbons.

Table I(B)16
EXPERIMENTAL RESULTS

Max. Temp (°C)		Pressure (atm)			Product			
Inner	Outer	Initial	Final	Decrease	Appearance	(Wt% or Coal)		
						Water Content	Solid Matter	Soluble - Benzene
100	120	100	100		Original form	5.9	94.1	
200	228	100	100		Original form	6.6	93.9	
300	340	100	99	1	Original form	8.0	92.0	
325	370	100	95	5	Pitch like	9.3	83.5	7.1
350	390	100	88	12	Pitch like	11.5	50.5	37.4
360	400	100	79.5	20.5	Pitch like	12.7	41.6	44.7
380	442	100	72.2	27.8	Low fluidity	15.2	19.9	56.6
425	450	100	70	30	High fluidity	12.6	17.3	51.4
450	450	100	68	32	Very high fluidity	12.3	17.3	60.3

ENCLOSURE (B)16

TABLE II(B)16
ANALYSIS OF GAS (VOL %)

Max. Inner Temp. (°C)	Gas Analysis					
	CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}	n
100	0.2	0	0	99.6	0	0
200	0.2	0	0	99.7	0	0
300	0.3	0	0.2	99.5	0	0
325	0.3	0.3	0.3	99.0	0	0
350	0.3	0.4	0.3	97.0	2.0	1.0
360	0.4	0.6	0.4	95.9	2.3	1.3
380	0.5	0.6	0.5	94.6	3.2	1.3
425	0.5	0.7	0.6	91.3	5.9	1.3
450	0.7	0.7	0.6	90.2	6.2	1.7

Table III(B)16
ULTIMATE ANALYSIS OF SOLID RESIDUE (%)

Max. Inner Temp(°C)	C	H	N	S	O	H/C
Original Coal	73.2	5.7	1.2	0.5	12.0	0.933
100°C	73.2	5.8	1.2	0.5	11.9	0.950
200°C	73.1	5.8	1.2	0.5	11.7	0.951
300°C	73.2	5.9	1.2	0.5	11.6	0.967

Table IV(B)16
ANALYSIS OF TOTAL OIL PRODUCED

Max. Inner Temp. (°C)	Ultimate Analysis (wt %)						Calorific Value (Cal/gm)	Sp. gr. (20/4 °C)	Molecular Weight Using	
									Diphenyl	Benzene
	C	H	O	N	S	H/C				
350	84.1	8.5	6.3	0.9	0.2	1.21	9178	1.1088	520	463
360	85.8	8.6	4.6	0.9	0.1	1.20	9253	1.0952	467	384
380	86.7	8.7	3.7	0.8	0.1	1.20	9612	1.0534	314	270
425	87.5	8.9	2.8	0.7	0.1	1.22	9636	1.0136	252	222
450	87.8	8.9	2.6	0.6	0.1	1.22	9663	0.9770	223	183

ENCLOSURE (B)16

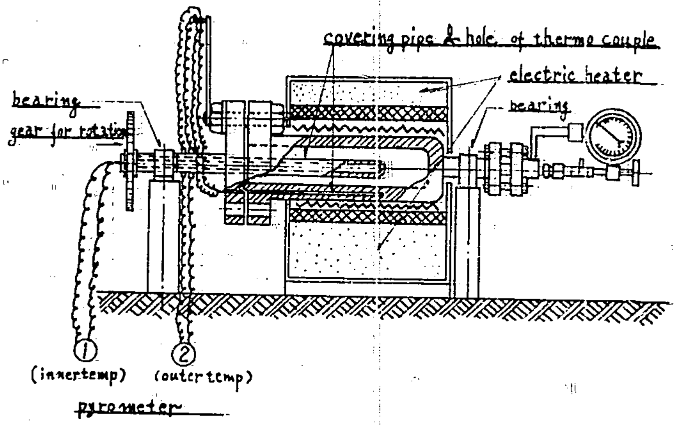

Figure 1(B) 16
DIAGRAM OF AUTOCLAVE

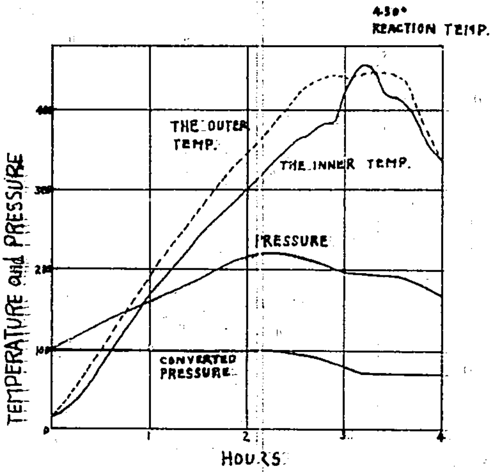

Figure 2(B)16
TEMPERATURE-PRESSURE-TIME CURVES

ENCLOSURE (B)16

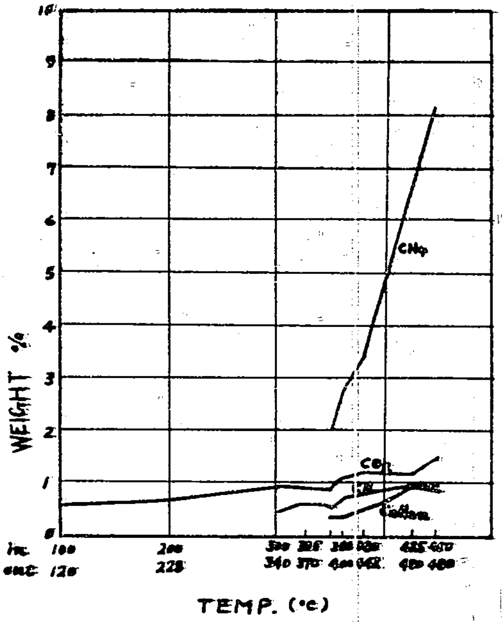

Figure 3(B)16
PRODUCTION OF GAS CONSTITUENTS

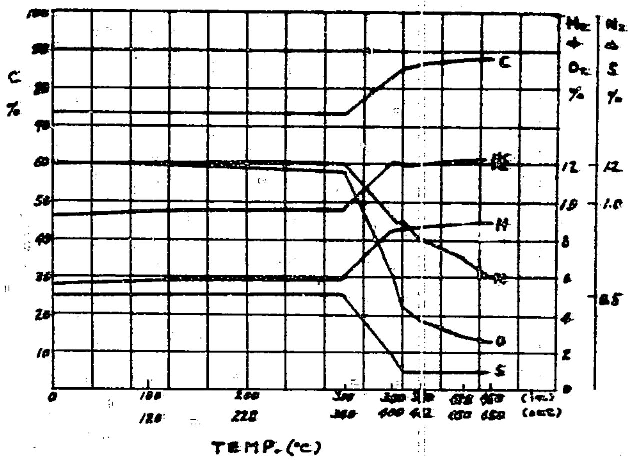

Figure 4(B)16
RESULTS OF ELEMENTAL ANALYSIS

ENCLOSURE (B) 17

COAL HYDROGENATION IN SEMI-COMMERCIAL PILOT PLANT

by

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Research Period: 1938-1939

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

December 1945

ENCLOSURE (B)17

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)17

SUMMARY

Three to three and one-half tons per day of OYAMA coal and NAEBUCHI coal were treated in the semi-commercial hydrogenation pilot plant, and the results were as shown in Table I(B)17.

I. INTRODUCTION

In previous experiments, the hydrogenation of brown coal had been studied in an autoclave and in a small continous pilot plant with a charge capacity of 5 kg of paste per hour.

To obtain data for design and operation of industrial plants, the present experiments in a semi-commercial scale unit were undertaken at TOKUYAMA during the period from August 1938 to October 1939.

II. DETAILED DESCRIPTION

A process flow sheet of the semi-commercial coal hydrogenation unit used in these experiments is given in Plate I(B)17. Photographs of this unit are also enclosed.

Coal was crushed to 20-60 mesh, washed with 3% $ZnCl_2$ solution, and ground to 150 mesh in a tube mill. The powder was then made into a paste, in the tube mill, by mixing with heavy recycle oil (in the ratio 2:3) from the bottom of the high-temperature separator tower.

The paste was heated to 130°C in a heat-exchanger, to 250°C with hydrogen in the pre-heater, and then brought to the final reaction temperature by internal electric heaters in the reaction tower.

The reaction mixture was agitated with recirculated hydrogen. The reaction products were separated in the high-temperature separator into light oil and gas from top, and heavy oil from the bottom. The latter was separated from solid substances by centrifuge, and was recycled to the paste mill.

Coal and paste used in these experiments had the analysis shown in Table II(B)17. The reaction product from the top of the high-temperature separator was composed of gas, tar, and water, and the bottom was a mixture of tar and solid matter, the latter consisting of unchanged coal and ash. Experimental results are summarized in Table III(B)17.

III. CONCLUSIONS

OYAMA coal, from the South Manchuria Railway Co., and NAEBUCHI coal, from the SAKHALIN Artificial Oil Co., were hydrogenated at 410°C under 200 kg/cm^2 of hydrogen, in the presence of a $ZnCl_2$ catalyst.

Five days of continuous smooth operation were made on OYAMA coal, and one day on NAEBUCHI, and fairly good yields of oil were obtained, as follows:

	OYAMA (wt.%)	NAEBUCHI (wt.%)
Liquid yield from coal	77.9	77.0
Hydrogen consumed for coal	7.97	7.4
Yield of light oil (below 180°C)	3.0	4.0
Yield of middle oil (180-280°C)	40.0	40.0
Yield of heavy oil (above 280°C)	53.0	52.0

ENCLOSURE (B)17

Difficulties were encountered during operation in uniform mixing of paste with hydrogen in the reaction tower, and centrifugal separation of the solid residue from the liquid product of the bottom tar.

Table I(B)17
RESULTS OF SEMI-COMMERCIAL HYDROGENATION OF OYAMA AND NAEBUCHI

	OYAMA	NAEBUCHI
Liquefied (wt.%)	77.9	77.0
H_2 consumed / pure coal(wt.%)	7.97	7.4
Tar yield (kg/day)	244	226

Table II(B)17
ANALYSIS OF COAL AND PASTE

		"A"	"B"
Coal		OYAMA	NAEBUCHI
Composition (wt. %)	Water	5.5	6.1
	Ash	7.0	11.5
	Fixed Carbon	46.4	38.1
	Volatile Matter	41.1	44.3
Calorific Value (cal)		7200	6814
Elementary analysis (wt %)	C	73.7	77.19
	H	5.7	6.24
	O (by diff.)	12.0	14.85
	S	0.5	0.37
	N	1.2	1.38
	H/C ratio	0.92	0.98
Paste Composition (wt %)	Carbon	39.2	42.7
	Ash	2.1	2.5
	Oil	51.9	52.3
	Water	6.8	2.5
Oil Used In Paste (wt %) (Distillation Test)	Below 280°C	16.0	
	280 - 320	18.5	
	Above 320	63.9	
	Water	0.7	
Fresh Hydrogen (vol. %)	CO_2	0.0	0.1
	CO	0.4	1.4
	H_2	93.7	91.8
	C_nH_{2n}	0.4	0.7
	C_nH_{2n+2}	1.0	1.0
	n	1.0	1.0

ENCLOSURE (B) 17

Table III(B)17
EXPERIMENTAL RESULTS

		"A"	"B"
Conditions	Length of Run (hr.)	120	28
	Average Reaction Temp.	415°C	410°C
	Average Pressure (kg/cm^2)	200	200
	Fresh H_2 (m^3/hr)	185	162
	Circulated H_2 (m^3/hr)	1000	1000
	Paste (kg/hr)	282	265
	Total Paste (kg)	33,840	7,461
	Temp. of High-Temp. Separator		
	Top	365°C	336°C
	Bottom	375°C	341°C
Yields of Products	Product from Top (kg)	15,825	
	Tar	15,825	2,960
	Water	3,884	490
	Product from Bottom (kg)		
	Tar	16,753	3,800
	Water	67	23
	Solid Residue	1,008	380
Gas Analysis (vol.%)	CO_2	0.5	0.4
	CO	1.3	2.6
	H_2	81.0	79.1
	C_nH_{2n}	1.2	1.0
	C_nH_{2n+2}	10.2	10.8
	n	1.2	1.6
Properties of Light Oil	Density d^{30}_4	0.937	0.924
	Distillation Tests		
	I.B.P.	83°C	78°C
	below 180°C (wt %)	6.6	9.6
	180 - 280	50.0	48.3
	280 - 320	19.9	18.6
	above 320	24.5	21.9
	Water	1.0	1.3
Properties of Heavy Oil	Water	0.4	0.6
	Solid	9.0	10.0
	Distillation Tests		
	below 220°C (wt %)	0.7	2.0
	220 - 280	5.2	6.4
	280 - 320	10.1	13.6
	above 320	74.3	67.1

ENCLOSURE (B)17

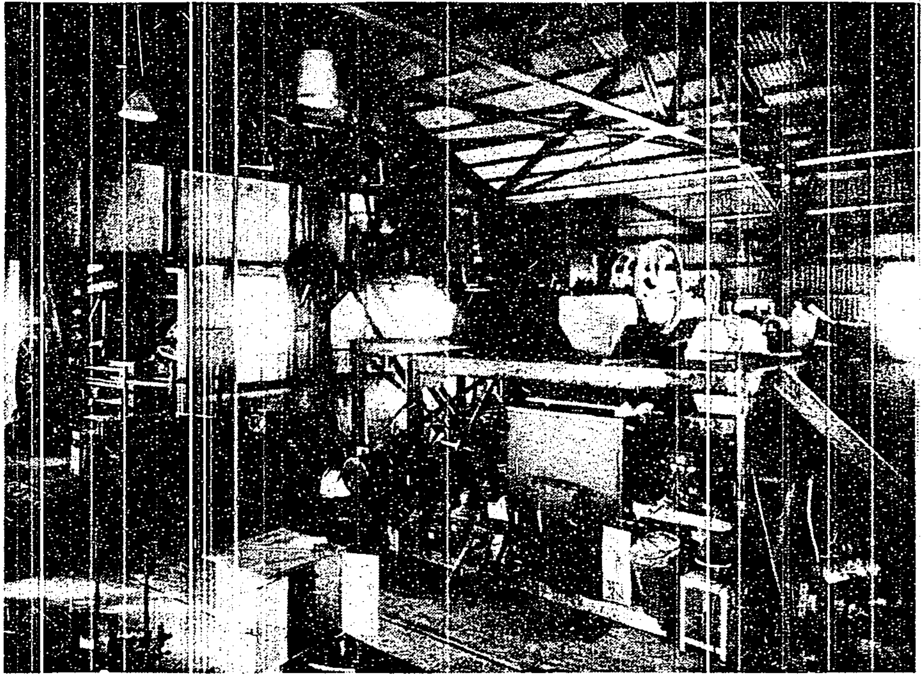


Figure 1(B)17
COAL WASHER

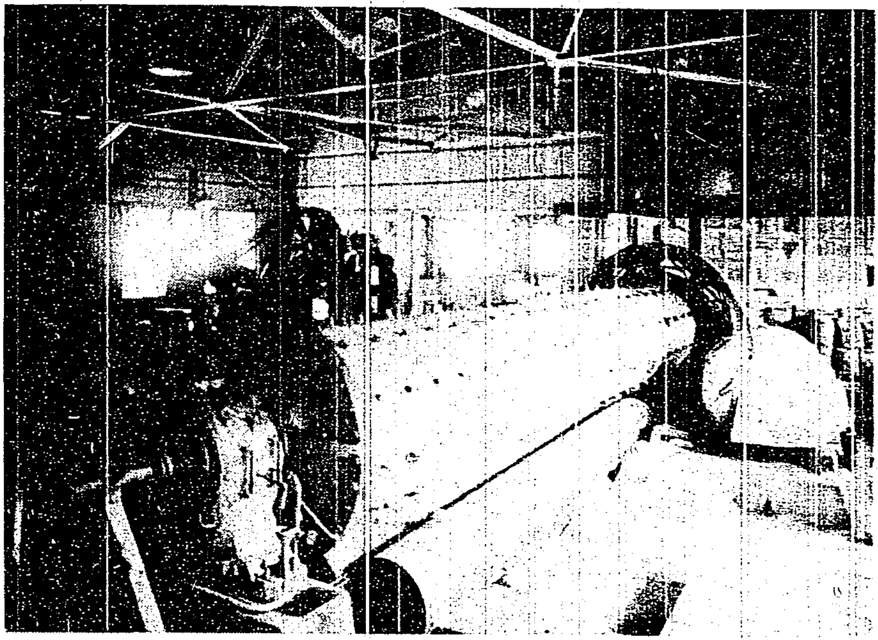
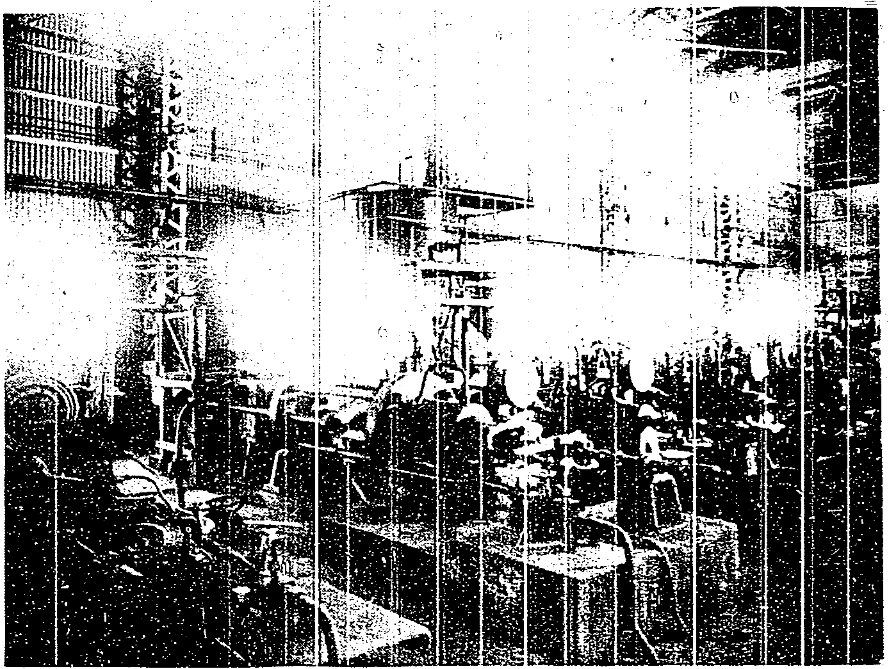


Figure 2(B)17
TUBE MILL FOR PREPARING PASTE

ENCLOSURE (B)17



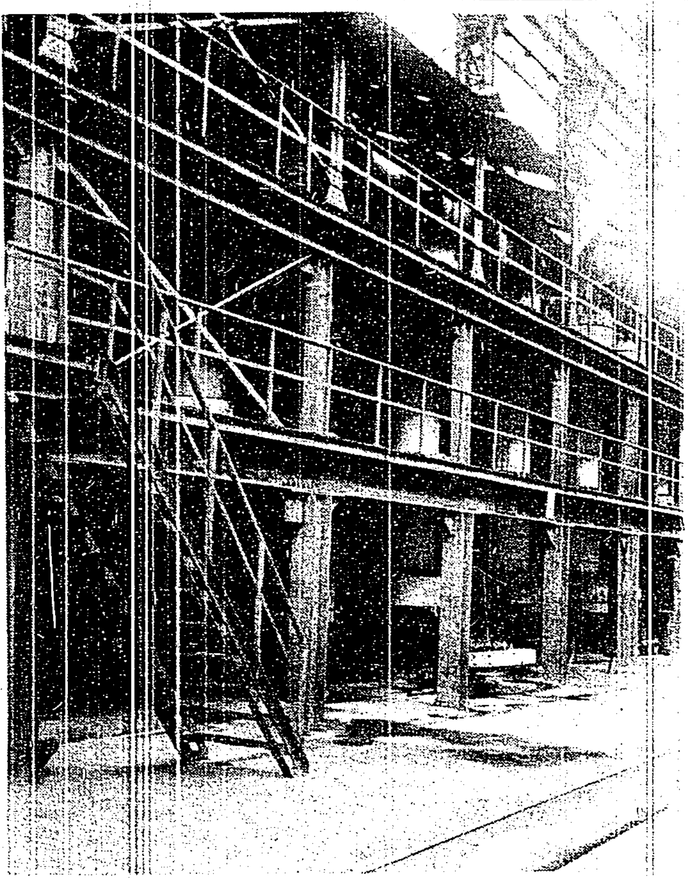


Figure 3(B)17
CONTROLLING PLATFORM
INCLUDING HIGH-PRESSURE
CHARGING PUMP

Figure 4(B)17
REACTION CHAMBER OF
COAL HYDROGENATION

PLATE I(B)17
FLOW CHART OF SEMI COMMERCIAL COAL
HYDRO GENATION PILOT PLANT

(THE 1st. NAVAL FUEL DEPOT)

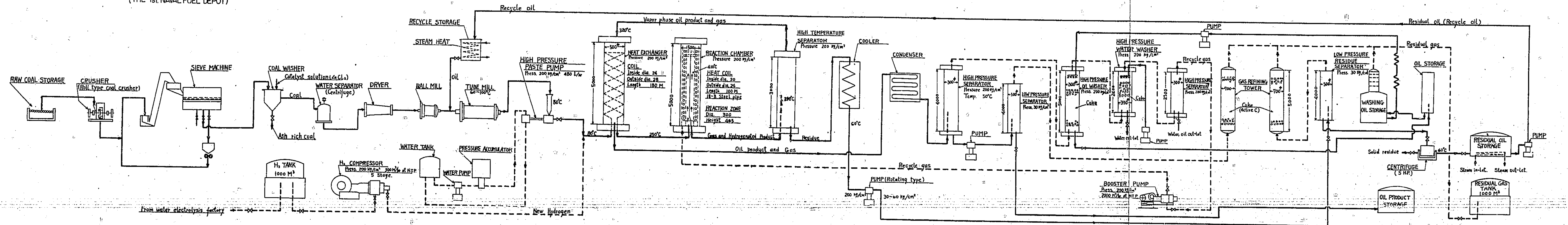


FIG. I

FLOW CHART OF SEMI-
COMMERCIAL COAL HYDRO-
GENATION PILOT PLANT

The 1st Naval Fuel Depot

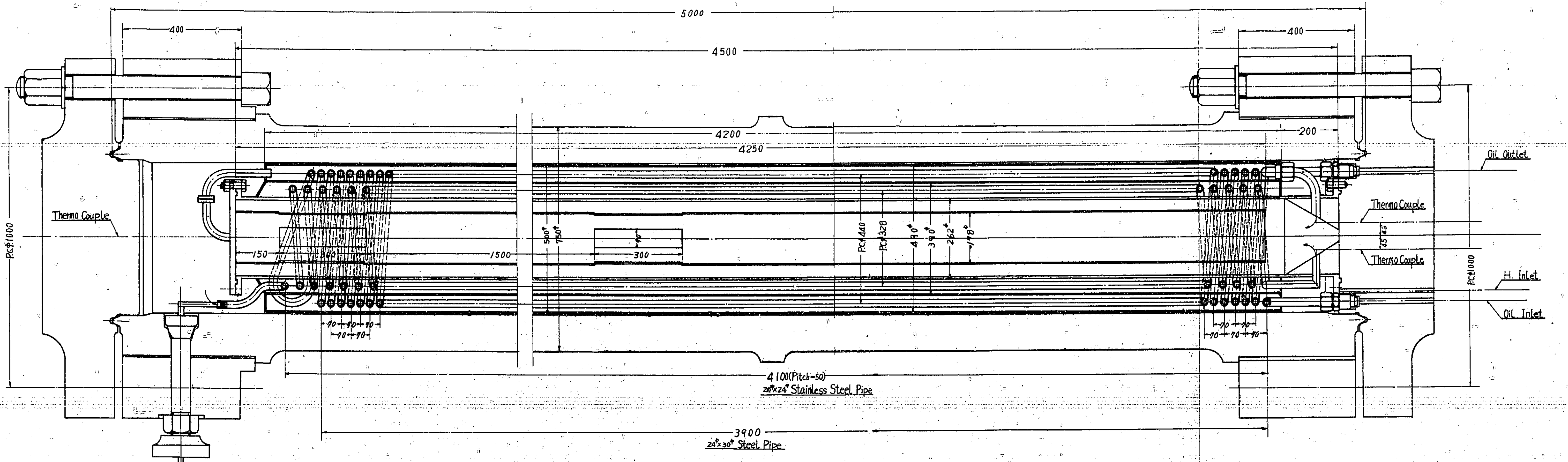
Prepared for
U.S. Naval Technical
Mission to Japan.

Date	Drawn by
18 Dec. 1945	K Sone

PLATE II(B)17

CROSS SECTION OF REACTION CHAMBER OF 07 TYPE EXPERIMENTAL APPARATUS

(TOKUYAMA NAVAL FUEL DEPOT)



TOKUYAMA NAVAL FUEL DEPOT

CROSS SECTION OF REACTION CHAMBER
OF 07 TYPE EXPERIMENTAL APPARARATUS

DEC. 19TH 1940

ENCLOSURE (B) 18

STUDIES ON CATALYSTS FOR COAL HYDROGENATION

by

CHEM. LIEUT. COMDR. K. MITSUI
CHEM. ENGINEER B. OKADA

Research Period: 1937 - 1939

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

December 1945

ENCLOSURE (B)18

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)18

SUMMARY

The catalyst used in the Bergius process, as applied to the hydrogenation of Japanese brown coals, was investigated and a mixed catalyst of the composition Fe_2O_3 : S : $Sn(OH)_2$ (100 : 17 : 1) was found to be the most suitable for the purpose.

I. INTRODUCTION

The catalyst employed in the Bergius process at the Naval Fuel Depot was $ZnCl_2.H_2O$, but owing to difficulties in supply, this investigation for finding a suitable catalyst composed of cheaper substitute materials was undertaken. This project was started in 1940 and completed in 1943.

II. DETAILED DESCRIPTION

A. Materials Used

1. Coal Brown coal from the Agochi district, Korea, was ground to powder of 60 mesh, and showed the following composition:

Water	15.5%	C	68.23%
Ash	8.2%	H	7.35%
V.m.	43.6%	S	0.73%
F.c.	32.7%	N	1.56%
		Ash	9.49%

2. Tar The tar, used to make the paste, was that fraction of dephenolated low temperature tar boiling from 270° to 320°. The dephenolated tar was prepared by washing with 10% caustic soda solution.

d^{30}_{4}	1.037
Benzene Insol	1.7%

Composition

C	86.75%
H	8.55%
N	0.85%
S	0.17%
Ash	0.1%

Distillation Test

I.B.P. (90°)	
90-270°	4.3%
270-300°	11.1%

300-350° 31.0%

350- 52.2%

3. Hydrogen Hydrogen, of 99% purity was obtained by electrolysis of water.

4. Catalyst The following catalysts were tested.

a $ZnCl_2.3H_2O$,

b. MoO_3, Na_2MoO_3, MoO_3 with C, $H_2[MoO_3(C_2O_4)\ (H_2O)]\ H_2O$,

c. $Sn(C_2O_4)_2.3H_2O$, $Sn(C_2O_4)_4.3H_2O$, $Sn(C_2H_2O_2)_2.2H_2O$,

d. $Sn(C_2H_2O_2)_4.2H_2O$, $SnCl_2.2H_2O$, $SnCl_4$, $Sn(OH)_2$, $Sn(OH)_4$,

e. $Sn(C_{17}H_{35}CO_2)_4$,

f. $Na_2MoO_4/SnCl_4(4 : 1)$, $MoO_3/SnCl_2(4 : 1)$

g. Fe_2O_3, $Fe(C_2O_4)_2.2H_2O$, $Fe_2(C_2O_4)_3.2H_2O$,

h. $Fe_2(C_2O_4)_3.2H_2O/NH_4Cl(10 : 1)$, $Fe(C_2O_4)_2.2H_2O/NH_4Cl(10:1)$,

i. $Fe(SO_4)$, $Fe_2(SO_4)_3$, FeS,

j. $Fe_2O_3/S(4 : 1)$, $Fe_2O_3/S(10 : 1)$, $Fe_2O_3/Sn(OH)_2(100 : 1)$,

k. Fe Stearate Soap/$Sn(OH)_2$ (100 : 1), $Fe_2O_3/S/Sn(OH)_2(100:17:1)$,

l. $Zn(C_2O_4)_2.3H_2O$, $Zn(C_2H_3O_2)_2.3H_2O$, $Zn(C_2H_3O_3)_2.3H_2O/NH_4Cl$ (10:1),

m. $Pb(C_2H_3O_2)_2.3H\ O$, $Pb(C_2H_3O_2)_2.3H_2O/NH_4Cl(10 : 1)$.

The catalysts were prepared from the metallic chloride or nitrate by precipitation and mixing of the components. They were dried at 110°C and powdered.

B. Apparatus

A cast iron cylindrical autoclave of 2.4 litres capacity was used. It was equipped with a thermometer and manometer, and was heated externally by electric resistance, and mounted to rotate horizontally.

C. Procedures

A paste was made by mixing oil and coal in the weight ratio of 1 : 1.

In each experiment, 150gms of the paste and 4.5gms of the catalyst to be tested were put into the autoclave, and hydrogen was introduced, from a cylinder, to produce 100 atmospheres of pressure at 0°C. The autoclave was heated at a rate of 2°C/min, to the required temperature and kept at this temperature for one hour. The changes in pressure during the reaction were observed at intervals of five minutes. When the reaction was finished, the volume and the density of the gas in the apparatus were measured and the chemical compositions of the gas, liquid and, solid reaction products were determined by the usual methods.

D. Experimental Results

Experimental results are summarized in Table I(B)18. The data are presented only for the most promising of the catalysts.

III. CONCLUSIONS

The simple catalysts which gave the best results were, $ZnCl_2 2H_2O$, MoO_3, $Sn(OH)_2$, and $Sn(OH)_4$.

The mixed catalyst which may be recommended in any respect was Fe_2O_3 : S : $Sn(OH)_2$(100 : 17 : 1). This catalyst was suitable for commercial usage and was better than $ZnCl_2.2H_2O$, previously used commercially due to a higher yield of tar and no corrosion difficulties. The cost of this mixed catalyst is slightly higher than $ZnCl_2.2H_2O$ due to tin content. It was prepared by mixing commercial grade ferric oxide (prepared by precipitation of $Fe(OH)_3$ and subsequent calcining), commercial grade sulphur and $Sn(OH)_2$ in the weight ratio of 100 : 17 : 1. The $Sn(OH)_2$ was prepared by precipitation from a 1 N solution of $SnCl_2$ with 10% NaOH, and drying in an oven at 110°C. This catalyst was used at the Fushun S.M.R. coal hydrogenation plant on the basis of these experiments and satisfactory results were obtained.

Table I(B)18
CATALYSTS FOR COAL HYDROGENATION

		Catalyst											
		$ZnCl_2.2H_2O$		Mo O_3		$Sn(CrO_4)_4.3H_2O$		$Sn(OH)_2$		Fe_2O_3	$Fe_2O_3.S.Sn(OH)_2$		$Sn(OH)_4$
Exp.No.		1	2	3	4	5	6	7	8	9	10	11	12
React. Temp. (°C)		400	420	420	450	375	400	385	400	400	410	420	400
Press. (max), kg/cm^2		260	277	287	298	270	270	275	278	282	260	260	292
Press. Drop, kg/cm^2		29	30	28	30	27.0	36.0	32	37	24.5	16.0	19.5	26
Yield (liquid and Solids) (gm)		131	127	85.7	129.6	96.8	130.4	117.7	125.5	104.0	-	-	113.5
Yield (by wt% of paste)		87	85	57	86	64	86.9	78.7	83.6	69.3	-	-	75.6
Water (wt% of tot. liquid)		24.5	25.7	27.5	28.9	25.0	26.3	25.3	25.3	23.7	13.0	13.0	24.3
Tar (<180°C)		10.5	11.3	3.0	6.8	2.6	8.2	7.1	11.1	4.9	4.2	5.6	5.9
Tar (180 - 320°C)		12.2	13.6	10.4	12.2	10.5	15.5	11.8	11.1	9.3	16.3	18.1	10.3
Tar (>320°C)		26.6	24.3	35.6	29.8	36.1	30.9	32.7	29.3	39.8	57.9	54.6	20.7
Residue		14.5	13.9	12.6	11.5	16.5	9.7	11.2	11.3	16.1	7.4	6.0	12.9
Gas Analysis	CO_2	1.8	1.8	1.7	0.9	2.2	1.8	2.2	2.0	2.4	0.6	0.6	2.1
	CO	0.7	0.6	0.8	1.0	0.4	0.8	0.6	1.0	1.1	0.8	1.0	1.0
	C_nH_{2n}	0.7	0.8	0.6	0.4	0.4	0.8	0.6	1.2	1.0	0.8	0.6	0.7
	H_2	87.5	86.9	89.8	89.8	90.6	86.1	91.2	89.1	90.2	90.0	89.0	90.6
	C_nH_{2n+2}	4.9	6.1	1.6	3.9	1.5	4.7	2.9	2.9	2.2	4.9	5.8	2.6
	n	1.2	1.2	1.0	1.2	2.0	2.0	2.0	2.0	1.5	2.7	2.0	1.5
Hydrogen consumed (gm)		7.7	8.0	7.5	7.7	7.0	9.3	7.6	9.1	6.6	4.9	5.7	6.8
Hydrogen (H_2/total, wt%)		37.3	38.8	36.4	37.3	33.9	45.1	36.9	44.2	32.0	24.2	28.4	33.0
Hydrogen (H_2/pure carbon in paste, wt%)		6.7	6.9	6.5	6.7	6.1	8.1	6.6	7.9	5.8	8.3	9.6	5.9
Yield of Tar (Total liquid product paste charged)		65.0	64.6	61.0	64.2	64.4	70.8	67.9	70.6	56.5	84.9	83.9	61.9

ENCLOSURE (B) 19

STUDIES ON THE FISCHER-TROPSCH SYNTHESIS

(In Three Parts)

by

ENG. LT. CMDR. A. NAKAI

Research Period: 1940-1941

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

December 1945

ENCLOSURE (B)19

LIST OF TABLES AND ILLUSTRATIONS

PART I

PART II

PART III

ENCLOSURE (B)19

PART I

ACTIVATION OF COBALT CATALYST BY HYDROGENATION

by
ENG. LT. CMDR. A. NAKAI

Research Period: 1940-1941

SUMMARY

Experiments were made to determine the best conditions for activation of the Standard Fischer-Tropsch cobalt catalyst employed for synthesis of oil from water gas.

The results disclosed that activation by hydrogen gas was excellent for Co-MgO-ThO_2-Kieselguhr catalyst (100:8:3:200 by weight), under conditions of 375-380°C, over 2500 gas space velocity and 1 1/2-2 hours reaction time. It was shown, for this case that about 50% of the cobalt in the reduced catayst was in metallic state, and the catalytic activity was also strongest in this instance.

It was also found that when the above catalyst was used for the synthesis of oil at normal pressure and 175-390°C, a gas contraction of 85% and a yield of over 160cc of oil (sp. gr. about 0.75) for each cubic meter of pure water gas (H_2:CO = 2:1 in volume ratio), were obtained.

I. INTRODUCTION

F. Fischer & H. Koch* reported that in the case of a Co-ThO_2-Kieselguhr (100:18:150) catalyst, reduction with hydrogen gas occurs only slightly at 300°C, and the most suitable temperature is 350°C with a reaction time of 4-5 hours. No research data had been reported on the activation of the Co-MgO-ThO_2-Kieselguhr catalyst in which magnesia replaced part of the rare thoria. In these experiments the effects of the reduction period and hydrogen gas velocity, in the temperature range of 375-380°C, on activation of the latter catalyst were studied.

II. DETAILED DESCRIPTION

A. Test Apparatus and Procedure

Figure 1(B)19 shows the test apparatus used. The contact oven, which was the chief part of this apparatus consisted of an aluminium block (90mm in diameter and 500mm in length) electrically heated, and through it, 4 reaction tubes were placed in parallel.

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* Brennstoff-Chemie 13, 67 (1932)

ENCLOSURE (B)19

Pure water gas, free from sulphur compounds, was made by blending electrolytic hydrogen with carbon monixide produced from formic acid and concentrated sulphuric acid.

To make the cobalt catalyst, 61.7 gm of $Co(NO_3)_2 \cdot 6H_2O$, 12.7 gm of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.78 gm of $Th(NO_3)_4 \cdot 4H_2O$ were dissolved in 250cc of distilled water, and mixed by stirring with 350cc of a solution containing 33.6 gm of Na_2CO_3·25 gm of Kieselguhr were next added, and the solution was filtered. The precipitate was washed with 1500cc of distilled water, dried and made into tablets 1-3mm in diameter. This catalyst had the approximate composition of Co-MgO-ThO_2-Kieselguhr 100:8:3:200 (by weight), the metals being mainly carbonates.

About 40cc of catalyst (corresponding to 4 gm of cobalt as metal) were introduced into the glass tube. After reduction with hydrogen, water gas was passed through at a velocity of 4 lit/hr (corresponding to a gas space velocity of 100) and a temperature of 375-380°C.

B. Experimental Results

1. The influence of reduction conditions, (varying hydrogen gas velocity and reduction time, but using a constant total volume of hydrogen) on catalytic activity is shown in Table I(B)19.

From the data it is noted that the catalyst which was reduced in the shortest time, showed the strongest activity.

2. The influence of reduction time on the catalytic activity, when the space velocity was held constant at 3750, is shown in Table II(B)19.

From these data it is noted that the optimum reduction period for 3750 SV is 1 1/2-2 hours.

3. The influence of hydrogen gas velocity on the catalytic activity is shown in Table III(B)19. In this experiment, the reduction time was held constant at 1 1/2 hours.

From these data, it is indicated that the optimum hydrogen gas space velocity was 3750-2500 for a reduction period of 1 1/2 hours.

4. It was clear that the catalyst prepared by precipitation achieved its activity for oil synthesis only after suitable treatment with hydrogen. To determine the optimum degree of reduction the following apparatus was devised. (See Figure 2(B)19).

Bottle "B" and the glass tube to 3-way cock "d" were filled with water from "F". "A" was an Erlenmeyer flask (about 100cc), in which about 2 grams of reduced catalyst had been placed, avoiding exposure to air.

Nitrogen gas was introduced at cock "b" and air displaced from flask "A". The nitrogen gas pressure in the apparatus was brought to atmospheric pressure.

Dilute sulphuric acid (1:1) was dripped into "A" from the burette "D". Hydrogen gas was evolved from the metallic cobalt and carbon dioxide gas from the carbonate mixtures. Both gases flowed to "B" through "c" and the water in "B" was drawn off to "C" through cock "e". To complete the reactions, the flask was heated gently, and then cooled to room temperature. The pressure in the apparatus was brought to atmospheric and the volume of water which flowed into "C" was measured.

Next, gases in "A" were displaced into "B" by adding water from "D", the gases in "B" were analyzed, and the amounts of CO_2 and H_2 generated from 1 gram of reduced catalyst were calculated. Experimental results for the catalysts described in Table II(B)19 are given in Table IV(B)19.

In the case of the most effective catalyst, 1 1/2 hours reduction time, 1 gram contained 0.3234 grams of cobalt by actual analysis. Therefore, the maximum hydrogen evolution from 1 gram of catalyst was,

$$22{,}400 \times \frac{0.3234}{58.94} \doteqdot 123 \text{ (cc)}$$

But the actual hydrogen gas evolution was only 58.7 cc. Therefore, the reduction degree was,

$$\frac{58.7}{123} \times 100 \fallingdotseq 48.0 \text{ (\%)}$$

It is apparent that the effective state of the cobalt catalyst did not contain only highly reduced cobalt metal, but lower oxides of cobalt were also present.

Table I(B)19
INFLUENCE OF REDUCTION CONDITION ON CATALYTIC ACTIVITY

	Temp. of Synthesis (°C)						
Temp. of Synthesis(°C)	176	185	190	195	200	Reduction Conditions*	
Time of Synthesis(hr)	8½	6¼	6¼	8½	9		
Gas Purity (%)	98.4	96.0	98.4	97.8	98.2		
Gas Composition(H_2:CO)	2.03	2.09	2.02	1.97	1.97		
Average Yield (1)	114.9	164.5	149.3	118.6	83.0	SV R.T.	1500, 1 hr
of Synthesis Oil (2)	103.5	160.2	155.6	124.8	91.5	SV R.T.	3750, 2 hr
cc/m^3 (3)	127.0	135.0	121.1	106.5	77.4	SV R.T.	2500, 3 hr

*SV Space Vol.
R.T. Reduct Time

ENCLOSURE (B)19

Table II(B)19
INFLUENCE OF REDUCTION TIME ON CATALYTIC ACTIVITY

		Temp. of Synthesis (°C)					Reduction Conditions*
		175	180	185	190	195	
Time of Synthesis(hr)		7	9	6	7½	8	
Gas Purity(%)		95.4	97.2	95.4	97.8	97.5	
Gas Composition(H_2:CO)		2.13	1.06	2.09	1.98	2.02	
Average	(1)	102.0 (86.2)	124.2 (87.0)	149.7 (86.2)	151.7 (83.7)	136.0 (83.3)	R.T. = 1 hr
Yield of	(2)	102.0 (86.5)	130.5 (88.5)	165.5 (87.0)	160.3 (87.0)	125.0 (84.0)	R.T. = 1½ hr
Synthesis Oil cc/m³	(3)	105.9 (87.4)	135.9 (87.4)	162.9 (86.8)	158.5 (86.8)	124.7 (82.6)	R.T. = 2 hr
(Gas contraction, vol %)	(4)	91.4 (75.4	118.4 (81.4)	127.7 (74.2)	121.4 (75.2)	118.2 (75.6)	R.T. = 3hr

*SV = 3750

Table III(B)19
INFLUENCE OF HYDROGEN GAS VELOCITY ON CATALYTIC ACTIVITY

		Temp. of Synthesis (°C)					Reduction Conditions*
		175	180	185	190	195	
Time of Synthesis(hr)		8	6½	6½	6	7	
Gas Purity(%)		93.9	96.6	97.5	96.9	98.4	
Gas Composition(H_2:CO)		2.15	1.88	2.05	2.07	2.01	
	(1)	113.8 (86.7)	124.7 (87.9)	151.8 (87.9)	148.5 (86.7)		SV = 3750
	(2)	107.0 (86.2)	116.8 (86.9)	149.7 (87.3)	148.5 (86.1)	138.0 (85.5)	SV = 2500
	(3)	100.4 (88.0)	102.8 (82.1)	107.7 (83.1)	120.5 (85.2	115.9 (85.2)	SV = 1250
	(4)	87.2 (70.3)	100.7 (75.3)		101.3 (82.1)	115.9 (85.2)	SV = 250

*R.T. = 1.5 hr

ENCLOSURE (B)19

Table IV(B)
GASES EVOLVED FROM REDUCED CATALYST

Reduction Time (hr)	Wt. of Cobalt in 1 gram Reduced Cat.	cc of Gas Evolved From 1 gm Red. Cat.		Reduction of Cobalt (%)
		CO_2	H_2	
1.5	0.3234	1.0	58.7	48
2	0.3196	1.0	74.7	62
3	0.8108	0.8	82.3	70

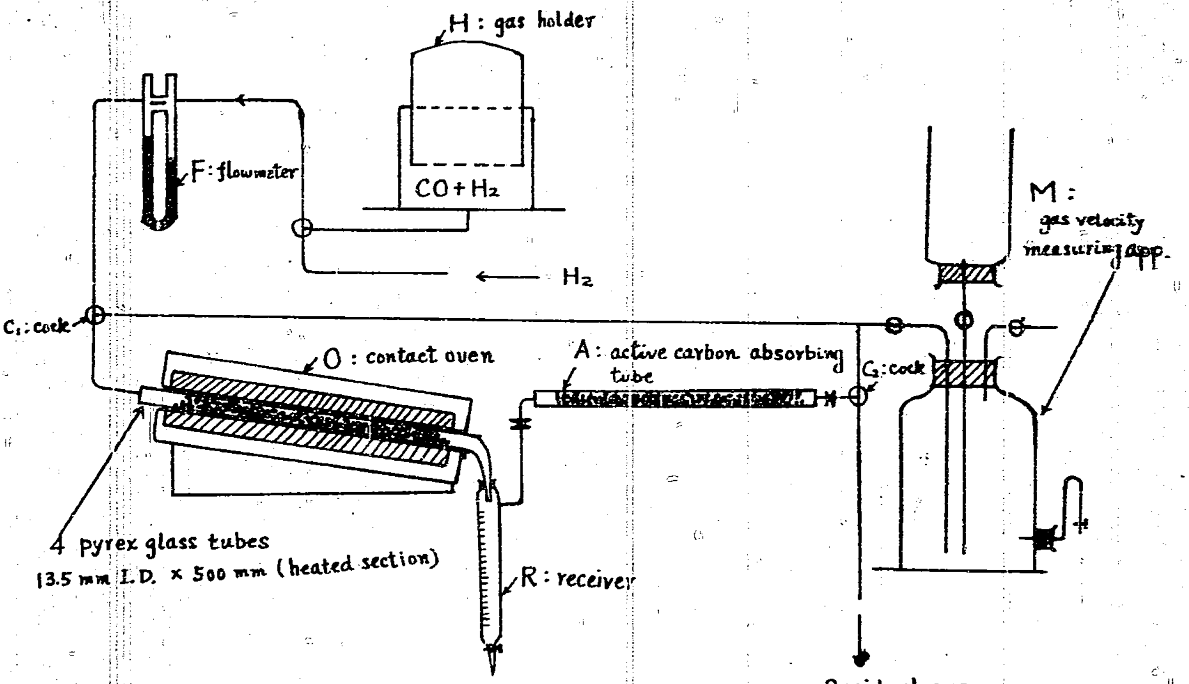

Figure 1(B)19
CATALYST TESTING APPARATUS

ENCLOSURE (B)19

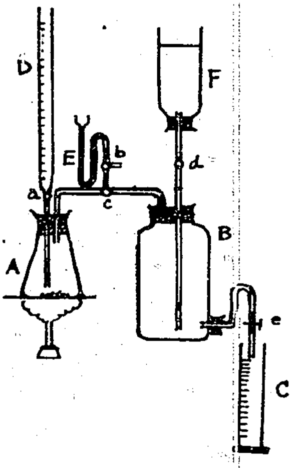

Figure 2(B)19
APPARATUS FOR DETERMINING
DEGREE OF CATALYST REDUCTION

ENCLOSURE (B)19

PART II

STUDIES ON IRON CATALYST

by

CHEM. ENG. LT. CMDR. A. NAKAI

Research Period: 1941-1942

SUMMARY

Experiments were made to investigate the effectiveness of iron catalysts for synthesis of oil from water gas at normal pressure. Detailed date on these experiments are not now available, but the significant results were as follows:

1. The catalyst Fe-Cu-ThO_2-MgO-Kieselguhr-K_2CO_3 (100:20:4:20:175-200:4), prepared by precipitation, was satisfactory at lower reaction temperatures, i.e., 235-240°C.

2. Thorium and magnesium were very effective promoters and served to lower the required reaction temperature.

3. For the purpose of activating the catalyst, it was better to circulate water gas rapidly at the reaction temperature.

4. The yield of synthetic oil with this iron catalyst was 61.6 gm/m^3 of water gas (H_2:CO=6:4 by volume) at 235°C.

I. INTRODUCTION

Many reports have been made concerning the use of iron catalysts for synthesis of oil from water gas. TSUNODA, MURATA and MAKINO* succeeded in obtaining 83cc of synthetic oil per cubic meter of water gas (H_2:CO 1:1) at 257°C using the catalyst Fe-Cu-Kieselguhr-K_2CO_3 (100:25:125:2, by weight). Later they** obtained a yield of 88cc or oil using the catalyst Fe-Cu-Mn-Kieselguhr-K_2CO_3 (100:25:2:125:2), and concluded that manganese was effective as a promoter. They confirmed, too, that magnesia was useful as a promoter, but oxides of uranium and thorium, and especially chromium and aluminium, were poisonous.

Generally, it was believed that for iron-catalyst,* addition of copper was absolutely necessary,** and that alkalies were very effective as promoters.

TSUNEOKA and his co-workers# found a new catalyst, consisting of the abovementioned catalyst plus boric acid (corresponding to 20% iron content) which gave a yield of 95cc of liquid products per cubic meter water gas (H_2:CO=2:1) at 240°C.

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*J. of Tech. Chem. Japan, 42 (1939) 202
**Ibid. 209
#Lect. of Kyoto Chem. Research Inst. 10 (1939) 2.

However, the required reaction temperature was high for commercial usage, and moreover, boric acid is not manufactured on a large scale in Japan. The following experiments were made primarily to find a catalyst without such weak points as these.

II. DESCRIPTION

The test apparatus was the same as described in Part I of "Studies on Fischer-Tropsch Synthesis". Catalysts were prepared by precipitation from nitrate mixtures and sodium carbonate solutions similar to the procedure for cobalt catalyst as described in Part I, except that the sodium or potassium carbonate was added after washing of the precipitates and before drying.

The following series of experiments were made:

1. The influence of metals or metallic oxides on the catalytic activity of the catalyst Fe-Cu-Kieselguhr-Na_2CO_3 (100:20:200:4) was investigated.

   Mn, Cr, Zn, ThO_2, U_3O_8, Al_2O_3 and MgO were tested as promoters, and it was observed that ThO_2, MgO and Al_2O_3 were effective in lowering reaction temperature, but Mn and Cr were poisonous.

2. The influence of metals or metallic oxides on the catalytic effect of the catalyst Fe-Cu-ThO_2-Kieselguhr-Na_2CO_3 (100:20:4:200:4) was investigated.

   Mn, Cr, Zn, Al_2O_3 and MgO were tested as promoters, and it was observed that MgO or Al_2O_3 was effective, especially the former.

3. Studies were made to determine the effect of varying thoria and magnesia contents on Fe-Cu-ThO_2-MgO-Kieselguhr-Na_2CO_3 catalyst.

   ThO_2 and MgO were varied over the range of 4 to 30 wt. % (of iron) and a catalyst of the composition 100:20:4:20:200:4 gave the best results.

4. A study was made of the effect of the types of alkalies used, and it was concluded that, sodium carbonate was the best to use in the precipitation step, but 4 % of potassium carbonate was the best alkali promoter for the above-mentioned iron catalyst.

5. The amount of Kieselguhr in standard iron catalyst Fe-Cu-ThO_2-MgO-Kieselguhr-K_2CO_3 was varied from 125 to 300 % of iron by weight, and it was found that the best content was 175-200 %.

6. The primary activation of the iron catalyst is accomplished by reduction with water gas. Experiments were made to investigate the effect of the rate of circulation (increased gas velocity) on rate of activation. The advantage of rapid circulation in decreasing reduction time is shown by Table V(B)19.

7. After the activation, as described in the preceeding paragraph, a single-stage conversion test was made using water gas (H_2:CO=6:4) at 235°C, atmospheric pressure, and gas velocity of 41/hr. 40cc of the catalyst, Fe-Cu-ThO_2-MgO-Kieselguhr-K_2CO_3 (100:20:4:20:200:4) were used. The average yield of liquid hydrocarbons was 61.6 gm/m^3 feed gas over a 50 hour reaction period.

ENCLOSURE (B)19

Table V(B)19
EFFECT OF CIRCULATION ON VOLUME % DECREASE OF WATER GAS USED IN ACTIVATION OF STANDARD IRON CATALYST

Reduction Time (hr)	6	8	12	16	18	22	24	26	Remarks
No Circulation			18.6	21.7	26.5	30.1	32.5	32.5	gas vel., 41/hr.
Circulation	24.7	31.3	37.4	41.0	42.2	45.2	45.2	45.2	circulated gas vel. 201/hr.

ENCLOSURE (B)19

PART III

STUDIES ON LIQUID PHASE SYNTHESIS WITH IRON CATALYST

by

CHEM. ENG. LT. CMDR. A. NAKAI

Research Period: 1942-1943

SUMMARY

Experiments were made to investigate the activity of iron catalysts in liquid phase synthesis of oil from water gas.

Significant results were as follows:

1. Fe-Cu catalysts, containing small amounts of alkali, had a strong oil synthesis activity, at temperatures under 250°C.

2. A similar catalyst, but containing no alkali, showed weaker activity for oil synthesis, but strong hydrogenating power at 250-270°C.

3. The catalysts, Fe-Cu-CaO, were prepared by precipitation from nitrate mixtures with an excess of sodium hydroxide. The catalysts Fe-CaO (100:100-150) and Fe-CaO-Cu (100:100-150:25) could be made into very hard tablets, and were suitable for liquid phase synthesis at 260-270°C, and pressure 10 kg/cm^2. The catalysts Fe-CaO(100:10)and Fe-CaO-Cu(100:10:25) had better activity than the afore-mentioned, but binders were required to make satisfactory tablets.

I. INTRODUCTION

Research on the synthesis of hydrocarbons from water gas was made chiefly for vapor-phase reaction conditions, which resulted in some difficulties in removing reaction heat in a large-scale apparatus. Reaction chambers of tubular design were used for controlling reaction temperature, but these chambers were expensive to construct and difficult to maintain.

A new, simpler method for removing reaction heat was proposed by the I. G. Co. in Germany, which was based on the circulation of synthetic oil through the reaction system.

F. Fischer and H. Pichler experimented with liquid phase synthesis using an iron catalyst suspended in water under 10-40 atmospheres of pressure and 200-250°C., but their results were unsuccessful.

The following experiments were made to determine a more suitable catalyst for the liquid phase synthesis.

II. DETAILED DESCRIPTION

The catalyst, containing 4 gm of iron, was mixed in a two-liter rotary autoclave with 200cc of Fischer-Tropsch synthetic oil, (iodine number of 8.83). Water gas was charged into the autoclave, to an initial pressure of 10 atmospheres at 15°C. The autoclave was heated electrically to the required reaction temperatures, held for the desired time, and then cooled to room temperature. The pressure drop was measured and the residual gas and oil analyzed.

III. EXPERIMENTAL RESULTS

A. Experiments with Fe-Cu-K_2CO_3 Catalyst

Catalysts were prepared by precipitating from iron and copper nitrate solutions with an excess (about 20% of theoretical) of sodium carbonate solution. This procedure was similar to that used for an iron catalyst, described in Part II of this enclosure.

Experimental data on these catalysts, summarized in Table I(B)19 show that, (1) the catalyst Fe-Cu-K_2CO_3 showed activity for oil synthesis at temperatures under 250°C, but variation of K_2CO_3 content had little influence on this activity, (2) the catalyst Fe-Cu (containing no alkali), showed lower synthesis activity than the former, but possessed hydrogenating power at 250-270°C.

B. Experiments with Fe-CaO and Fe-CaO-Cu Catalyst.

These catalysts were prepared by precipitating from nitrate mixtures with a large excess (about 100% of the theoretical amount) of sodium hydroxide solution, and the precipitate was washed with 1/20 N sodium hydroxide.

Data on these catalysts, given in Tables VII(B)19, and VIII(B)19, show that, (1) the catalyst Fe-CaO was active at a reaction temperature of 260-270°C., and its activity was better with lower CaO content, (2) the catalyst Fe-CaO-Cu was more reactive than the former at lower temperatures and the CaO content had less influence on the synthesis activity, (3) the catalyst with high CaO content was very hard and made excellent tablets.

IV. CONCLUSIONS

The best catalyst for the liquid phase reaction appeared to be Fe:CaO:Cu (100:150:25). The amount and quality of oil formed in these experiments was not determined, and it would be necessary to perform experiments on a larger continous-pilot plant scale to establish the economic attractiveness of this process.

All work on Fischer-Tropsch synthesis was stopped in 1943. The work covered in these three sections of "Studies on the Fischer-Tropsch Synthesis" represents all of the work done by the Naval Research Department on development of the process.

ENCLOSURE (B)19

Table VI(B)19
EXPERIMENTS WITH Fe-Cu AND Fe-Cu K_2CO_3 CATALYSTS

Catalyst	Final* Press. kg/cm^2	Synthesis (Temp. °C)	Synthesis (Time, hr)	Contraction (Vol. %)	Iodine Value, After Reaction
No Catalyst Used	10	230-285	5.5	0	54.11**
Fe-Cu Catalyst Ratios 100:25	4.2	248-270	5.5	58	8.83#
100:25	6.8	220-250	4	32	48.56
Fe-Cu-K_2CO_3 Catalyst Ratio 100:25:2	6.0	220-250	4	40	42.80
100:25:4	6.1	220-250	4.5	39	44.14
100:25:6	6.1	220-250	4	39	45.43
100:25:6	6.1	240-270	4	39	45.98
100:25:8	6.1	220-263	4	39	47.87
100:25:25	6.2	218-252	4	38	48.65
100:25:25	6.0	240-270	4	40	49.07
100:25:50	8.3	223-254	4	17	48.61

*In all cases initial pressure was 10 kg/cm^2
**Partial cracking occurred
#Synthesis and hydrogenation occurred

ENCLOSURE (B)19

Table VII(B)19
EXPERIMENTS WITH Fe-CaO CATALYST

Catalyst (Fe-CaO)	Final* Press. kg/cm^2	Synthesis Temp. (°C)	Synthesis Time (hr)	Contraction (Vol. %)
100:5	4.5	270	2	55
100:10	4.8	260	2	52
100:20	4.2	270	2	58
100:100	5.0	270	2	50
100:100	7.2	260	2	28
100:150	6.0	270	2	40
100:150	7.0	260	2	30
100:200	6.0	270	2	40
100:200	7.0	260	2	30

*In all cases initial pressure was 10 kg/cm^2

Table VIII(B)19
EXPERIMENTS WITH Fe-CaO-Cu CATALYST

Catalyst (Fe-CaO-Cu)	Final* Press. kg/cm^2	Synthesis Temp. (°C)	Synthesis Time (hr)	Contraction (Vol. %)
100:10:5	4.3	260	2	57
100:10:10	4.0	260	2	60
100:10:25	3.7	260	2	63
100:100:25	4.8	260	2	52
100:150:25	4.0	260	2	60
100:200:25	4.2	260	2	58

*In all cases initial pressure was 10 kg/cm^2

ENCLOSURE (B) 20

STUDIES ON COAL

by

CHEM. ENG. LIEUT. C. M. KUMAMOTO

Research Period: 1940-1942

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

December 1945

ENCLOSURE (B)20

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)20

SUMMARY

This work was carried out to investigate the nature of coal in MANCHUKUO and in North China. About 50 kinds of the North China coal and 40 of the Manchukuo coal were investigated.

Test results showed that the North China coal was suitable for high temperature carbonization, whereas, the Manchukuo coal was better for low-temperature carbonization or liquefaction by hydrogenation.

I. INTRODUCTION

This work was begun in April, 1940. About 90 kinds of coal were investigated. It was desired to study, in detail, the chemical factors affecting caking properties of typical coals, but this project was ordered to stop in May, 1942.

The key research personnel working on the project were Eng. Cmdr. Dr. M. HAGIHARA and Eng. Lt. Cmdr. M. KUMAMOTO.

II. DETAILED DESCRIPTION

A. Description of Test Methods

1. Proximate Analysis. Moisture, volatile matter, ash, and fixed carbon were measured by the standard British method.

2. Ultimate Analysis. After grinding and drying the coal at 105 5°C, the content of carbon and hydrogen were determined by combustion. Nitrogen was determined by Kjeldahls' method, and sulphur by the Eschka method. The gross calorific value was measured by the bomb method.

3. Hydrogenation Test. 300 grams of coal (sized through to 60 mesh) and 15 grams of $ZnCl_2$ were put into an autoclave of 2.5 liters volume. After replacing the air by hydrogen gas, the hydrogen pressure was increased to 100 kg/cm^2 (no oil used). The autoclave was heated gradually and 3 hours were required to raise the temperature to 420 °C. After one hour at this temperature, the pressure was released and the hydrogenated product removed. The moisture and benzene-soluble material in the reactant were measured. The yield of liquid and the reactivity were calculated by the following formulae:

$$A = \%\ \text{Yield of liquid} = \frac{\text{total liquid product(wt)}}{\text{ideal coal(wt)}} \times 100$$

(The ideal coal is defined as the volatile matter plus fixed carbon contained in the coal.)

$$B = \%\ \text{Reactivity} = \frac{\text{ideal coal} - (\text{residue} - \text{ash})}{\text{ideal coal}} \times 100$$

(The residue is the material remaining after removal of moisture and benzol soluble material from the product.)

4. Carbonization Test. The Gray-King method was used.

5. High-temperature Carbonization Test. The Lessing method was used.

6. Caking Properties. Caking properties were determined by the usual observation of the residue from the volatile matter test, and also from the high-temperature carbonization test. It was desired to study the chemical factors affecting caking properties, especially oxygen content of typical coals, but this project was abandoned.

III. EXPERIMENTAL RESULTS

Experimental results are summarized in Table I(B)20 and Table II(B)20.

IV. CONCLUSIONS

Apparently the Manchukuo coal has more water and less fixed carbon than the North China coal. Most Manchukuo coal is a form of brown coal, but the North China coal is bituminous.

Practically all of the North China coal is suitable for high-temperature carbonization, as compared with only 16% of the Manchukuo coal.

The average yield of liquid by hydrogenation of Manchukuo coal is 64.1%, and of the North China coal is 41.9%. The Manchukuo coal is better suited for hydrogenation or low-temperature carbonization.

ENCLOSURE (B)20

Table I(B)20
TESTS ON NORTH CHINA COAL

Coal Field		Proximate Analysis (%)					Ultimate Analysis (%)					Cal. Value (gm-cal)	Hydrogenation (%)		Low Temp. Carbonization			High Temp. Carbonization			Caking Property
		Moist.	Vol.M.	Fix.C	Ash	Fuel Ratio	C	H	N	S	O		A	B	Coke wt %	Tar wt %	Gas wt %	Coke wt %	Tar wt %	Gas wt %	
Tatung	No.1	3.6	29.2	64.1	3.1	2.19	85.1	5.6	0.9	0.7	7.9	7.890	61.8	80.2	82.9	5.9	7.4	71.5	9.8	11.1	none caking
	No.2	3.0	29.4	61.2	6.4	2.08	84.1	5.8	1.0	0.6	8.6	7.549	53.5	77.8	83.6	6.2	5.7	69.3	7.9	12.6	none caking
	No.3	4.3	30.6	62.3	2.8	2.03	83.5	5.4	0.9	0.7	9.6	7.860	64.9	82.8	82.6	6.2	4.6	66.9	9.3	16.8	good caking
	No.4	3.6	31.8	57.4	7.2	1.81	84.6	5.3	0.9	0.8	8.5	7.450	59.6	81.4	77.3	4.5	13.7	68.2	7.9	16.9	good caking
Hwa Yong	No.1	1.9	12.1	73.7	12.3	6.09	90.8	4.5	1.0	0.6	3.1	7.284	0.0	0.0	98.5	0.0	1.3	89.4	0.0	7.7	none caking
	No.2	4.8	33.2	57.3	4.7	1.73	78.1	5.3	1.1	0.2	15.5	7.440	73.3	95.1	79.6	13.1	6.2	65.8	14.9	8.6	none caking
Yang Shen		3.6	7.5	81.7	7.2	10.89	92.3	3.2	1.4	0.9	2.1	7.878	0.0	0.0	97.9	0.0	1.6	90.3	0.0	6.4	none caking
Kailuan	No.1	0.9	29.1	44.9	25.1	1.54	84.0	6.9	1.4	1.5	6.2	6.084	62.7	74.8	80.9	8.7	6.6	75.6	9.4	9.6	good caking
	No.2	1.2	30.6	49.3	18.9	1.60	84.2	6.7	1.6	2.2	5.4	6.724	52.0	75.1	79.4	11.4	7.2	71.9	12.1	12.7	good caking
	No.3	1.5	25.8	40.0	32.7	1.55	83.9	6.7	1.5	1.2	6.8	5.306	57.1	73.5	83.7	8.2	4.7	75.0	7.7	11.6	good caking
	No.4	1.2	26.6	40.7	31.5	1.53	82.2	7.4	1.3	1.4	7.7	5.426	60.2	69.4	81.2	8.9	5.5	74.2	8.0	12.0	good caking
	No.5	0.9	30.1	49.8	19.2	1.65	85.4	6.5	1.4	1.9	4.7	6.716	57.8	74.7	80.4	10.4	6.5	77.7	9.9	10.1	good caking
Tanyshan	No.1	1.1	29.5	45.7	23.7	1.32	76.9	6.3	1.5	1.4	14.0	6.156	44.1	47.7	83.6	11.5	4.8	73.5	11.8	9.6	good caking
	No.2	1.3	28.6	52.0	18.1	1.82	79.4	5.6	1.3	1.6	12.2	6.788	34.5	50.3	82.9	10.8	6.3	72.2	11.9	12.2	good caking
	No.3	1.5	28.4	52.0	18.1	1.83	71.2	5.5	1.6	1.3	14.4	6.797	46.3	56.4	83.6	10.9	5.3	73.7	10.2	12.1	good caking
Tany Ghochuan	No.1	1.8	28.5	45.4	24.3	1.59	173.5	6.5	1.5	1.0	17.4	6.217	43.8	69.6	81.7	9.8	8.4	73.7	8.4	13.9	good caking
	No.2	1.3	29.8	48.9	20.0	1.64	77.6	5.8	1.5	1.1	13.9	6.713	29.6	77.5	82.4	11.8	5.4	75.6	11.0	12.5	good caking
	No.3	1.9	25.9	39.2	33.0	1.51	82.5	5.9	1.6	1.2	8.8	5.231	26.4	68.9	87.4	8.4	4.0	76.9	6.9	10.6	good caking
	No.4	1.3	25.9	47.4	25.4	1.83	80.3	5.3	1.5	0.9	12.0	6.063	26.0	80.0	84.9	9.9	5.0	75.9	9.8	15.4	good caking
	No.5	1.5	31.1	48.6	18.8	1.56	77.8	6.1	1.4	2.1	12.7	6.700	37.0	72.0	87.6	10.3	1.9	74.4	9.4	11.5	good caking
Chao-Kyong	No.1	1.7	29.1	45.8	23.4	1.57	81.5	5.3	1.6	0.7	10.9	6.086	52.1	61.8	81.9	10.0	6.1	72.2	9.3	13.9	good caking
	No.2	1.7	34.5	47.5	16.3	1.38	82.9	5.5	1.4	2.2	7.9	6.871	48.5	76.8	77.5	12.9	7.0	69.8	13.4	11.8	good caking
	No.3	2.7	27.4	38.0	31.7	1.39	82.5	5.4	1.4	0.9	9.8	5.324	51.5	62.2	83.7	8.7	5.0	68.5	11.3	18.1	good caking
	No.4	2.0	28.2	44.3	25.5	1.57	81.5	5.2	1.4	0.8	11.3	5.820	47.1	62.1	80.8	9.3	5.9	74.6	9.2	11.5	good caking
	No.5	2.0	33.4	48.2	16.4	1.44	83.0	5.5	1.4	2.2	7.9	6.840	47.6	73.7	80.5	11.4	6.1	70.7	8.9	15.7	good caking

Table I(B)20 (cont'd)
TESTS ON NORTH CHINA COAL

Coal Field		Proximate Analysis (%)					Ultimate Analysis (%)					Cal. Value (gm - cal)	Hydrogenation (%)		Low Temp. Carbonisation			High Temp. Carbonisation			Caking Property
		Moist.	Vol.M.	Fix.C.	Ash	Fuel Ratio	C	H	N	S	O		A	B	Coke wt %	Tar wt %	Gas wt %	Coke wt %	Tar wt %	Gas wt %	
Linshi	No.1	1.8	24.9	49.2	24.1	1.98	83.9	5.2	1.4	1.8	7.7	6.335	34.5	64.9	87.9	7.1	4.7	77.6	7.2	10.6	good caking
	No.2	1.5	27.2	54.4	16.9	2.00	81.9	5.0	1.5	2.9	8.2	5.966	43.5	76.0	87.5	6.2	6.1	75.5	8.0	14.2	good caking
	No.3	1.9	25.0	41.1	32.0	1.64	83.3	5.4	1.5	1.1	8.8	5.351	41.7	60.5	88.5	6.7	3.7	73.5	5.6	11.3	good caking
	No.4	1.4	24.8	49.3	24.5	1.94	84.9	5.3	1.5	1.2	7.2	6.115	59.9	63.6	86.8	5.8	7.1	77.2	8.1	11.0	good caking
	No.5	1.1	27.3	53.1	18.5	1.92	81.8	5.2	1.2	2.1	5.7	6.838	48.4	74.8	84.9	8.0	7.0	75.4	7.6	12.4	good caking
Ching Ching	No.1	1.2	32.5	55.1	11.2	1.69	80.4	5.8	1.4	1.6	10.8	7.701	58.3	75.4	94.0	2.9	3.1	80.9	6.5	11.4	good caking
	No.2	1.2	30.0	56.4	12.4	1.88	82.5	5.5	1.5	1.2	9.3	7.588	45.9	52.3	94.0	2.4	3.6	77.2	5.1	16.8	good caking
	No.3	1.2	24.8	66.2	7.8	2.67	85.8	5.6	1.5	3.5	3.6	7.829	26.6	33.4	88.6	9.1	2.2	85.5	3.2	9.6	good caking
	No.4	1.1	21.0	62.9	15.0	2.99	83.7	6.6	1.5	0.7	7.9	7.244	9.6	22.9	88.9	7.8	3.3	79.4	6.7	12.6	good caking
Cheng Feng	No.1	1.3	25.3	61.1	12.3	2.42	85.4	5.2	1.4	1.7	6.3	7.574	56.9	70.1	90.4	2.1	6.9	82.9	3.5	11.7	good caking
	No.2	1.0	23.2	59.0	16.8	2.54	85.4	5.6	1.4	1.4	6.3	7.202	49.0	58.1	90.1	3.4	5.4	82.9	6.6	8.1	good caking
	No.3	1.0	23.5	70.1	5.4	2.98	86.9	5.4	1.4	1.9	4.4	8.187	42.2	58.5	89.4	5.4	4.8	70.9	4.4	22.9	good caking
	No.4	1.3	21.0	69.2	8.5	3.29	88.9	5.4	1.7	0.6	3.4	7.889	28.7	28.1	86.7	6.7	5.6	78.5	7.9	11.6	good caking
Poshang	No.1	0.8	21.0	64.5	3.7	3.03	88.4	4.8	1.4	0.6	4.8	7.303	41.7	72.5	88.5	6.8	5.5	81.0	5.8	11.4	good caking
	No.2	1.8	22.5	56.0	19.7	2.49	84.1	5.0	1.5	3.4	6.0	6.725	27.7	32.2	88.7	5.7	5.4	79.9	6.4	11.4	good caking
	No.3	5.3	20.8	54.7	19.2	2.63	79.5	4.3	1.5	4.6	10.1	6.101	19.0	37.2	86.9	0.5	6.5	79.2	1.5	10.6	none caking
	No.4	2.2	22.1	58.7	17.0	2.65	82.3	5.2	1.6	3.4	7.5	7.072	41.3	44.9	87.0	6.3	6.5	79.4	6.3	12.2	good caking
Huah-pao	No.1	2.7	23.1	56.1	18.1	2.43	71.3	6.3	1.5	1.1	19.9	6.545	55.2	81.2	78.2	15.7	5.3	67.2	10.7	12.5	good caking
	No.2	3.2	33.4	45.1	18.3	1.35	71.0	5.3	1.4	1.3	20.9	6.464	39.2	56.4	80.8	11.9	6.8	66.3	11.7	13.3	good caking
	No.3	3.0	33.7	53.5	9.8	1.59	75.8	5.1	1.5	0.6	17.0	7.244	47.3	77.8	78.9	14.0	6.6	66.9	9.3	15.2	good caking
	No.4	2.8	37.0	49.0	11.2	1.32	72.7	5.5	1.2	4.6	16.1	7.279	44.5	61.6	77.1	15.8	6.5	63.1	15.4	13.5	good caking
	No.5	2.2	33.7	45.7	18.4	1.36	64.3	5.1	1.4	4.8	23.5	6.538	18.9	43.6	73.5	10.2	15.8	67.8	11.7	12.2	good caking
Chin Choro	No.1	1.1	26.8	63.8	8.3	2.34	76.2	5.4	1.6	0.8	15.7	7.778	11.2	18.3	84.8	9.7	5.5	69.7	11.8	1.58	good caking
	No.2	1.3	30.2	60.2	8.3	2.00	78.2	5.9	1.7	4.2	9.9	7.986	16.7	19.9	93.1	3.1	3.8	71.7	11.1	16.9	good caking

ENCLOSURE (B)20

Table II(B)20
TESTS ON MANCHUKUO COAL

Coal Field Coal Field		Proximate Analysis (%)					Ultimate Analysis (%)					Hydregenation (%)		Caking Property	Low Temp. Carbonization (%)		
		Moist.	Vol.M.	Fix.C.	Ash	Fuel Ratio	C	H	N	S	O	A	B		Coalite	Tar	Gas
Salinor		19.8	55.7	20.8	3.7	0.37	74.6	7.3	1.3	0.3	16.4	49.4	87.1	none caking	52.3	7.4	16.3
Sincheng		13.6	37.7	44.9	3.8	1.19	75.9	5.4	1.2	0.6	16.8	59.7	91.5	none caking	70.8	11.9	10.5
Padogo	No.1	15.9	35.4	39.8	8.9	1.12	76.1	5.2	1.1	2.3	15.2	64.6	88.2	none caking	70.9	7.0	12.5
	No.2	14.1	35.8	40.0	10.1	1.11	76.2	4.7	1.3	1.7	16.1	68.6	91.6	none caking	67.1	8.0	12.9
Taiping		10.8	36.2	49.4	3.6	1.36	78.3	6.2	0.9	1.4	13.3	81.3	92.5	none caking	71.1	10.9	9.8
Sun Kiawan		11.0	35.3	44.2	9.5	1.25	77.9	4.2	1.2	0.9	15.8	65.5	92.4	none caking	65.3	6.9	10.5
Peipiao	No.1	11.9	39.6	41.9	6.6	1.06	77.4	3.9	1.0	2.9	14.8	69.1	89.8	none caking	69.5	16.2	6.1
	No.2	13.1	38.1	43.2	5.6	1.13	76.8	5.1	0.9	1.4	15.8	64.8	91.6	none caking	71.5	7.8	8.8
	No.3	11.4	40.1	42.4	6.1	1.06	76.3	5.0	0.9	1.4	15.6	65.2	91.9	none caking	65.6	11.3	8.2
	No.3	7.2	36.5	52.4	9.9	1.43	86.0	6.1	1.2	0.2	6.7	64.9	80.4	caking	94.3	11.5	9.2
	No.4	2.1	33.7	44.7	19.5	1.32	82.0	5.7	1.2	0.6	9.5	65.9	81.2	caking	78.6	11.0	6.1
	No.5	2.2	33.8	44.8	19.4	1.33	84.7	5.7	1.2	0.4	8.0	67.3	80.2	caking	75.1	12.4	8.2
	No.6	2.0	35.7	50.3	12.0	1.40	86.8	5.8	1.2	0.3	6.4	65.8	81.3	caking	74.1	12.4	8.5
Hsian	No.1	9.3	36.2	46.2	8.3	1.27	74.0	5.5	1.2	0.8	18.3	68.2	93.2	none caking	72.7	6.5	12.0
	No.2	9.4	36.2	45.1	9.3	1.24	77.9	5.8	2.0	1.5	12.9	63.0	87.0	none caking	68.3	10.1	11.6
Talcheng	No.1	11.2	30.7	40.4	17.7	1.31	75.8	5.7	1.0	0.5	17.0	65.1	83.0	none caking	75.4	3.3	6.3
	No.2	10.5	41.5	41.6	6.4	1.00	75.6	5.9	1.5	0.7	17.3	64.1	91.1	none caking	64.3	10.3	9.4
	No.3	11.0	34.3	35.6	17.7	1.00	78.8	6.2	2.4	0.7	12.6	70.8	89.7	none caking	68.9	9.8	8.6
Chiaoho	No.1	7.5	28.6	39.1	23.8	1.37	77.3	4.9	1.4	0.6	15.7	67.0	82.1	none caking	76.1	8.9	17.6
	No.2	6.7	31.0	37.5	24.8	1.21	79.3	6.1	1.2	0.7	12.7	78.1	88.3	none caking	92.2	9.1	7.8

ENCLOSURE (B)20

Table II(B)20 (cont'd)
TESTS ON MANCHUKUO COAL

Coal Field		Proximate Analysis (%)					Ultimate Analysis (%)					Hydrogenation (%)		Caking Property	Low Temp. Carbonization (%)		
		Moist.	Vol.M.	Fix.C.	Ash	Fuel Ratio	C	H	N	S	O	A	B		Coalite	Tar	Gas
(Hido Kasi)	No.1	22.0	48.3	12.5	17.2	0.26	72.1	6.3	1.7	0.3	19.6	58.2	86.1	none caking	60.8	10.3	11.2
	No.2	23.7	47.3	15.3	13.7	0.30	71.0	6.3	1.7	0.3	20.7	50.5	92.0	none caking	50.0	20.5	10.1
	No.3	23.0	46.7	21.3	9.0	0.46	70.0	6.3	0.2	0.3	23.3	48.7	92.6	none caking	61.7	11.2	13.8
Biyong		18.8	42.1	8.9	30.2	0.21	70.0	8.0	1.4	0.4	20.2	71.7	83.4	none caking	62.7	3.2	20.5
Feng Turho	No.1	16.8	49.2	18.4	15.6	0.37	72.0	7.0	1.6	0.2	19.1	67.0	87.8	none caking	57.4	18.5	14.8
	No.2	20.8	42.2	13.1	13.9	0.55	71.5	6.6	1.9	0.3	19.8	59.0	88.7	none caking	58.8	12.2	11.4
	No.3	19.5	44.5	25.9	10.1	0.58	69.3	5.7	1.8	0.2	22.8	66.9	93.6	none caking	58.7	12.8	11.2
Hunchun		18.7	32.8	32.2	16.3	0.98	70.3	5.0	1.0	0.3	23.3	53.8	77.3	none caking	65.5	9.3	14.5
Holung	No.1	16.4	30.4	39.2	14.0	1.29	76.1	5.1	1.1	0.7	17.0	72.8	95.4	none caking	69.4	12.1	5.8
	No.2	11.3	28.3	40.4	20.0	1.43	75.7	5.5	1.0	1.6	16.6	61.7	77.7	none caking	79.9	3.2	5.7
Laotoang	No.1	10.5	33.5	43.1	12.9	1.29	79.3	5.1	1.2	0.5	13.9	69.6	88.3	none caking	72.9	1.1	10.3
	No.2	11.5	32.1	39.5	16.8	1.23	78.2	6.2	1.0	0.5	14.1	73.4	91.4	none caking	74.7	14.8	5.5
	No.3	7.3	33.6	42.3	16.8	1.25	79.1	5.0	1.1	0.4	14.4	72.1	88.0	none caking	75.2	8.9	8.5
Mishang	No.1	1.8	20.2	52.8	25.2	2.61	84.0	5.9	1.1	0.6	8.4	54.1	58.2	none caking	85.5	5.0	7.2
	No.2	1.0	21.2	62.0	15.8	2.92	86.8	5.7	1.2	0.7	5.0	66.0	64.6	none caking	86.1	5.5	7.2
	No.3	1.5	19.9	64.2	14.4	3.22	88.3	5.5	1.0	0.7	4.5	48.6	52.5	none caking	87.6	6.2	6.0
	No.4	1.2	20.2	60.3	18.8	2.98	88.3	5.1	1.1	0.7	4.8	41.3	60.0	none caking	85.9	6.1	7.0
Hokang	No.1	2.7	30.6	53.5	13.2	1.75	83.4	5.7	0.9	0.2	9.8	67.1	85.1	none caking	81.5	7.5	7.6
	No.2	2.4	34.8	51.6	11.2	1.48	83.2	5.3	0.9	0.2	10.4	64.8	83.7	none caking	75.7	12.6	8.7
	No.3	2.3	34.1	52.6	11.0	1.54	83.3	5.3	0.8	0.8	10.3	66.8	85.7	none caking	74.4	10.9	9.4
	No.4	1.9	36.5	42.3	14.3	1.30	82.5	6.1	0.7	0.2	10.5	66.0	86.6	none caking	75.7	11.8	7.7

ENCLOSURE (B) 21

STUDIES ON SHALY COAL TAR

by

CHEM. ENG. LT. CMDR. M. KUMAMOTO

Research Period: 1945

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

December 1945

ENCLOSURE (B)21

LIST OF TABLES
AND ILLUSTRATIONS

ENCLOSURE (B)21

SUMMARY

A study was made of the suitability of the distillation products of shaly coal tar for use as boiler fuels. The distillate boiling between 200°C and 350°C is suitable for this purpose. The yield of this product is about 52.9% (by weight) and the physical properties are as follows:

Sp. gr. (25/4) 0.9813

Flash point .... 34.3°C

Freezing point .... 7°C

Viscocity at 30°C,
sec. (Redwood No.1) 64.3

In this work some interesting facts were discovered Unexpected boiling occurs violently at 346°C, distillation temperature, and the phenomenon is due to the alkali-soluble matter. Also when the distillate of the tar is mixed with oil, such as petroleum, shale oil, and soya bean oil, a deposit will be seen. Such a deposit is due to olefine hydrocarbons, mainly di-olefines. Acid materials **tend to prevent this deposition.**

I. INTRODUCTION

Studies on the carbonization of shaly coal were underway at this station, and it was desired to utilize the tarry product formed during this process.

This work was undertaken in an attempt to find a product which would be suitable for use as a boiler fuel. A fuel having a freezing point below (+) 15°C and forming no deposits when mixed with other fuels was desired.

The project was started in January, 1945 and was not completed. The key personnel that worked on project were Chem. Eng. Lt. Cmdr. M. KUMAMOTO and Chem. Eng. Lt. F. HOSINO.

II. DETAILED DESCRIPTION

A. Test Apparatus

The test apparatus for determining the decomposition of tar is shown in Fig. 1(B)21

B. Test Procedure

About 315 grams of shaly coal tar samples were fractionated and the temperatures of the oil and the vapor were observed.

At higher temperatures, gases were evolved and the gas volume was measured. The determination of paraffin was carried out by Holde's Method.

For observation of deposits which occurred by mixing with other fuels, the boiler fuel from this tar was mixed with others in various ratios and kept standing in the open air for 13 days. Upon inclining the mixture, a deposit could be seen at the bottom of the vessel.

C. Experimental Results

When the shaly coal was dry-distilled, crude tar was obtained with a 2 to 4% yield, based on charging stock. The differences of yield were due to variation in the amount of ash in shaly coal. The crude tar has the following properties:

Sp. gr. (20/20)	1.136
Water	6.0
Solid matter included	1.35 %
10% NaOH soluble	32.5 %
Ash	0.19 %
Flash point	99.0°C
Freezing point	11.0°C
Viscocity at 50°C (sec.) (Redwood No. 1)	124

Decomposition temperature is determined by means of measuring the gas volume evolved during distillation. These data are shown in Table I(B)21 and Figure 2(B)21.

The decomposition temperature is about 240°C, and the amount of gas evolved increases with increasing temperature. It is interesting that an unexpected boiling occurs at 346°C, distillation temperature. Therefore, it is necessary to distill in vacuo in order to prevent decomposition, and to keep the distillation below 340°C, for the purpose of safety. Such unexpected boiling is due to the alkali-soluble matter. This is known because in the distillation of tarry acid, the same phenomenon is observed, but does not occur if the oil has had sufficient alkali washing.

An investigation was made of the resulting freezing point and deposition which occurred when mixed with other fuels such as petroleum, soya bean oil, and shale oil.

Crude shaly coal tar was distilled and 10°C fractionations over 200°C were obtained. For each fraction, we determined the above properties. The results are recorded in Table II(B)21.

Paraffin waxes which have the most effect on freezing point begin to appear in the 250° to 260°C fraction, and the amount increases with increasing temperature. Therefore, to remove the paraffin waxes commercially, distillation must be carried out in 2 steps; the first step is 200°C to 270°C and the second step 270° to 340°C. Acidic materials, 10% NaOH soluble, are, for the most part, included in the fraction below 270°C.

Several boiler fuels were prepared and their properties are given in Table III(B)21.

If the acidic material is removed, the freezing point will be raised. For example, in the case of alkali-washed oil, the freezing point is + 25°C and the freezing point of untreated oil is +7°C.

Results of mixing the 200°C - 340°C untreated distillation products with other oils are tabulated in Table IV (B)21.

Since no deposits were observed when the oil had been washed with 80% H_2SO_4, and since alkali washing did not materially effect the formation of deposit, it can be concluded that deposition is due to the presence of olefines in the oil.

Thus, to obtain as much boiler fuel as possible, it is necessary to distill the tar, and the boiling range of 200°C to 340°C is suitable.

The prepared boiler fuel has the following properties:

Yield	52.9%
Sp. gr. (25/4)	0.9813
Red. No. 1	
Vis. at 30°C, sec.	64.3
Flash point	34.3°C
Freezing point	7°C
Ash point	0.0°C
10% NaOH-Soluble	32.0%

D. Summary of Data

A tar-distiller must be concerned with distillation of tar for the preparation of boiler fuel, and the distillate between 200°C and 340°C should be used for this purpose. The yield is about 52.5%.

In regard to the distribution of paraffin waxes and acidic matter, paraffin waxes begin to appear in the 250°C to 260°C fraction and the amount increases with increasing temperature. However, acidic matter is for the most part included in the lower fractions.

At 346°C distillation temperature, an unexpected boiling occurs which is thought to be due to the alkali-soluble material.

A deposit, which is thought to be due to olefines, and mainly di-olefine hydrocarbons, occurs when the oil from tar is mixed with other fuels such as petroleum, shale oil, or soya bean oil. This deposit may be prevented by treating the distilled oil with 10% H_2SO_4.

III. CONCLUSIONS

As a result of this experiment, the decomposition temperature of shaly coal tar was determined, the distribution of paraffin waxes and acidic materials was investigated, as well as the influence of olefine and acidic material on the deposition.

ENCLOSURE (B)21.

Table I(B)21
DETERMINATION OF THE DECOMPOSITION OF TAR

Time	T_2	T_1	Distillate (cc)	Gas (cc)
0.00	20			
19	40			
20	60			
28	80			
53	100			
1.03	110	100	I.D.	
16	120	100	12	
24	140	103	15	
29	160	103	16	
33	180	103	17	
38	200	103	—	
46	220	103	19	
57	240	103	—	
2.04	260	164	20	
8	255	195	27	
9	260	203	30	
14	270	215	44	
19	290	230	65	2
26	310	243	88	—
32	330	350	108	9
35	335	254	127	26
36	340	257	131	39.0
39	350	370	141	95.5
40	352	276	145	110
41	358	280	151	134
43	363	285	160	172

Remarks: T_2 = Oil temperature (°C)
T_1 = Distillation temperature (°C) atomospheric pressure.

Table II(B)21
DISTRIBUTION OF PARAFFIN WAXES AND ACID MATERIALS

Boiling Range °C	Yield (%)	10% NaOH Soluble(%)	Paraffin Wax (%)
I.D.-200	3.71	32.0	
200-210	3.17	39	
210-220	2.88	38	
220-230	4.55	37.5	
230-240	3.81	34.0	
240-250	3.76	35.7	
250-260	3.62	31.0	0.75
260-270	4.94	26.5	1.32
270-280	1.50	24.0	—
280-290	0.69		4.55
290-300	2.44		7.64
300-310	2.13		9.59
310-320	2.41		13.78
320-330	8.27		17.21
330-340	12.57		20.15

ENCLOSURE (B)21

Table III(B)21
PROPERTIES OF PREPARED OILS

Oil	Preparation(°C)			Properties	
	First step	Second step	Sp. gr.(25/4)	Freezing pt. (°C)	Viscosity(sec) Redwood No. I
A	200-340 untreated		0.9707	+7	64.3
B	200-270 Alkali treated	270-340 untreated	0.9667	+25	64.7
C	200-270 Alkali treated	270-340 Alkali-treated and dewaxed	0.9510	+2	43.3
D	200-270 untreated		0.9645	below -16	43.2
E	200-270 untreated	270-340 dewaxed	0.9655	-2	

Table IV(B)21
EFFECT OF MIXING 200-340°C OIL WITH VARIOUS OTHER OILS

Deposition on Mixing with			
Treatment	Petroleum Oil	Soya bean oil	Shale Oil
None	Deposit	Deposit	Deposit
80% H_2SO_4	No Deposit	No Deposit	No Deposit
10% H_2SO_4	No Deposit	No Deposit	Trace
10% NaOH	Deposit	Deposit	Deposit

ENCLOSURE (B)21

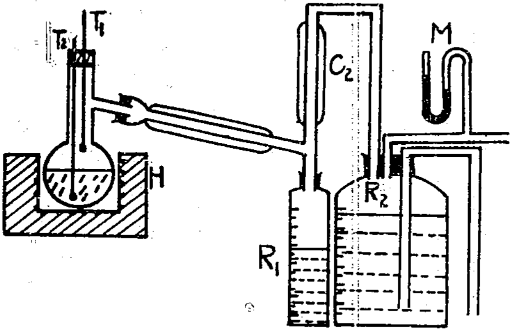

Figure 1(B)21

TEST APPARATUS FOR DETERMINING THE DECOMPOSITION TEMPERATURE

T_1 = Thermometer for distillation temp.
T_2 = Thermometer for oil temp.
R_1 = Receiver for distillate
R_2 = Gas holder
C_1,C_2 Condenser
H Heater

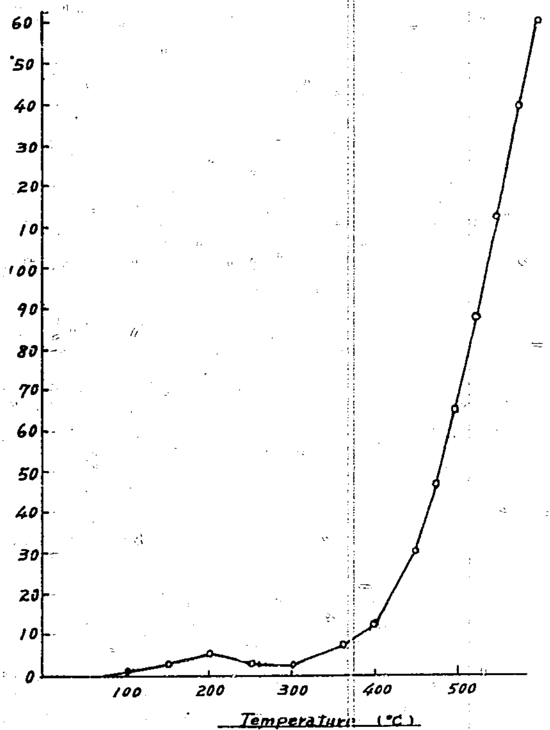

Figure 2(B)21
GAS VOLUME EVOLVED AT DIFFERENT TEMPERATURES

ENCLOSURE (B) 22

STUDIES ON A SIMPLIFIED APPARATUS FOR CARBONIZATION OF SHALY COAL

by

CHEM. ENG. LIEUT. R. SUSUKI

Research Period: 1944-1945

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

December 1945

ENCLOSURE (B)22

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)22

SUMMARY

A simplified apparatus for carbonization of shaly coal was studied with the object of obtaining bunker fuel from its product, tar. After preliminary tests on pilot-plant scale, a plant was designed with a carbonization capacity of about 30 T/day of shaly coal. This plant consisted of four blast-furnace type carbonization retorts, each having about 2m^3 inner volume and equipped with tubular condenser, exhauster and packed columns. In March, 1945, a test plant was operated continuously for 20 days, and about 12 tons of tar were produced (about 2% of shaly coal). From these tests it was determined that the ash content of shaly coal should be less than 65% and the size should be greater than 50mm. Construction of 200 of the 30 T/day plants was started in March, 1945. Forty plants are located at FUKUOKA (Fourth Naval Fuel Depot) and the balance are located at various mines in KYUSHU. About 80 plants were finished by the end of the war.

I. INTRODUCTION

A. History of Project

In December, 1944, orders came to study this project. After fundamental experiments on 1.8 T/day and 7 T/day pilot plants, a treating apparatus of about 30 T/day charge capacity was designed.

The following points were specifically requested for this project:

1. Minimum usage of critical materials.
2. Ease of operation.
3. High capacity.
4. Mass production of apparatus beginning in March, 1945.

B. Key Research Personnel Working on Project

Chem. Eng. Lieut. R. SUSUKI
Chem. Eng. Sub Lieut. R. KAWASHIMA

II. DETAILED DESCRIPTION

A. Apparatus and Procedures

The general layout of the plant is illustrated in Figure 1(B)22. This plant was designed to minimize cracking by removing quickly, by suction fan, tar which is produced by the carbonization of low calorific-value, high ash-content shaly coal. The raw coal is fed into the charge hopper and travels slowly downwards. The retort is heated by the gas generated from the fixed carbon remaining in the shaly coal after it has passed through the carbonization zone. Thus, in this retort, the sensible heat of the gas in employed directly in raising the temperature of the shaly coal up to 700°-800°C. It flows upward through the retort, counter current to the coal, carrying along volatile matter evolved from the coal during distillation.

The temperatures employed in this retort are:

1. Temperature of hot gas leaving retort, 200°-280°C.

ENCLOSURE (B)22

2. Temperature of carbonization zone, 300°-800°C.
3. Temperature of combustion zone, 800°-1,100°C.

The construction materials required for the complete plant are:

Iron and steel	6.8 tons
Fire bricks	5,500 ea.
Fire mortar	5.0 tons
Cement	5.0 tons

This plant can be constructed in about 15 days.

B. Experimental Results

1. Material and Heat Balance (Based on 20 days average results).

a. Material balance (yields per ton of shaly coal).

Input

Shaly coal	1.00 tons
Air	1.88 tons
Total	2.88 tons

Output

Tar	0.022 tons
Ash	0.75 tons
Condensed water	0.10 tons
Non-condensed gas	1.90 tons
Loss	0.11 tons
Total	2.88 tons

b. Heat balance (Basis: 100 kg of shaly coal)

Input	K cals	Percent
Shaly coal (gross cal. value)	265,000	99.6
Water Vapor in air (gross cal. value)	960	0.4
Total	265,960	100.0

Output	K cals	Percent
Tar (gross cal. value)	17,000	6.4
Ash (gross cal. value)	76,500	28.8
Flue gas (gross cal. value) (Non-condensed gas)	149,000	56.0
Tar (sensible heat)	170	0.04
Ash (sensible heat)	6,025	2.27
Flue gas (sensible heat) (Non-condensed gas)	1,710	0.64
Steam in Flue gas (sensible heat)	235	0.09
Condensed Water (sensible heat)	5,670	2.13
Heat in cooling water	2,070	0.78
Heat loss of radiation	7,580	2.85
Total	265,960	100.0%

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2. Physical and Chemical Properties of Feed stock and Products.

a. Feed Stock (Shaly coal from 4th Naval Fuel Depot, FUKUOKA).

Proximate Analysis (%) (as charged)

Moisture	1.30
Volatile matter	22.03
Fixed carbon	15.05
Ash	61.62
Total	100.00

Gross Calorific value, 2,650 K cal/kg.

b. Products.

Properties of the tar are discussed in a subsequent report by Chem. Eng. Lt. Cmdr. M. KUMAMOTO.

Proximate Analysis of Ash (%)

Moisture	0.59
Volatile Matter	2.71
Fixed carbon	6.37
Ash	90.33
Total	100.00

Gross calorific value, 817 K cals/kg.

Orsat Analysis of Non-Condensed Flue Gas

CO_2	8.1
O_2	7.1
C_2H_4	0.4
CO	0.2
H_2	2.3
CH_4	6.4
N_2	75.5

Gross calorific value 700 K cals/m^3.
Condensed water was not analysed.

3. Operating Difficulties.

a. When the particle size distribution of shaly coal varies over a large range (e.g. from powder to 200mm dia.) or ash content of the coal is more than 65%, ash accumulates in the bottom of the retort, and, in this hand-discharged retort, the formation of bad clinkers occurs.

b. Small size coal, less than 55mm in diameter, and especially high content of powder, caused bad distribution of blast in the retort.

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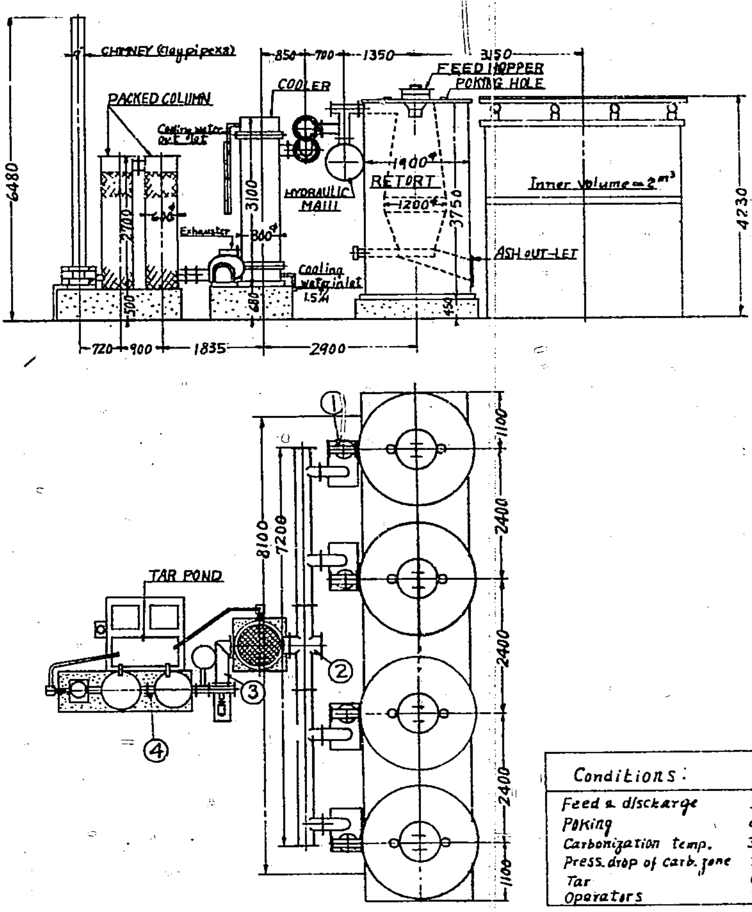
c. The tar loss from the chimney was about 7-9 gm/m^3 of g (e.g. 75-85 lit/day.

III. CONCLUSIONS

A. In spite of the difficulties mentioned above, mass production of this type plant was begun by the Imperial Navy in March, 1945, in order to quickly produce tar for the fleet.

B. The physical and chemical properties of shaly coals were different at every coal mine, so the design details of this apperatus (especially the retort structure), were left up the the engineers of each coal mine.



Conditions:	
Feed & discharge	30 T/D
Poking	every hour
Carbonization temp.	300°~800°C
Press. drop of carb. zone	2~5 mm WG
Tar	600 l/D
Operators	6 men

Item	Packed column	Exhauster	Coolar	Hydraulic main
Description	Bamboo Rasching Ring packed at random 30 X 30 mm 0.5 M³ packed	Turbo-fan at 50 mm WG 47 M³/min	Tubular 2"φ (H-2000) Gas-pipe x44 Cooling Surface = 21.6 M²	200 L Drum
% Tar removed	5+25 %	50 %	15 %	5 %

Gas Temp. (°C)	Gas Velocity (M/sec)	press. (mm-WG)
① 150-250	4.0	-2~-5
② 120-80	3.5	-5~-10
③ 55-40	3.5	-15~-30
④ 50-35	10.5	+50~+75

Figure 1(B)22

SIMPLIFIED CARBONIZATION APPARATUS FOR SHALY COAL

ENCLOSURE (B)22

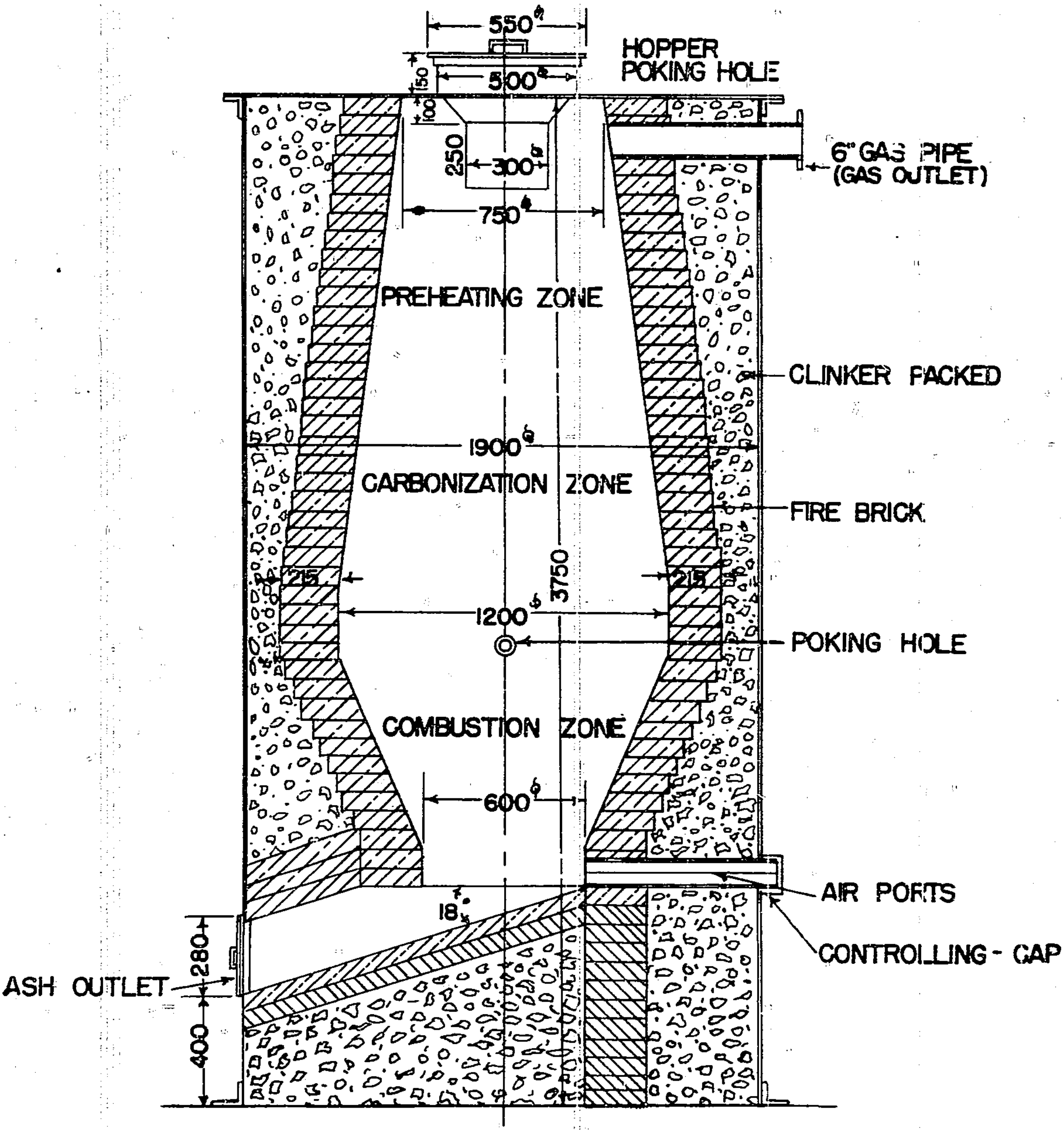


Figure 2(B)22
CROSS-SECTION OF CARBONIZATION RETORT

ENCLOSURE (B) 23

STUDIES ON THE EXTRACTION OF COAL

by

ENG. LIEUT. CMDR. M. KUMAMOTO

Research Period: 1940-1944

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

December 1945

ENCLOSURE (B)23

LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (B)23

SUMMARY

A study was made of the extraction of Fushun coal with basic oil obtained from shale oil. It was found that this basic oil was an effective solvent and 77% of the coal was dissolved by 4-stage extraction at atmospheric pressure. By extracting under hydrogen pressure, the amount of coal dissolved was increased. By distilling off basic oil from the final solution, an ashless coal can be precipated which is suitable for carbon electrodes.

I. INTRODUCTION

In April, 1940, orders were given to study this project. After experiments on laboratory scale, a pilot plant of 10 liters/hr capacity was designed and constructed, but was not operated because the basic oil could not be obtained from MANCHUKUO in 1944. A flow sheet of the pilot plant is given in Plate I (B)23. No large-scale plants using this process have been built.

The key research personnel working on the project were Chem. Eng. Lt. M. MOCHIZUKI and Chem. Eng. Lt. Cmdr. M. KUMAMOTO.

II. DETAILED DESCRIPTION

A. Apparatus and Procedure

A rotating-type autoclave of 5 liters capacity was used for this project. The coal was ground and sized to pass a 60 mesh screen. Basic oil produced at FUSHUN was used as a solvent.

One part (by weight) of dried coal and three parts of oil were mixed to a paste in the autoclave.

After air in the autoclave was replaced by hydrogen, the pressure of hydrogen was raised to 100 kg/cm^2. The rotating autoclave was heated gradually and held at the desired reaction temperature for the required time. After cooling and releasing the pressure, the products were removed from the autoclave and filtered through a glass filter. The residue of filtration was washed, first with pyridine until the filtrate was colorless, and then with benzene until the odor of pyridine disappeared.

The washed residue was then dried and weighed. The percentage of extraction was calculated by the following formula:

$$\text{Percentage of Extraction} = \frac{(\text{weight of sample coal}) - (\text{weight of residue})}{\text{weight of sample coal}} \times 100$$

B. Experimental Results

The properties of Fushun coal and the basic oil obtained from shale oil are given in Tables I(B)23 and II(B)23. The basic oil was obtained by caustic neutralization of the sludge from acid treatment of shale oil. This oil was rich in quinoline and related compounds.

The effect of temperature, time, and pressure on the extraction were investigated and the results are given in Tables III(B)23, IV(B)23 and V(B)23.

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It was found that the extraction of coal is possible under atmospheric pressure at boiling temperature of the solvent. Consequently, further experiments were made to investigate extraction of coal at atmospheric pressure. The basic oil was fractionated into several cuts.

At first the extraction of coal was carried out with the lowest boiling solvent fraction, then the residue was extracted with the next higher boiling range fraction, and so on.

Experimental results are shown in Table VI(B)23 for 4-step extraction and in Table VII(B)23 for 3-step extraction. Both series of extractions were carried out under atmospheric pressure with no hydrogen present.

III. CONCLUSIONS

1. The influence of temperature, time and hydrogen pressure on the solvent extraction was investigated and it was found that the temperature effect was the most significant. Optimum conditions for extraction in presence of hydrogen were found to be 1-2 hours, 350-400°C and 50-100 kg/cm^2.

2. Extraction of the coal in the presence of hydrogen under pressure increased the percentage of coal dissolved. This is believed to be due to the peptization of the coal being facilitated as a result of slight hydrogenation. Up to 89% of the coal was dissolved under 100 atm. of hydrogen pressure, whereas at atmospheric pressure, using 4-stage extraction, a 77% extraction was obtained.

3. The solution of basic oil and dissolved coal was not considered as a source of boiler fuel due to scarcity and poisonous nature of the solvent. By distilling off the basic oil, an ashless coal can be obtained which is suitable for manufacture of carbon electrodes.

Table I(B)23
ANALYSIS OF FUSHUN COAL

Proximate Analysis (%)		Ultimate Analysis (%)	
Moist	4.16	C	73.7
Vol. M.	47.52	H	6.6
Fix. C.	41.67	S	0.7
Ash	6.65	N	1.7
		O	17.3

ENCLOSURE (B)23

Table II(B)23
DISTILLATION OF BASIC SHALE OIL

Boiling Range (°C)	Yield (%)	Remarks
From I.P. to 200	2	"Distillation above
From I.P. to 225	8	250°C was
From I.P. to 250	14	made under vacuum of
From I.P. to 275	26	10mm Hg"
From I.P. to 300	42	Distillation temperatures
From I.P. to 325	60	were corrected to atmos-
From I.P. to 350	85	pheric pressure.

Table III(B)23
EFFECT OF TEMPERATURE*

Reaction Temp. (°C)	Percentage Extract (%)	Final Pressure (kg/cm^2)
250	8.0	99.8
300	21.3	99.4
350	87.1	98.6
400	88.5	91.3
450	68.2	83.7

* Sample in each case contained 115gm coal, 310gm solvent, and was reacted for 2 hours under an initial pressure of 100 kg/cm^2.

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Table IV(B)23
EFFECT OF PRESSURE*

Initial Pressure with H_2 (kg/cm^2)	Percentage of Extract (wt.%)
0	67.7
30	83.3
50	88.1
80	89.0
100	87.0

* Sample in each case contained 100gm coal, 300gm solvent and was reacted for 2 hours under a reaction temperature of 350°C.

Table V(B)23
EFFECT OF TIME*

Reaction Time (hr)	Percentage of Extract (wt.%)	Final Pressure (kg/cm^2)
½	65.6	99.4
1	84.5	99.0
2	85.4	98.3
4	78.0	90.8

* Samples in each case contained 105gm coal, 301gm solvent. and was reacted under a temperature of 350°C with initial pressure (H_2) of 100 kg/cm^2.

Table VI(B)23
4-STEP EXTRACTION*

Step	Matter Extracted (gm)	Solvent		Reaction Temp. (°C)	Percentage of Extract (wt.%)
		Volume (cc)	Boiling Range (°C)		
1	400	2000	I.D. to 250	230	7.5
2	235	1012	250 to 300	280	11.9
3	213	1065	300 to 350	330	23.0
4	119	342	350 to 400	380	35.0
				Total	77.4

Table VII(B)23
3-STEP EXTRACTION*

Step	Matter Extracted (gm)	Solvent		Reaction Temp. (°C)	Percentage of Extract (wt.%)
		Volume (cc)	Boiling Range (°C)		
1	400	2000	230 to 280	250	11.4
2	203	745	280 to 330	300	13.3
3	214	592	330 to 360	350	27.0
				Total	51.7

* In each case, reaction time was 1 hour.

ENCLOSURE (B)23

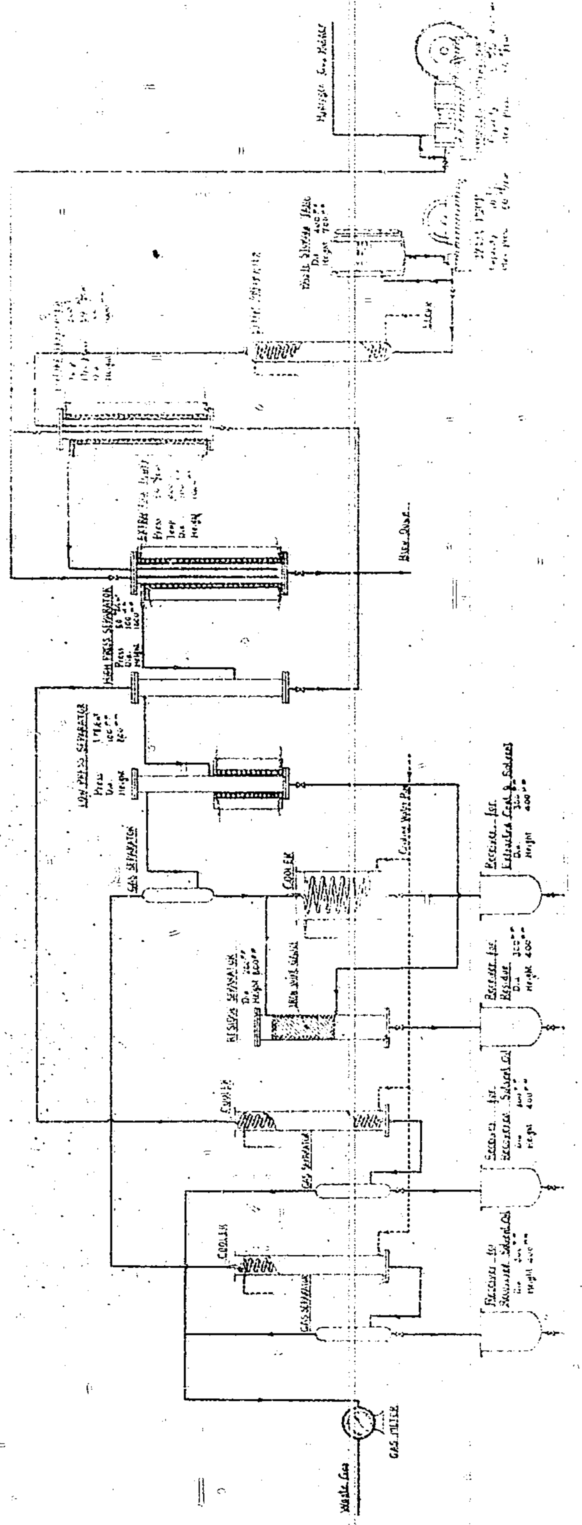

Figure 1(B)23

FLOW SHEET OF PILOT PLANT FOR SOLVENT EXTRACTION OF COAL

ENCLOSURE (B)23

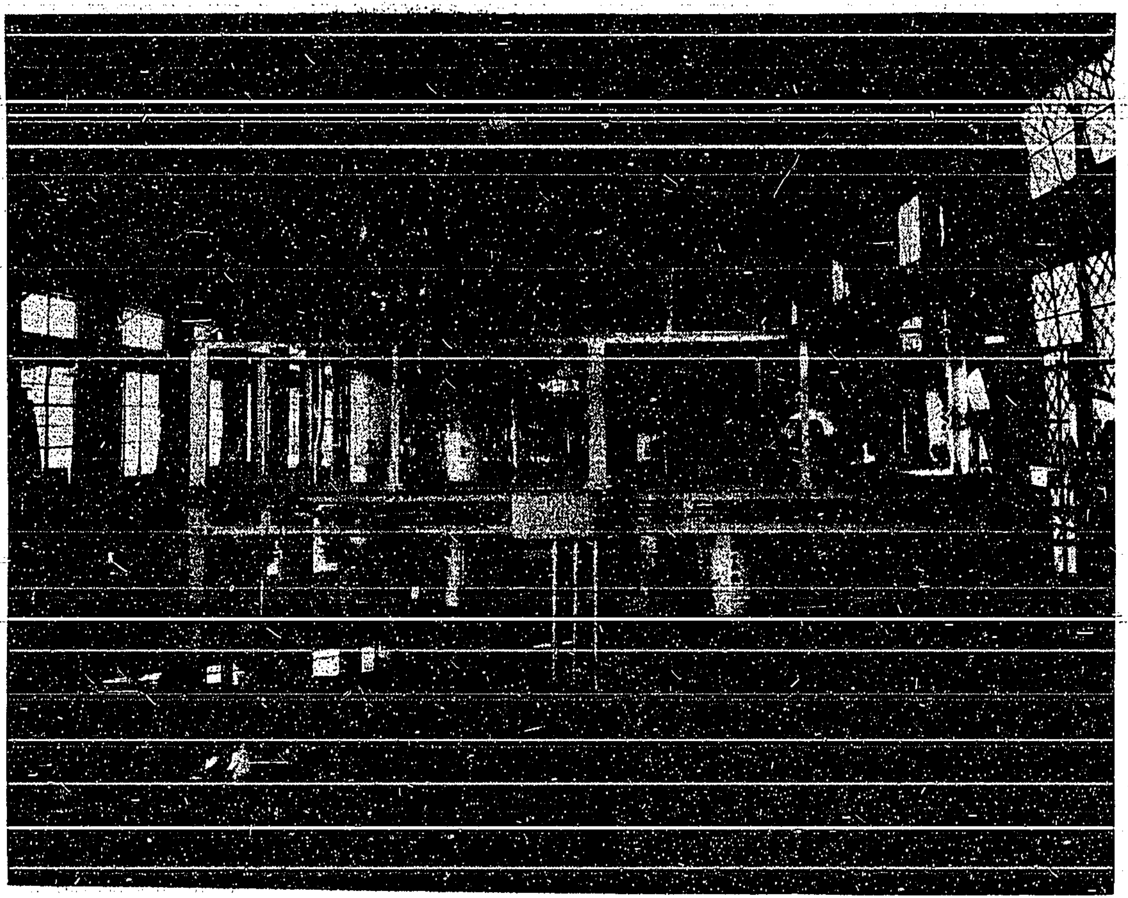

Figure 2(B)23

SOLVENT EXTRACTION PILOT PLANT OF BASIC OIL FROM SHALE

ENCLOSURE (C)

ENCLOSURE (C)

LIST OF JAPANESE REPORTS ON CONVERSION OF COAL TO OIL, FIRST NAVAL FUEL DEPOT, OFUNA

(Forwarded through ATIS to the Washington Document Center)

ENCLOSURE (C)

ATIS No. for all Documents Listed Below is 4579

NavTechJap No.	Title	Author	Year
ND26-0008.1	The Manufacture of Industrial Hydrogen.	H. FUJIMOTO	12-29
ND26-0008.2	Thermal Cracking of Diphenyl Ether and Diphenyl Oxide in a High Pressure Hydrogen Atmosphere.	T. OGAWA	24-2-31
ND26-0008.3	Dehydration of Diphenylene Oxide in a High Pressure Hydrogen Atmosphere.	T. OGAWA I. TAKAHASHI	12-3-31
ND26-0008.4	Thermal Decomposition of a-and b-Dinaphthylene Oxide in a High Pressure Hydrogen Atmosphere.	T. OGAWA	30-5-31
ND26-0008.5	Thermal Decomposition of Tetrahydro Diphenylene Oxide in a High Pressure H_2 Atmosphere.	T. OGAWA	30-5-31
ND26-0008.6	Thermal Decomposition of Phenol in a High Pressure Hydrogen Atmosphere.	T. OGAWA I. TAKAHASHI	30-5-31
ND26-0008.7	Thermal Changes of Aromatic Compounds under High Pressure Hydrogen.	S. YAMAGUCHI G. FUJII	17-2-33
ND26-0008.8	Preparation of Hydrogen by Cracking of Methane.	T. NAMIKAWA M. YAMAMOTO	6-35
ND26-0008.9	Hydrogenation of Coal.	T. YOKOTA	10-11-35
ND26-0008.10	Liquid Fuel in Germany, Especially the Hydrogenation of Brown Coal.	K. ANDO	27-4-36
ND26-0008.11	Studies on Coal Hydrogenation. I. Influence of the size of Paste. II. Influence of Viscosity on Paste. III. Activity of Ferric Oxide as a Catalyst.	T. OGAWA T. TAKAHASHI	1- 6-36
ND26-0008.12	Studies on Coal Hydrogenation. IV. Influence of Reaction Temperature. V. Influence of Reaction Pressure. VI. Influence of Reaction Time. VII. Influence of Heating Velocities on Coal.	T. OGAWA T. TAKAHASHI	10-6-36

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ND26-0008.13	Thermal Treating of Coal Tar in High Pressure Hydrogen Atmosphere	T. OGAWA T. TAKAHASHI	15-10-36
ND26-0008.14	Hydrogenation of Coal in England and Germany.	Y. OSHIMA	22-11-37
ND26-0008.15	Catalytic Hydrogenation of Anthracene.	T. YOKOTA	28- 7-38
ND26-0008.16	On the Reaction of Coal Hydrogenation.	K. MITSUI	10- 4-39
ND26-0008.17	Studies on Coal Hydrogenation XXI. Hydrogenation Test of Various Coals in Japan.	T. SUZUKI I. TAKAHASHI	1-10-39
ND26-0008.18	Studies on Coal Hydrogenation. On the Physical Properties of Charging Paste.	T. SUZUKI R. YUMEN	10- 4-40
ND26-0008.19	Studies on Coal Hydrogenation. VI. On the Reaction Mechanism.	T. SUZUKI T. TAKAHASHI A. MORITA	25-11-41
ND26-0008.20	On the Hydrogenation of Aromatic Hydrocarbon Mixture.	T. SUZUKI	25-11-41
ND26-0008.21	On the Catalytic Hydrogenation of Phenol with reduced Nickel Oxide.	I. WATANABE	10-21-41
ND26-0008.22	On the Catalytic Hydrogenation of Anthracene with Nickel Oxide.	I. WATANABE	15-12-41
ND26-0008.23	The Mean Chemical Reaction Velocity on the Catalytic Surface in Hydrocracking of Oha Light Oil.	K. MITSUI R. YUMEN A. MORITA U. SATO	17-12-41
ND26-0008.24	On the Catalytic Reduction of a Mixture of Phenol and Anthracene with Nickel-Oxide.	I. WATANABE	17-12-41
ND26-0008.25	Influence of Space Velocity on the Hydrogenation of Coal.	K. MITSUI B. HASEIDA K. SONE H. NISHIKAWA	5- 5-43
ND26-0008.26	Nickel Catalyst for Catalytic Hydrogenation.	K. MITSUI U. SATO	16- 6-43
ND26-0008.27	On the Chemical Analysis of the Hydrogenation products of Monovinyl Acetylene.	T. YAMAMOTO Y. MIZUTANI	16- 8-43
ND26-0008.29	On the Mechanism of the Catalytic Hydrogenation with Molybdenum Sulphide.	K. MITSUI K. TAMURA A. KAMOGAWA	9- 4-44

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NavTechJap No.	Title	Author	Year
ND26-0008.30	On the Reaction Capacity of a Pilot Plant for the Hydrocracking of Gasoline.	K. MITSUI R. YUMEN M. YANAGITA H. NISHIKAWA O. SATO	25- 4-44
ND26-0008.31	Fischer-Tropsch's Method.	M. TAKEI	5- 7-38
ND26-0008.32	Low Temperature Carbonization of Coal Part I.	N. TAMAKI S. YAMAGUCHI H. SHIMAMURA F. KAWASE T. IRIYE S. MAITANI	7-27
ND26-0008.33	Low Temperature Carbonization of Coal. Part II, Davidson's Plant. Part III, Dry Distillation of Shale Rock.	N. TAMAKI S. YAMAGUCHI H. SHIMAMURA	12-27
ND26-0008.34	Low Temperature Carbonization of Coal. Part IV, Thyssen's Plant.	N. TAMAKI S. YAMAGUCHI H. SHIMAMURA	4-28
ND26-0008.35	Low Temperature Carbonization of Coal Part V, Small Vertical Type Plant.	N. TAMAKI S. YAMAGUCHI H. SHIMAMURA	5-28
ND26-0008.36	LoW Temperature Carbonization of Coal Part VI, Brown Coal of Chosen. (Korea)	N. TAMAKI S. YAMAGUCHI H. SHIMAMURA	11-28
ND26-0008.37	Studies on the Low Temperature Carbonization of Coal.	S. YAMAGUCHI S. MAITANI	6-29
ND26-0008.38	Reports on the Low Temperature Carbonization of Coal and Brown Coal from Korea.	N. TAMAKI T. NAMIKAWA S. YAMAGUCHI H. SHIMAMURA S. MAIYA	7- 7-30
ND26-0008.39	Reports on the Low Temperature Carbonization of Coal. (Fushun Coal).	T. NAMIKAWA H. SHIMAMURA S. MAIYA	1- 8-30
ND26-0008.40	On the Asphalten in the Low Temperature Coal Tar.	S. YAMAGUCHI	25- 4-31
ND26-0008.41	Reports on the Low Temperature Carbonization of Coal Part III.	S. YAMAGUCHI S. MAIYA S. KITAMURA	15- 5-31
ND26-0008.42	On the Components of Low Temperature Coal Tar.	R. NAKAI	15- 8-31

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NavTechJap No.	Title	Author	Year
ND26-0008.43	Studies of the Manufacture of Phenol from Acidic Matters in Low Temperature Carbonization Tar.	C. FUJIO A. SHIRAI H. SHIMAMURA T. HAYANO	7-34
ND26-0008.44	Gas Producer Using Powdered Coal.	T. NAMIKAWA H. SHIMAMURA M. YAMAMOTO	1-12-30
ND26-0008.45	Reaction between Methane and Steam in the Presence of Catalyst.	H. FUJIMOTO S. KUBO	9-33
ND26-0008.46	Complete Gasification of Coal, Part II, Relation of Cokes to Carbon Dioxide.	T. NAMIKAWA	1- 9-33
ND26-0008.47	Studies on the Complete Gasification of Coal Part III, Experiments with Commercial Furnace.	T. NAMIKAWA S. DOI M. YAMAMOTO	21- 4-33
ND26-0008.48	Complete Gasification of Coal. Part I, Relation between Carbonization and Heating Velocity.	T. NAMIKAWA	1- 9-33
ND26-0008.49	Complete Gasification of Coal Part IV. Relation between Carbonization Speed of Coal and the Electrical Conductance of Cokes.	T. NAMIKAWA	11-34
ND26-0008.50	Complete Gasification of Coal. Part V, Effect of Ash on the Formation of water Gas.	T. NAMIKAWA	11-34
ND26-0008.51	Complete Gasification of Coal. Part VI, Cracking of Methane by White Heaked Cokes.	T. NAMIKAWA	3-35
ND 26-0008.52	Complete Gasification of Coal. Part VIII, Effect of Carbonization Speed on the Combustion of Cokes. Part IX, Effect of Carbonization Speed on the Temperature-rise by the Combustion of Cokes. Part X, Effect of Volume of White Heated Layer of Cokes on the Formation of Water Gas.		
ND26-0008.53	Complete Gasification of Coal, Reaction of Cokes to Steam.	T. NAMIKAWA H. KUNISUE	9-35

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ND26-0008.54	Studies on the Perfect Gasification of Coal. Dry Distillation of Coal in the Atmosphere of Gas and Steam.	T. NAMIKAWA H. KUNII	5-36
ND26-0008.55	Studies on the Perfect Gasification of Coal. Part XII. Influence of Heating Velocity of Coal.	T. NAMIKAWA H. KUNII	9-37
ND26-0008.56	Studies on the Perfect Gasification of Coal. Part I. On the Influence of Metallic Oxides in the Reaction of Steam in Coal.	T. ITAKURA T. FUJII	2-10-39
ND26-0008.57	Rapid Determination Method of Ash in Heijo's Coal.	T. YOSHIHIRO T. KONO	9-26
ND26-0008.58	Studies on Water Contained in Coal.	S. SUMIMOTO K. OKUMA	12-27
ND26-0008.59	Studies on Coal.	S. KOMATSU	10-28
ND26-0008.60	Quantitative Testing Method of Water in Coal.	T. OGAWA S. SUMIMOTO F. NEMOTO	12-28
ND26-0008.61	Quantitative Testing Method of Volatile Matters in Coal.	T. OGAWA S. SUMIMOTO F. NEMOTO	12-28
ND26-0008.62	Quantitative Testing Methods of Ash in Coal	T. OGAWA S. SUMIMOTO F. NEMOTO	12-28
ND26-0008.63	Utilization of Residue from Coal Washing. Part I.	T. YOSHIHIRO T. KONO	3-29
ND26-0008.64	Testing Method of Coal. (Determination of Moisture in Coal.)	T. OGAWA T. YOSHIHIRO	15- 8-30
ND26-0008.65	Specific Heat of Coal.	T. YOKOTA E. ISOGAI	15-12-31
ND26-0008.66	Researches on Coal.	S. SUMIMOTO	8-35
ND26-0008.67	Soya-Bean Industry in Manchuria and Brown Coals in Korea.	T. NAMIKAWA T. TAKEI	1- 9-36
ND26-0008.68	Coal Resources in China.	T. NAMIKAWA T. TAKEI	12- 2-37
ND26-0008.69	Coal Resources in East Siberia.	M. SASAKI T. TAKEI	8- 6-38

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NavTechJap No.	Title	Author	Year
ND26-0003.70	Carbon-Dust Explosion.	N. OSAKA	5-12-39
ND26-0003.71	Coal Resources in the South Asia-District.	K. MITSUI T. KIKKAWA	31- 3-44
ND26-0003.72	Experiments on the Cracking of Shale Oil.	K. KUDO K. KOIKE Y. MIYATA	9-27
ND26-0003.73	Basic Compounds of Shale Oil.	T. EGUCHI	11-28
ND26-0003.74	The poisonous Characteristics of Shale Oil.	INADA	16- 3-33
ND26-0003.75	Shale and Its Chemical Industry in the World	T. NAMIKAWA T. TAKEI	10- 6-36
ND26-0003.76	Thermal Cracking of Shale Oil in High Pressure Hydrogen Atmosphere.	T. OGAWA I. TAKAHASHI K. MUNECHIKA	10-36

ENCLOSURE (D)

RESTRICTED

ENCLOSURE (D)

REPORT ON RESEARCH ON THE FISCHER TROPSCH PROCESS AT THE KYOTO IMPERIAL UNIVERSITY

ENCLOSURE (D)

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ENCLOSURE (D)

I. INTRODUCTION

This report summarizes technical information pertaining to research on the Fischer-Tropsch process carried on by Prof. G. KITA and staff at the Kyoto Imperial University. The following Japanese personnel were interviewed by representatives of the Petroleum Section of NavTechJap during the period 15-17 January 1946:

Prof. G. KITA - Retired
Prof. S. KODAMA - In charge of Fischer-Tropsch
Asst. Prof. K. TARAMA

The details of the work at KYOTO are described in detail in various publications (mostly in German), copies of which were secured. This report serves only to outline the scope of the work and to present certain significant points covered in the interviews.

II. HISTORY OF WORK

Work on the Fischer-Tropsch synthesis under Prof. KITA at the Institute of Physical and Chemical Research was started in 1927, one year after publication of Franz Fischer's first paper in Brennstoff Chemie on "Die Erdol" Synthesis".

The work was begun from a purely scientific view-point and the first papers were published in 1929 by Mr. S. KODAMA, Prof. KITA's first assistant. The early work was concerned primarily with testing various types of catalysts and investigation of operation variables, in small laboratory-scale glass apparatus at normal pressure. Work on alloy catalysts was started in 1934.

In 1937 work was started an iron catalysts for use at normal pressure. This work continued through the war with a view toward developing a satisfactory substitute for cobalt in existing plants. During the period 1937-1941, studies were made in a semi-commercial normal pressure pilot plant at the Institute, with a charge capacity of about $100m^3$/hr of water gas. At the request of the Japanese Army this plant was transferred in 1942 to the Army Fuel Research Institute at FUCHU for use in the testing of natural iron catalysts.

In 1939 work was started on the middle pressure synthesis (10-15 atm), with special emphasis on the use of iron catalysts. All work at middle pressure at the University was done in small, single tube apparatus, containing about 40cc of catalyst, and with synthesis gas charge capacity of about 4 liters per hour (atm. press. and temp.). Pilot plant tests on the middle pressure synthesis were made in a small, 10 m^3/hr. unit constructed at RUMOI, Hokkaido, by the MITSUI interests. A full-scale reactor was installed in the Takikawa Fischer-Tropsch plant in 1943, to test iron catalysts, and it was planned to install an additional 15 sets.

In 1944 studies were made at KYOTO on the natural iron catalyst discovered by Prof. MATSUBARA at the Tokyo Imperial University. Tests were made at both normal and middle pressure, and studies were made on additives to improve the effectiveness of this catalyst.

During the period 1938-1945, studies were also made of the application of the Fischer-Tropsch principle for production of propanes and butanes for use in aviation gasoline synthesis.

Theoretical investigations on the Fischer-Tropsch reaction mechanism, including X-ray studies, were carried on during the period 1937-43.

For the future it was planned to continue studies on reaction mechanism, and also to develop an iron catalyst for middle pressure which would permit operation at temperatures lower than required with present iron catalysts.

III. NORMAL PRESSURE CATALYST STUDIES

It was stated that no catalyst superior to the conventional cobalt-thorium catalyst had been developed. Activity equal to that of cobalt was obtained on laboratory test scale with a nickel catalyst of the composition:

$$Ni + 15\% Mn + 3\% ThO_2 + 125\% \text{ Kieselguhr}$$

This catalyst, however, was very sensitive to traces of alkali (Na_2CO_3) and in preparation of same, the wash had to very carefully controlled to obtain the optinum alkali content.

In 1937, after rights to use and prepare the German cobalt catalyst had been secured by the MITSUI interests, work at KYOTO was concentrated on the development of a cheap iron catalyst as a substitute for cobalt in normal pressure synthesis. Many catalysts were tested, and are described in detail in the several publications listed in Part A of Appendix 1. It was found that boric acid was an effective additive for iron catalysts, and that the most effective catalyst developed for normal pressure operation had the following composition:

$$Fe + 25\% Cu + 2\% Mn + 125\% \text{ Kieselguhr} + 15\% H_3BO_3 + 3\% K_2CO_3$$

Experiments showed that the H_3BO_3 promoted the adsorption of active hydrogen, whereas alkali promoted adsorption of carbon monoxide. The product from a high alkali catalyst was also less saturated than from a high acid catalyst. The effects were almost independent, so that when H_3BO_3 was added to a catalyst, alkali would also be added to increase the adsorption of carbon monoxide. It was found that for middle pressure synthesis, the use of H_3BO_3 was actually harmful, apparently due to over-adsorption of hydrogen as result of the higher partial pressure.

After the natural catalyst was discovered, Kyoto University undertook, at the request of Tokyo University, tests on this catalyst at both normal and middle pressures. The natural catalyst utilized was a base yellow earth or ochre obtained form NIWASAKA, in FUKUSHIMA Prefecture, between TOKYO and SENDAI, and from certain other areas in Japan. A typical analysis(%) is as follows:

Moisture........	6.4
Ignition Loss...	20.7
Fe_2O_3	64.8
Undetermined ...	8.1
	100.0

X-ray diffraction analysis of this material indicated the crystal form to be alpha $Fe_2O_3 \cdot H_2O$. The ore also probably contained some SiO_2 and $CaCO_3$.

The best natural earth normal pressure catalyst tested at KYOTO had the following composition:

$$\text{Ochre} + 1\% Cu + 1\% H_3BO_3 + 6\% K_2CO_3$$

A comparison of several of the more promising normal pressure catalysts is given in Table I(D). In the case of the Kyoto Laboratory, the tests were made in small laboratory glass apparatus. Gasoline was the material absorbed on silica gel or by a dry-ice condenser, and kerosene was the product from the water condenser.

From this table it is noted that the best natural catalyst gave a yield of 86 gm/m^3, which was lower than results of the best synthetic iron catalyst, (98-102 gm/m^3,) which in turn was lower than results of the best cobalt catalysts, 151-158 gm/m^3. It was stated that, at normal pressure, the synthesis reactions were as follows for iron and cobalt catalysts.

Catalyst	Reaction
Iron	$2\,CO + H_2 \rightarrow CH_2 + CO_2$
Cobalt	$CO + 2H_2 \rightarrow CH_2 + H_2O$

In the case of iron catalysts, however, when gas with a CO:H$_2$ ratio of 2:1 was used, catalyst life was very short due to carbon poisoning of the surface. When gas with higher hydrogen content was used, the life was longer, but yields were lower as compared with cobalt catalyst.

In Table III(D) are summarized pilot plant tests on miscellaneous catalysts. The normal pressure catalyst, Fe + 25% + 2% Mn + 125% kieselguhr + 20% H_3BO_3 4% K_2CO_3, was also tested in a fullscale reactor at the Miike Synthetic Oil Co., but results were unsatisfactory since only 225°C reaction chamber temperature could be reached whereas the minumum for this catalyst was 235°C.

Data on pilot plant tests in normal pressure units at OMUTA are contained in publications listed in Part E. of Appendix I.

IV. MIDDLE PRESSURE CATALYST STUDIES

Increasing the reaction pressure greatly favors the iron catalyst, and work within recent years has been concentrated on a study of various catalysts and suitable operating conditions for the so-called middle pressure synthesis. In Table IV(D) laboratory data are summarized which show the effect of increasing pressure, (and also the effect of increasing K_2CO_3 content), on an iron-copper-kieselghur base catalyst. It is noted that optimum yields are obtained in the range of 10-15 atm., and with 6% K_2CO_3 content.

In Table II(D) laboratory data are summarized comparing various middle pressure catalysts.

A catalyst of the composition Fe +25%Cu +125% kieselguhr + 4-6% K_2CO_3 was manufactured in the 200 litre/day catalyst-manufacturing plant for tests at TAKIKAWA. Later it was found that the addition of magnesium increased oil yields, and it was stated that the best middle pressure catalyst developed to date has the composition:

Fe + 25%Cu + 5% Mg + 125% kieselguhr + 6% K_2CO_3.

Test data on this catalyst are also given in Table II(D). The opinion was advanced that, under operating conditions of 15 atm. pressure, 220-240°C, reaction temperature and synthesis gas with H$_2$:CO ratio of 1:1, yields equal to those of cobalt would be obtained. Furthermore, a catalyst life of 6 months should be expected, compared with 2 months for a cobalt catalyst. It was predicted that this performance could be realized on commercial scale.

The only natural iron oxide catalyst tested at middle pressure at KYOTO is shown in Table II(D). This same catalyst was also manufactured by the Japanese Army Fuel Research Institute at FUCHU, for use in full scale tests at TAKIKAWA. It was believed that further improvement could be made by study of new promoters for the natural catalyst, especially in the direction of increasing copper content.

In part B of Appendix I is a list of the papers obtained from the University relating to research on middle pressure synthesis.

V. CATALYST PREPARATION

A. Precipitated Iron Catalysts - Middle Pressure

The following procedure was used for preparation of a catalyst of the composition Fe + 25% Cu + 125% kieselguhr + 6% K_2CO_3. This catalyst was manufactured at the Kyoto Imperial University for full scale testing at TAKIKAWA.

Metallic iron (10 kg) and copper (2.5 kg) in the form of plates about 5-10 inches square, were dissolved in the theoretical quantity of 52% commercial nitric acid. Electrolytic grades of iron and copper were used, although it was stated that ordinary mild steel could be utilized. A stainless steel vessel 70cm in diameter and 80cm high, equipped with a stirrer, was used. Temperature was maintained at 50-70°C by external water cooling. The solution was removed to a stainless steel precipitation vessel, 1 meter x 1 meter (capacity 750 lit), equipped with a 60 RPM stirrer. 12.5 kg of kieselguhr were added. The dieselguhr was obtained from the Island of OKI in the Japan Sea, and was a natural kieselguhr graded by water sedimentation. This particular material had been standardized on at KYOTO since 1939 for use in all catalyst work. No further treatment was given to the kieselguhr prior to use.

While maintaining stirring, 20% Na_2CO_3 was added in 10 minutes until a pH of 7.8 was reached. The Na_2CO_3 solution was made by dissolving commercial grade Na_2CO_3 in city water, containing some chlorine. (It was stated that distilled water might be more desirable, but the supply was limited at the University.) Stirring was continued for 30 minutes at room temperature; then the solution was pumped with a diaphragm pump through 18-8 stainless steel lines, to a cast iron filter press equipped with thirty 24-inch plates and cotton filter cloth. The filtering required a period of about one hour, and the filter cake was washed with city water for a period of 6-7 hours.

The cake was removed by hand and transferred to a 1.3m x 1.3m. enamel lined cylindrical wash vessel. $1.5m^3$ of water was added and the mixture stirred for one hour, at room temperature, with a high speed movable stirrer to make a slurry. The slurry was again transferred with the diaphragm pump to the filter press, and the filter cake washed 5-6 hours with city water at room temperature until the pH of the wash water dropped to 7.0-7.1. The cake was then transferred to a dough mixer containing two rotating spiral-type knives in a horizontal trough about 1.5m. long. A saturated solution of K_2CO_3 (containing 0.6 kg of K_2CO_3) was added and kneading continued for two hours. The mix was then transferred to enamel-lined trays about 5cm x 80cm x 50cm, and placed in a circulating hot-air type drier maintained at 90°C. After five hours the half-dried catalyst was removed and pressed by hand through copper wire screen containing 20 mesh per linear inch. The pressed material was placed again in the drier and held at 90°C for five hours. The dried catalyst was sifted over 20-mesh copper screen to remove fines, and the final material was packaged in wooden boxes or steel drums for shipment.

The procedure for activating the middle pressure catalyst was to introduce the catalyst into the reactor and reduce with the regular synthesis gas at 250°C and normal pressure for a period of 24 hours. Then the temperature was decreased to 180°C, requiring about 10 hours, and the pressure raised to the operating level. The temperature was then raised to the required reaction temperature, 220°C, in about 30 hours.

A more effective catalyst developed for middle pressure synthesis had the follwoing composition:

$$\text{Fe} + 25\%\ \text{Cu} + 5\%\ \text{Mg} + 125\%\ \text{kieselguhr} + 6\%\ K_2CO_3$$

This catalyst is prepared by an identical procedure as described above except that MgO, $MgCO_3$ or $MgNO_3$ is added to the cupric and ferric nitrate solution in the solution vessel. Although 5% of Mg is added in this step, the actual content in the final catalyst is less than this due to incomplete precipitation.

B. Natural Iron Catalyst - Middle Pressure

The best natural catalyst had the following composition:

$$\text{Ochre} + 0.5\%\ \text{Cu} + 0.5\%\ \text{Mn} + 6\%\ K_2CO_3$$

For preparation of this catalyst, OCHRE, a natural iron ore, was obtained from NIWASAKA, Fukushima Prefecture, between TOKYO And SENDAI. The ochre was washed at the mining plant prior to delivery. Chemically pure grades of $Cu(NO_3)_2$ and $Mn(NO_3)_2$ in concentrated solutions were added in the required amounts; then K_2CO_3 in concentrated solution was added in the required amount and the massknеaded. In the Army method used at FUCHU, the kneaded mass was pressed through 20 mesh screen and dried prior to shipment. At KYOTO, more dilute solutions were used to permit easier and more thorough kneading. The moist mass was then partially dried, pressed through 20-mesh screen, and dried as described above.

C. Iron Catalysts - Normal Pressure

The procedure is similar to that described above for either precipitated or natural catalysts, except that H_3BO_3 in the required amount is added with the saturated K_2CO_3 solution.

I. MISCELLANEOUS

In connection with the use of iron catalysts, it was found necessary to remove all forms of sulphur, although their sensitivity was lower than that of cobalt at normal pressure, and even less at middle pressure. Halogens are also definitely poisonous to this catalyst and lead, tin, and phosphorous may also be harmful. Gases such as oxygen, carbon dioxide and nitrogen are not harmful.

In connection with the synthesis of iso-octane, considerable work was done on the preparation of gaseous hydrocarbons from carbon monoxide and hydrogen. It was stated that a process had been developed whereby, by using a catalyst of the composition,

$$\text{Fe} + 25\%\ \text{Cu} + 125\%\ \text{kieselguhr} + 3\%\ K_2CO_3$$

and operating at 15 atm, 275-280°C, and with a $CO:H_2$ ratio of 1:1, about 44%

of the synthesis gas could be converted into light hydrocarbons containing 50% of propanes and 20% of butaines. Refer to Part D of Appendix I for a list of publications obtained relating to work on this project.

In Appendix II is given a list of patents relating to the Fischer-Tropsch synthesis obtained by Professor KITA and staff at the KYOTO Imperial University.

ENCLOSURE (D)

Table I(D)
LABORATORY COMPARISON OF CATALYSTS FOR NORMAL PRESSURE SYNTHESIS

Composition of Catalysts	Composition of Raw-gas. ($CO:H_2$)	Gas Flow L/hr	Reaction Temp. (°C)	Oil Yield (cc /m^5)			Life of Catalysts	Name of Investigator
				Kerosene	Gasoline	Total		
Co-15%Mn-150% Kieselguhr	1:2	4	200	72.5	72	144.5	more then one month	Fischer & Koch
Co-18%ThO_2-150% Kieselguhr			190	100	53	153	about two months	
Co-5%Cu-12%U_3O_8-4%Mn-100%KSG		6	195			158.2	-	TSUTSUMI
Co-7%Cu-5%ThO_2-2.5%U_3O_8-125%KSG		4	200	97	54	151	-	KITA Laboratory
Fe-25%Cu-2%Mn-125% Kieselguhr-2%K_2CO_3	1:2	4	230	52	22	74	22nd day 27 cc/m^3	KITA Laboratory (40 c.c. Catalyst)
			240	43	36	79	17th day 42 cc/m^3	
Fe-25%Cu-2%Mn-125% Kieselguhr-15%H_3BO_3-3%K_2CO_3			230	62	33	95	18th day 17 cc/m^3	
			240	59	39	98	about one month	
			250	44	49	93	22nd day 48 cc/m^3	
Fe-25%Cu-2%Mn-125%Kieselguhr-20%H_3BO_3-4%K_2CO_3			240	66	36	102	about one month	
Ochre-1%Cu-4% K_2CO_3	1:2	4	240	45	29	74	-	KITA Laboratory (40 c.c. Catalyst)
Ochre-1%Cu-5% K_2CO_3				40	33	73	30th day 39 cc/m^2	
Ochre-5%Cu-4% K_2CO_3				44	35	79	-	
Ochre-1%Cu-1% H_3BO_3-6% K_2CO_3				52	34	86	30th day 62 cc/m^3	
Ochre-1%Cu-5% H_3BO_3-8% K_2CO_3				51	35	86	30th day 57 cc/m^3	

ENCLOSURE (D)

Table II(D)
COMPARISON OF CATALYSTS FOR MIDDLE PRESSURE SYNTHESIS LABORATORY TESTS AT KYOTO IMPERIAL UNIVERSITY

	Composition of Catalysts	Gas Comp.	Gas Flow over 40 cc cat.	Press	Temp.	Yield inc. wax.	Life of Catalysts (mean yield for each week)																	
		$CO:H_2$	L/hr	Kg /cm^2	°C	g / m^3	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Cobalt	Co+8%MgO+5%ThO_2+200 Kies.(1)	1:2	4	10	185	143	139	143	138	135	140	136	128	137	143	137	125	133	118	111				
					190																95	110	121	124
Iron	Fe+25%Cu+125%Kies.+4%K_2CO_3	1:1			190	41																		
					200	67																		
					210	83	83	84	79	76	74	72												
					220	101							92	87	85	79	78	79	-	70	65	70		
					230	105																		
					240	115																		
					250	106																		
	Fe+25%Cu+125%Kies+6%K_2CO_3			15	210	120																		
	Fe+25%Cu+5%Mg+125%Kies+6%K_2CO_3			10	210	111																		
				15	190	70																		
Natural	Ochre+0.5%Cu+5%Mn+6%K_2CO_3			10	210	74																		
					230	99																		
					250	112																		

(1) Catalyst from OMUTA.

ENCLOSURE (D)

Table III(D)
SUMMARY OF LARGE SCALE PILOT PLANT CATALYST TESTS

	Pressure	Composition of Catalyst	Gas Comp.	Gas Flow	Reaction Temperature	Avg. Yield Inc. Wax	Max. Life of Catalyst	Distillation								Olefine Content %		Iodine No.	
								Gasoline				Kerosene							
			CO:H$_2$	m^3/hr	°C	m^3	month	Initial b.pt.	10%	50%	90%	Initial b.pt.	10%	50%	90%	gasoline	kerosene	gasoline	kerosene
Co$^{(1)}$	norm.	Co+12%ThO+200% Kies. or Co+5%Mg+7%ThO+200% Kies.	1:2	1000	180-200	125g.	4	25	39	79	137	142	183	227	315	40	12		
Co$^{(1)}$	mid.		1:2	1000	180-200	145g.	6									17	6		
Co$^{(2)}$	norm.	Co+10%Cu+5%ThO$_2$+25% U$_3$O$_8$+125% Kies.	1:2	100	200-210	102^{cc}	1	29	41	79	155	96	138	180	232			59	17
Fe$^{(2)}$	norm.	Fe+25%Cu+2%Mn+125% Kies.+20%H$_3$BO$_3$+4% K$_2$CO$_3$.	1:2	100	235	86^{cc}	1	40	58	93	172	102	154	205	282			167	60
Fe$^{(3)}$	mid.	Fe+25%Cu+2%Mn+125% Kies. +20%H$_3$BO$_3$+7% K$_2$CO$_3$	1:1	10	230	106^{cc}	6	32	48	77	150	51	88	159	271	74	61		

(1) Estimated from the results of Fischer's publication.
(2) Results of pilot plant in Kyoto Imperial University. 100 m^3/hr.
(3) Results of pilot plant in RUMOI, Hokkaido.

ENCLOSURE (D)

Table IV(D)
EFFECT OF PRESSURE AND ALKALI CONTENT ON OIL YIELD* FROM Fe + 25% Cu + 125% KIESELGUHR BASE CATALYST

K_2CO_3 added % of Fe	Press. kg/cm²	Gas Contraction %	Gas Consumption CO:H_2	Composition of Reaction Gas						Yield of Reaction Products g/m³				
				CO_2	Heavy HC	CO	H_2	CH_4	N_2	H_2O	Gasoline	Kerosene	Paraffin	Total Liquid H.C.
2%	3	21.9	0.90	5.0	0.4	37.5	40.9	3.4	12.8	29.4	7.2	5.9	6.1	19.2
	6	29.0	0.87	6.2	0.6	36.2	38.7	4.5	13.8	46.6	10.7	9.2	10.0	29.9
	10	34.0	0.87	7.0	0.7	34.9	37.2	5.5	14.7	41.9	13.4	13.4	32.8	59.0
	15	35.0	0.75	5.8	0.7	37.3	36.6	5.3	14.3	35.8	12.9	14.1	51.8	78.8
	20	32.9	0.72	4.7	0.5	39.1	36.8	4.9	14.5	54.6	10.7	15.0	30.5	56.2
4%	3	19.1	1.64	9.6	0.5	33.0	42.9	2.5	11.5	12.2	9.7	4.1	13.1	26.9
	6	26.2	1.48	12.9	0.6	29.2	41.2	3.4	12.6	25.8	18.4	6.7	27.0	52.1
	10	36.1	1.53	21.3	6.0	17.9	38.0	6.0	15.8	40.2	20.4	15.8	58.4	94.6
	15	37.5	1.39	20.9	1.0	21.2	37.0	4.7	15.2	52.0	21.9	17.9	66.0	105.8
	20	33.4	1.12	12.9	0.8	30.8	37.3	3.8	14.4	63.7	17.1	13.4	59.8	90.3
6%	3	28.8	1.26	9.1	0.3	33.7	41.5	2.5	12.9	7.3	4.4	5.6	9.3	19.3
	6	35.2	1.42	13.2	0.4	27.7	41.6	2.9	14.2	10.0	7.1	5.1	42.6	54.8
	10	47.5	1.47	20.2	0.7	16.3	40.3	4.4	18.1	18.6	12.3	8.7	76.9	97.9
	15	54.6	1.49	27.5	1.1	6.8	39.0	5.3	20.3	32.3	15.1	30.0	74.0	119.1
	20	54.9	1.31	26.9	1.2	11.6	33.8	5.9	20.6	45.1	15.1	39.2	61.5	115.8
8%	3	25.2	1.10	6.0	0.2	37.7	41.6	2.8	12.3	7.5	3.1	0.5	3.5	7.1
	6	29.1	1.20	8.3	0.3	34.6	41.1	2.5	13.4	12.7	3.8	2.5	13.9	20.2
	10	32.3	1.15	8.1	0.3	34.7	40.6	2.7	13.6	18.4	5.4	3.5	36.4	45.8
	15	47.2	1.41	23.5	0.8	15.9	37.4	4.8	17.6	33.7	13.5	15.4	77.2	106.8
	20	51.6	1.28	24.9	0.9	15.7	34.3	4.8	19.4	56.2	16.8	29.9	68.4	114.8
Avg. feed gas analysis:				0.2	0.0	43.5	45.1	1.8	9.4					

*Data are average for one weeks operation at each reaction pressure.

Reaction Conditions

Catalyst 40cc
Temperature .... 210°C
Gas Flow .... 4 lit/hr

ENCLOSURE (D)

APPENDIX I

LIST OF DOCUMENTS (JAPANESE AND GERMAN) ON FISCHER-TROPSCH RESEARCH OBTAINED AT KYOTO IMPERIAL UNIVERSITY

(Forwarded Through ATIS to Washington Document Center)

A. On the Studies of Gasoline Synthesis from CO and H_2 Under Normal Pressure. (ATIS No. 4597)

NavTechJap. No.	Paper No.	Subject	Author	Date*
	Note:	ND26-0026.1 is one volume comprising the following 31 papers.		
ND26-0026.1	1.	Research for catalysis by Heating Curve Method. Part A.	S. KODAMA	1937
ND26-0026.1	2.	Research for catalysis by Heating Curve Method. Part B.	S. KODAMA	1937
ND26-0026.1	3.	Formation of Liquid Hydrocarbons by Co, Cu and Thoria Catalysts.	S. KODAMA	1937
ND26-0026.1	4.	Effect of Beryllium oxide, Magnesium Oxide Zinc Oxide and Cadmium on Co and Cu Catalysts.	S. KODAMA	1937
ND26-0026.1	5.	Effect of Titanium Oxide, Zirconium Oxide and Selenium Oxide on Co & Cu Catalysts.	S. KODAMA	1937
ND26-0026.1	6.	On the Formation of Hydrocarbons by Fe Catalyst.	S. KODAMA	1937
ND26-0026.1	7.	Effect of Alkali on Fe-Cu Catalyst.	S. KODAMA K. FUJIMURA	1937
ND26-0026.1	8.	On the Fe-Cu Catalyst.	K. FUJIMURA	1937
ND26-0026.1	9.	On the Co-Cu-MgO Catalyst.	K. FUJIMURA	1937
ND26-0026.1	10.	Effect of Promotors on Co-Cu-MgO Catalyst.	K. FUJIMURA	1937
ND26-0026.1	11.	On the Synthesis of Petroleum by Catalytic Reduction of CO at Ordinary Pressure.	K. FUJIMURA	1937
ND26-0026.1	12.	On the Synthesis of Petroleum by Catalytic Reduction of Co at Ordinary Pressure.	T. TSUNEOKA K.FUJIMURA	1937
ND26-0026.1	13.	Study on Ni Catalyst. Part A.	T. TSUNEOKA	1937

*Institute of Physical and Chemical Research Journal

ENCLOSURE (D)

NavTechJap No.	Paper No.	Subject	Author	Date*
ND26-0026.1	14.	Study on Ni Catalyst. Part B.	T. TSUNEOKA	1937
ND26-0026.1	15.	Study on Ni Catalyst. Part C.	K. FUJIMURA	1937
ND26-0026.1	16.	Study on Ni Catalyst. Part D	T. TSUNEOKA	1937
ND26-0026.1	17.	General Propeties and Composition of Products.	K. FUJIMURA T. TSUNEOKA	1937
ND26-0026.1	18.	Effect of Sulphur Compounds on Ni Catalysts.	K. FUJIMURA T. TSUNEOKA K. KAWAMITSI	1937
ND26-0026.1	19.	Ratio of H_2 and Co in Raw Gas.	K. FUJIMURA T. TSUNEOKA	1937
ND26-0026.1	20.	Effect of N_2, methane, CO_2 in Raw Gas.	T. TSUNEOKA	1937
ND26-0026.1	21.	Relation Between Raw Gas Composition and Reaction Temperature and Degree of Saturation of Gasoline.	T. TSUNEOKA	1937
ND26-0026.1	22.	Possibility of use of alloy	T. TSUNEOKA	1937
ND26-0026.1	23.	Study on Extraction and Washing of Alloy Catalyst.	T. TSUNEOKA	1937
ND26-0026.1	24.	Effect of Grain Size, Treating by H_2 and Oxidation Conditions of Alloy Catalyst.	T. TSUNEOKA	1937
ND26-0026.1	25.	General Properties and Composition of Synthetized Petroleum by Alloy Catalyst.	T. TSUNEOKA Y. MURATA	1937
ND26-0026.1	26.	Synthesis Reaction and Gas Contraction.	T. TSUNEOKA Y. MURATA	1937
ND26-0026.1	27.	Study on Series of Ni-Co and Co Alloy Catalysts.	T. TSUNEOKA M. MURATA	1937
ND26-0026.1	28.	Study on Series of Ni Alloy Catalysts.	T. TSUNEOKA M. MURATA	1937
ND26-0026.1	29.	Study on the Effect of Reaction Tube Diameter and Catalyst Layer Length.	T. TSUNEOKA Y. MURATA	1937

*Institute of Physical and Chemical Research Journal

ENCLOSURE (D)

NavTechJap No.	Paper No.	Subject	Author	Date*
ND26-0026.1	30.	Effect of Amount of Catalyst on Reaction.	T. TSUNEOKA M. MURATA	1937
ND26-0026.1	31.	Effect of Flow Rate of Gas on Reaction.	Y. MURATA S. ISIKAWA T. TSUNEOKA	1937
ND26-0026.2	32.	Study on Construction Material of Reaction Chamber.	T. TSUNEOKA	1937
ND26-0026.3	33.	Study on Construction Material of Reaction Chamber.	T. TSUNEOKA	1937
ND26-0026.3	33.	Relation between Freespace Volume in Reaction Chamber and Reaction Rate; Effect of Packing Material with Catalyst.	T. TSUNEOKA Y. MURATA	1937
ND26-0026.4	34.	Analytical Test of Alloy Catalysts.	T. TSUNEOKA	1937
ND26-0026.5	35.	Fine Structure of Alloy Catalyst.	T. TSUNEOKA R. KURODA	1937
ND26-0026.6	36.	Relation between Activity of Catalyst its Hysteresis of High Temperature Treatment.	T. TSUNEOKA R. KUROKA	1937
ND26-0026.7	37.	Study on Space Velocity of Gas.	T. TSUNEOKA J. NISHIO	1938
ND26-0026.8	38.	Condition of Synthesis and Unsaturation of Product.	T. TSUNEOKA Y. MURATA	1938
ND26-0026.9	39.	Superiority of Ni-Co Catalyst Prepared by Precipitation Method.	T. TSUNEOKA Y. MURATA	1938
ND26-0026.10	40.	Effect of Mixture Ratio	T. TSUNEOKA Y. MURATA	1938
ND26-0026.11	41.	On the Activation of Catalyst by Air Slow Oxidation.	I. KATAYAMA Y. MURATA	1938
ND26-0026.12	42.	Study of Purification of Raw Gas for Gasoline Synthesis. Part A. Elimination of organic Sulphur Compounds at Low Temperature.	T. TSUNEOKA W. FUNASAKA	1938

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NavTechJap No.	Paper No.	Subject	Author	Date*
ND26-0026.13	43.	Study of Purification of Raw Gas for Gasoline Synthesis. Part B. Elimination of Organic Sulphur Compounds at High Temperature.	T. TSUNEOKA W. FUNASAKA	1938
ND26-0026.14	44.	Elimination of Organic Sulphur by Lux Mass.	W. FUNASAKA I. KATAYAMA	1939
ND26-0026.15	45.	Elimination of Organic Sulphur Compounds by Synthetic Fixing Reagent.	W. FUNASAKA I. KATAYAMA	1939
ND26-0026.16	46.	Preparation of New Fe-Catalyst and its Superiority.	T. TSUNEOKA Y. MURATA	1939
ND26-0026.17	47.	Influence of Composition of Raw Gas in Use of Fe Catalyst.	T. TSUNEOKA Y. MURATA	1939
ND26-0026.18	48.	Effect of Adding Amount of Cu and Alkali on Fe Catalysts.	T. TSUNEOKA Y. MURATA	1939
ND26-0026.19	49.	Effect of Metal and Metal Oxide Promotors and Precipitation Reagents on Fe-Cu-Alkali Catalysts.	T. TSUNEOKA Y. MURATA	1939
ND26-0026.20	50.	Elimination of Organic Sulphur Compounds from Water Gas.	W. FUNASAKA	1940
ND26-0026.21	51.	On a Intensive Fixing Reagent of Sulphur which can Purify Water Gas at 200-250°C.	W. FUNASAKA	1940
ND26-0026.22	52.	Influence of Raw Material, Carrier and Alkali on Fe-Catalyst; and Effect of Packing Materials.	Y. MURATA S. MAKINO	1940
ND26-0026.23	53.	Effect of Aluminium, Ag and Other Promotors on Fe Catalyst.	S. MAKINO K. KOIDE	1940
ND26-0026.24	54.	Influence of CO_2 on Catalyst.	Y. MURATA T. YAMADA	1939
ND26-0026.25	55.	Influence of N_2, CH_4, O_2 and Ammonia Gas in Raw Gas on Fe Catalyst.	Y. MURATA T. YAMADA	1939
ND26-0026.26	56.	Distillation Analysis of Synthetic Gasoline. (1)	S. KODAMA	1939

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NavTechJap No.	Paper No.	Subject	Author	Date*
ND26-0026.27	57.	Promotors on Fe-Cu Catalysts.	Y. MURATA Y. TAZUKI	1940
ND26-0026.28	58.	Effect of Cu on Fe Catalyst	Y. MURATA M. YASUDA	1940
ND26-0026.28	59.	Promotion Effect of Boric Acid on Fe-Cu Catalyst.	Y. MURATA M. YASUDA	1940
ND26-0026.29	60.	Effect of Cu on Fe Catalyst.	Y. MURATA H. YASHIRO	1940
ND26-0026.30	61.	Reaction Temperature and Durability.	Y. MURATA Y. YOSHIOKA	1940
ND26-0026.30	62.	Durability of Fe Catalyst and Composition of Raw Gas.	Y. MURATA Y. YOSHIOKA	1940
ND26-0026.30	63.	Fe Catalyst and Raw Composition.	Y. MURATA S. SAITO	1940
ND26-0026.31	64.	On the Preparation of Fe Catalyst by Precipitation.	Y. MURATA M. NAKAGAWA	1941
ND26-0026.31	65.	On the Reduction of Fe Catalyst by H_2 and Thermal Treatment.	M. MURATA E. TASHIRO	1941
ND26-0026.31	66.	On the Reduction of Fe Catalyst.	Y. MURATA M. UMEMURA	1941
ND26-0026.32	68.	Distillation Analysis of Synthetic Gasoline.	K. TARAMA Y. TAZUKI	1941

B. Investigation of Synthesis of Petroleum Under Middle Pressure. (ATIS No. 4598)

NavTechJap No.	Paper No.	Subject	Author	Journal
ND26-0027.1	1.	On the Catalytic Reaction of CO and H_2 Under High Pressure.	E. TAHARA Y. SAWADA D. KOMIYAMA	J. Soc. Chem. 1941
ND26-0027.2	2.	On the Peculiarity of Synthesis of Petroleum Under Pressure-especially Durability of Catalyst.	S. KODAMA S. TAHARA I. FUKUSHIMA S. ISODA S. KOMASAWA K. KIMURA	ibid. 1942

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NavTechJap No.	Paper No.	Subject	Author	Journal
ND26-0027.2	3.	Effect of Reaction-temperature and Alkali Content for Fe-Cu-Mn-Boric Acid Catalyst.	S. KODAMA S. TAHARA I. FUKUSHIMA S. ISODA S. KOMAZAWA K. KIMURA	ibid. 1942
ND26-0027.2	4.	Effect of Alkali, Boric Acid, Cu, Kieselguhr Content for Iron Catalyst	S. KODAMA S. TAWARA I. FUKUSHIMA S. ISODA S. KOMASAWA K. KIMURA	ibid. 1942
ND26-0027.3	5.	Investigation on Technical Use of Iron Catalyst for Synthesis of Petroleum.	S. KODAMA S. TAHARA Y. HONG	Conference of Synthetic Petroleum. 1943.

C. Physico-Chemical Investigation of Gasoline Synthesis. (ATIS No. 4599)

NavTechJap No.	Paper No.	Subject	Author	Journal
ND26-0028.1	1.	Activated Adsorption of H_2, CO, CO_2 and H_2O by Cobalt.	S. KODAMA K. TARAMA S. MATSUMURA	J. Soc. Chem. Ind. Japan 1940.
ND26-0028.1	2.	Activated Adsorption of H_2, CO, CO_2 and H_2O by Iron.	S. MATSUMURA	1940
ND26-0028.1	3.	Activated Adsorption and Mechanism of Gasoline Synthesis Reaction,	S. MATSUMURA	1940
ND26-0028.2	4.	Adsorption Velocity of H_2 by Cobalt.	S. MATSUMURA	1941
ND26-0028.3	5.	Adsorption Velocity of H_2 by Co-Kieselguhr Catalyst	S. KODAMA S. MATSUMURA T. ANDO	1941
ND26-0028.3	6.	Adsorption Velocity of H_2 by Co-Th-Kieselguhr Catalyst.	T. ANDO	1941
ND26-0028.4	7.	Adsorption Velocity of H_2 by Iron.	S. KODAMA S. MATSUMURA K. TARAMA	1942
ND26-0028.4	8.	Adsorption Velocity of H_2 by Fe-Kieselguhr Catalyst	S. KODAMA S. MATSUMURA T. ANDO	1942
ND26-0028.4	9.	Adsorption Velocity of H_2 by Fe-Catalyst for Gasoline Synthesis.	S. KODAMA S. MATSUMURA	1942

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NavTechJap No.	Paper No.	Subject	Author	Journal
ND26-0028.5	12.	X-ray Studies on Gasoline Synthesizing Iron Catalyser.	S. KODAMA H. TAHARA	1942
ND26-0028.6	13.	X-ray Investigation of Iron Catalyst for Benzene Synthesis.	H. TAHARA	KYOTO Imperial U. Lecture

D. The Synthesis of Gaseous Hydrocarbons from CO and H_2. (ATIS No. 4600)

NavTechJap No.	Paper No.	Subject	Author	Journal
ND26-0029.1	1.	Effect of Reaction Temperature on Fe-Catalyst.	S. KODAMA K. TARAMA T. OSHIMA K. FUJITA	J. Soc. Chem. Ind. Japan 1941
ND26-0029.1	2.	Effect of Synthetic Gas Velocity on Fe-Catalyst.	K. FUJITA	1941
ND26-0029.2	3.	Promoter Action of Cu, Mn, K_2CO_3 and H_3BO_3 on Fe-Catalyst.	S. KODAMA K. TARAMA A. MISHIMA K. FUJITA M. YASUDA	1943
ND26-0029.2	4.	Effect of Reaction Temperature on Fe-Catalyst with Various Promoters.	M. YASUDA	1943
ND26-0029.3	5.	Effect of K_2CO_3 Content on Fe-Catalyst.	M. YASUDA	1943
ND26-0029.3	6.	Effect of H_3BO_3 Content on Fe-Catalyst.	M. YASUDA	1943
ND26-0029.4	7.	Effect of Reaction Temperature on Co-Catalyst.	S. KODAMA K. TARAMA T. TAKASAWA K. FUJITA T. TESHIMA	1945
ND26-0029.4	8.	Effect of Synthetic Gas Composition on Fe-Catalyst.	T. TESHIMA	1945
ND26-0029.4	9.	Effect of Kieselguhr Content on Fe-Catalyst.	S. KODAMA K. TARAMA T. TAKASAWA M. ITO T. TESHIMA	1945
ND26-0029.4	10.	Effect of Various Carriers on Fe-Catalyst.	T. TESHIMA	1945

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E. Pilot Plant Test of Gasoline Synthesis. (ATIS No. 4601)

NavTechJap No.	Paper No.	Subject	Author	Journal
ND26-0030.1	9.	The 9th Report on Gasoline Synthesis. (The 1st Test by $100m^3$/hr. Scale Convertor.)	S. KODAMA	Reports of the Inst. forChem. Research 1941.
ND26-0030.2	11.	Pilot Plant Test of Gasoline Synthesis.		Journal of Chem. Eng. 1941.

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APPENDIX II

LIST OF PATENTS RELATING TO THE FISCHER-TROPSCH PROCESS KYOTO IMPERIAL UNIVERSITY

Pat.No.	Date of Application	Date of Issue	Title	Content	Inventor
98205	1931, May, 22	1932, Nov., 11	Manufacture of gasoline by reduction of CO.	Normal pressure, Co, Cu, ThO_2 & MgO or U_2O_3 catalyst.	G. KITA S. KODAMA K. FUJIMURA
106560	1933, Apr., 5	1934, Jun, 15	Manufacture of gasoline by reduction of CO.	Normal Pressure Ni-catalyst: utilization of inpure Ni (Cu $< 0.5\%$).	K. FUJIMURA S. TSUNEOKA
126845	1937, Dec., 17	1938, Oct., 6	Steam generator utilizing heat of chemical reaction.	Arrangement of cooling pipes in reaction chamber.	S. SUGAHARA S. KODAMA S. TSUNEOKA T. FUJITA
129242	1938, Apr., 14	1939, Mar., 20	Two stage method of producing oil from water gas.	1st stage: Fe catalyser. 2nd stage: Co- or Ni- catalyst.	G. KITA S. KODAMA Y. MURATA
134661	1937, Sep., 13	1940, Feb., 8	Manufacture of hydrocarbon.	Adiabatic synthesis by 5% reaction and recirculation.	G. KITA S. KODAMA
134662	1938, Apr., 4	1940, Feb., 8	Treatment of gasoline synthesis.	Activation of catalysts by slow oxidation.	G. KITA, Y. MURATA, S. TSUNEOKA, I. KATAYAMA, K. KOIDE
139554	1939, Nov., 1	1940, Nov., 4	Removal of sulphur from gases.	Cu(OH), Kieselguhr, 10-100% NaOH by 200-400°C.	G. KITA W. FUNASAKA
142908	1938, Sep., 23	1941, Apr., 7	Reaction chamber for oil synthesis.	Arrangement of cooling pipe.	S. SUGAHARA S. KODAMA T. FUJITA
142939	1938, Aug., 24	1941, Apr., 12	Manufacture of synthetic liquid fuel.	Low activity catalyst near inlet of reaction chamber.	G. KITA, S. KODAMA, T. FUJITA, Y. MURATA.
143373	1937, Oct., 15	1941, May, 8	Oil synthesis by iron catalyst from CO & H_2.	Normal pressure, Fe-, Cu, Kieselguhr, and alkali catalyst. Reduction by reaction gas.	G. KITA, S. TSUNEOKA, Y. MURATA, S. MAKINO
144803	1939, Aug., 24	1941, Aug., 1	Oil synthesis from CO and H_2.	Reduction by high speed gas flow, save of reduction time.	G. KITA, Y. MURATA
144921	1939, Oct., 28	1941, Aug., 9	Liquid fuel synthesizing reaction chamber.	Device of insertion of cooling tubes in the reaction chamber.	S. KODAMA G. HASHIMOTO

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Pat.No.	Date of Application	Date of Issue	Title	Content	Inventor
147086	1939, Feb., 3	1941, Dec., 9	Gasoline synthetic iron catalyser.	Fe-catalyser with boron compound.	G. KITA, K. KOIDE, Y. SAWADA, Y. MURATA
147087	1940, Mar., 25	1941, Dec., 10	Two stage method of producing oil from water gas.	1st stage: low reaction temperature. 2nd stage: high reaction tempezature.	G. KITA, Y. MURATA, Y. YOSHIOKA.
147126	1938, Aug., 27	1941, Dec., 11	Oil synthesis by iron catalyser from CO and H_2.	Fe, Cu, Mn or Al-catalyst.	G. KITA, S. MAKINO, Y. MURATA, K. KOIDE.
150548	1940, Mar., 25	1942, May, 13	Manufacture of oil.	Recirculation using slightly hydrogen excess initialgas.	G. KITA S. KODAMA Y. MURATA
150952	1940, Nov., 25	1942, Jun., 4	Manufacture of liquid hydrocarbon.	Recirculation of hydrogen seperated from reaction gas.	G. KITA S. KODAMA S. TSUNEOKA Y. MURATA
154262	1941, Apr., 11	1942, Dec., 16	Oil synthesis.	Activation of Fe-catalyser by H_2 rich reduction gas.	G. KITA S. KODAMA Y. MURATA
155493	1941, Mar., 13	1943, Mar., 16	Activation of oil synthetic catalyst.	Activation of catalyst by preliminary heat treatment.	G. KITA S. KODAMA Y. MURATA
158987	1941, Oct., 3	1943, Jun., 10	Hydrocarbon synthesis from CO and H_2.	Middle pressure Fe-catalyst, more alkali than normal pressure Fe-catalyst.	S. KODAMA H. TAHARA Y. MURATA

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RESEARCH ACTIVITIES OF THE IMPERIAL FUEL RESEARCH INSTITUTE

KAWAGUCHI

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ENCLOSURE (E)

SUMMARY

This report records and summarizes technical data on the Imperial Fuel Research Institute, at Kawaguchi, Saitama Prefecture, Japan, by the Petroleum Section of NavTechJap during the period 16-28 January 1946.

The Institute is an agency of the Japanese Department of Commerce and Industry, engaged almost totally in research on the subject of utilization of coal substances native to the Japanese home islands. Its field of activity embraces studies on the production of both liquid and solid fuels from coals. Specifically, low temperature carbonization, coal hydrogenation and the Fischer-Tropsch Synthesis have been the principal media of approach to the production of such fuels.

The Institute has operated a six-retort carbonization assay plant since 1921. This installation has a throughput capacity of 6 tons per day. Non-coking bituminous coals of Japan have been thoroughly studied in this plant. At present, interest is centered upon the carbonization of brown coals found principally in Central Honshu.

The Fischer-Tropsch plant was operated from early in 1938 to 1940, this work being discontinued when the MITSUI interests began full scale plant operation at MIIKE. The Institute's plant never attained more than 30% of design capacity, which was 200kg of total crude oil product per day. Failure was partly due to poor catalysts, and partly to faulty and cumbersome converter design.

The coal hydrogenation plant was operated between 1936 and 1940, being abandoned when the FUSHUN and AGOCHI commercial coal hydrogenation plants began operations. The Institute's plant had a throughput of 3 to 5 tons of paste per day, representing 1.5 to 2.5 tons of coal input. It was operated only as a liquid phase unit, hence produced mainly heavy oil. When Japanese high-volatile low rank bituminous coals were processed in this plant at 200 atmospheres pressure, 80% or more liquefaction was obtained.

Although this plant apparently operated at rated capacity and with relatively little difficulty, no outstanding process or equipment developments were attained as a result of its operation. This was partly due to over-simplification in its design and partly to failure to incorporate the vapor phase step.

From 1944 until the end of the war, the Institute was under the administrative supervision of the newly formed Department of War Production, which abolished the Department of Commerce and Industry. At the end of hostilities, prewar status was regained. The war program of the Institute directly concerned with military activities comprised seven projects, none of which were reduced to commercial practice.

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I. JAPANESE PERSONNEL INTERVIEWED

The following personnel of the Imperial Fuel Research Institute were interrogated and supplied verbal information or submitted written documents from which this report was compiled.

Mr. Y. BAN	Director of the Institute.
Mr. T. SHIMURA	Assistant Director and Supervisor of the Fischer-Tropsch Group.
Mr. M. KUROKAWA	Supervisor of the Coal Hydrogenation Group.
Mr. N. SAITO	Supervisor of the Carbonization Group.

II. LOCATION AND GENERAL DESCRIPTION

The Imperial Fuel Research Institute (Nenryo-Kenkyusho), of the Japanese Department of Commerce and Industry, is located in the town of KAWAGUCHI, Saitama Prefecture, Honshu. KAWAGUCHI is situated just north of TOKYO, from which it is separated by the ARAKAWA River. The Institute covers an area of 483,624 square feet, all of which is quite level, hence completely utilizable for building construction. In this area are a total of more than forty buildings, of which about fifteen are totally devoted to laboratory and pilot plant operations and administration. Total building floor space, that is, laboratories plus shops, warehouses, service buildings, etc., amounts to more than 180,000 square feet. Pilot plants and some laboratories are housed in sheet iron structures; the administration building and some laboratories are concrete. Figure 1(E) is a layout plan of the grounds and buildings.

III. HISTORICAL

The Institute was founded in 1921, and at that time was under the jurisdiction of the Department of Commerce and Forestry. About 1923, this Department was reorganized and divided to form the Departments of Commerce and Industry, and Agriculture and Forestry. The Institute became part of the Department of Commerce and Industry, and so remained until 1944, when the Department was placed under military administrative supervision and given the name Department of War Production, as nearly as the new title could be translated. At the end of the war military supervision ceased, and the pre-war name and status were regained.

IV. GENERAL DESCRIPTION OF ACTIVITIES

A. Normal Activities

At the time of its organization, the field of investigation assigned to the Institute was to study and promote processes for the economical utilization of coal substances native to the Japanese home islands. These comprise mainly low rank and low grade bituminous coals, brown coals and lignite. Their chemical nature is, therefore, such that they are not attractive to most industrial consumers. Research activities were later extended to include utilization of natural gas and petroleum.

Coal studies most intensively pursued have related to complete gasification, low temperature carbonization, and combustion in industrial furnaces. Before the war, the Institute's technologists were active in studying the direct gasification of coal in one step. They claim credit for developing processes now used in commercial plants serving TOKYO, YOKOHAMA, and KOBE. A continuous program of coal carbonization has been carried on, aiming toward the production of an acceptable substitute for charcoal for domestic heating and cooking. Institute technologists believe that general acceptance of low temperature semi-coke or "coalite" from brown coal would practically revolutionize the Japanese home fuel situation. In the rural districts and towns of moderate size (i.e., less than 50,000 population) in central and southern Japan, wood and wood charcoal are universally used for both heating and cooking; also a large proportion of the people in the larger cities use charcoal exclusively. In TOKYO, for example, it is estimated that about 40 per cent of the homes use no fuel other than charcoal. Successful application of low temperature carbonization to this market would also make available large quantities of low temperature tar, which is particularly valuable in Japan as a petroleum substitute.

Because of Japan's poor position with respect to natural petroleum, the Institute has conducted research on synthetic liquid fuel production from coal by the Bergius and Fischer-Tropsch process since 1931 and 1933, respectively. However, no industrial process or equipment applications have evolved from this work, and experimentation has a dwindled since 1940. Present personnel state that the Japanese government has withdrawn support of these projects because of the pressing need for work in more direct utilization of Japanese coals during the reconstruction period.

Studies on the utilization of Japanese raw materials other than coal, gas, and petroleum have been very limited. The Institute is in no way connected with the metallurgical or mineral industries. A small amount of work is done on agricultural wastes (such as straw and chaff), and forestry products, particularly in problems dealing with obtaining liquid fuels from such sources.

A continuous program of coal assay is carried on for the benefit of both public interests and the industries. Similarly, coal sampling, coal dressing, studies of coke properties, coal combustion tests, tar treatment and the like are continuous problems. No fundamental research is done which is not directly connected with fuel problems.

B. WAR ACTIVITIES

Present personnel state that throughout the war the major part of the Institute's work continued to be along the lines of fuel production for civilian or normal industrial use. A few specific war projects were assigned when the military group was in control (1944-1945), the general subject titles of which are the following:

1. Hydrogenation of Daido Coal.
2. Low-Temperature Carbonization of Coaly Shale.
3. Carbonization of Pine Wood.
4. Preparation of Aviation Gasoline from Pine Root Oil.
5. Catalytic Cracking of Low-Temperature Tar.
6. Synthesis of Triptane.
7. Explosive Combustion of Coal Dust.

Results of this work are summarized in Section IX.

C. PROPOSED FUTURE ACTIVITIES

As an outcome of the war, Japan has lost her most valuable coal fields of former days, that is, in Korea, Manchuria, and China. She has also lost a fairly important source of oil in the poor quality shale deposits of FUSHUN. These circumstances are cited as evidence of the necessity for concentrating to a greater degree than in the past on extending the fields of utilization of native Japanese coals and related materials.

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V. PRESENT PERSONNEL ORGANIZATION

Total personnel now numbers 121, which is considered the normal complement. The employees are classified as follows:

Director	Mr. Y. BAN
Assistant Director	Mr. T. SHIMURA
Mechanical Engineers	2
Physicists	1
Research Chemists	18
Assistants	25
Clerks	3
Laborers and Operators	70

The laborer classification includes skilled as well as unskilled workers.

During the time when the Institute was under the control of the Army and Navy, personnel was increased to 166, classified as follows:

Director	Mr. Y. BAN
Assistant Director	Mr. SHIMURA
Research Chemists & Engineers	25
Assistants	38
Clerks	3
Laborers	98

The annual budget for a normal year is 500,000 yen, of which 200,000 yen is paid out in salaries. The average wage of the professional man is 3,000 yen per year, the assistant 2,000 yen, and the laborer 5 yen per day. Salaries have recently been increased by 10%, this increase being granted to offset present currency inflation. The Institute is financed entirely by government funds, administered by the Department of Commerce and Industry.

VI. COAL HYDROGENATION PROCESS

A. Laboratory Work

The first experiments on direct coal hydrogenation began in 1931. The principal object of this work was to study in a comprehensive manner the hydrogenation of Japanese coals, the results of such experimentation to be applied to development of a commercially-feasible synthetic liquid-fuel process. The statistical technical information obtained on the behavior of the various coals was to be made available for general distribution to those interested in development of industrial hydrogenation. It was considered the duty of the government to provide such information for the industry. This work was carried on as a continuous project until about the last two years of the war, and has involved a very large number of tests using high pressure autoclaves with charging capacities from ½ liter to about 5 liters.

More specifically, the purpose of these investigations may be outlined thus:

1. To study a wide variety of Japanese coals with respect to their suitability for liquefaction by direct hydrogenation. Over 100 coals have been assayed.
2. To study the effect of catalysts on the liquefaction reactions.
3. To study the kinetics of depolymerization-hydrogenation reactions.

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4. To study hydrogenation of the complex separable constituents of coal.

5. To study vapor phase hydrogenation of products obtained by primary liquefaction or dry distillation of coal.

Results of this work have been prepared for distribution in the form of technical papers and bulletins, some have also been published in technical journals. Copies of all these bulletins (written in Japanese) were obtained, but not translated except for their titles, which are as follows:

1. The Hydrogenation of Phenols, Part I.
2. Studies on the Liquefaction of Coal, Part II. (Test Results of Japanese Coals)
3. The Hydrogenation of Low-Temperature Tar.
4. The Hydrogenation of Heavy Oils.
5. The Hydrogenation of Phenols, Part II. (On the Preparation of Hydrocarbons from Low-Temperature Tar Acids).
6. Studies on the Liquefaction of Coal, Part III.
7. The Preparation of Benzol from High-Temperature Tar by Hydrogenation.
8. Studies on the Liquefaction of Coal, Part V. (Action of Catalysts on the Coal Paste)

(ATIS and ND numbers for these publications will be found in Appendix I of this report).

The material contained in these bulletins is of general technical and scientific interest, and so has bearing on the broad subject of coal hydrogenation, but cannot be said to be the basis for any specific process, or improvements applicable to any specific process.

According to the present personnel, the most important general conclusions obtained from this work are:

1. Practically all coals of the Japanese islands were found suitable for hydrogenation. In general, Hokkaido and Sakhalin coals are more easily liquefied than those of the central and southern regions of Japan.

2. The action of catalysts on coal hydrogenation is two fold:

   a. Acceleration of the reactions of depolymerization-hydrogenation. Catalysts effective for this purpose are oxides and sulfides of tin, lead, and nickel.

   b. Acceleration of hydrocracking reactions. Catalysts suitable for this purpose are oxides and sulfides of molybdenum, zinc, iron, and copper. Halides capable of acting as a source of hydrogen halide at elevated temperatures are also extremely effective hydrocracking catalysts.

3. Mixtures of hydrocracking catalysts (such as MoO_3) with alumina gel or with halides (such as NH_4Cl) were more effective than either used alone. The alumina gel is said to catalyze decomposition of asphaltic bodies. Depolymerization catalysts (such as SnO or PbO), when mixed with halides (such as NH_4Cl or CHI_3), were likewise more effective than either component alone.

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B. Semi-Plant Work

In 1934, the Institute began the operation of a semi-pilot-plant scale liquid-phase coal hydrogenation plant, capable of treating 3 to 5 tons of paste per day. Usual practice was to use paste in which the ratio of coal to vehicle was 1:1, hence the amount of coal treated was 1.5 to 2.5 tons per day. The product was heavy oil which, in a complete hydrogenation plant, would have been split into two parts, one going to the vapor phase step, and the other (after separation of solid matter), to vehicle storage for paste making.

The entire hydrogenation system except the hydrogen compressor was designed and built by the Kobe Iron Works. The operating staff consisted of 1 research chemist (group leader), 3 assistants, 5 operators, 2 analysts, 1 producer gas operator, and 1 hydrogen plant operator.

As a matter of record, this is Japan's second hydrogenation plant with respect to age. The oldest is the one built at TOKUYAMA and later moved to OFUNA.

The object of experimentation with this plant was to compare plant and laboratory results on the hydrogenating characteristics of a few representative Japanese coals which gave good liquefaction yields in laboratory tests, and also to determine whether Japanese-engineered and Japanese-built plant equipment could be made to serve in this particular high pressure field.

It was planned, if satisfactory performance was obtained, to continue expanding the scale of operation to a demonstration plant of commercial size.

This plant was operated for a total of about 5000 hours between 1934 and 1940. Its operation was discontinued when full scale plants began running at FUSHUN and AGOCHI. There seemed to be no immediate need for further pilot plant experimentation by the government.

The flow diagram of the plant is shown in Figure 2(E). Process hydrogen was manufactured by electrolysis of water in a small Knowles generator having a capacity of 16 m^3 per hour. Low pressure hydrogen storage consisted of a gasholder system of 115,000 cu. ft. total capacity. A ballast vessel of 110 liters free volume was placed between the compressor and the hydrogenation system. Producer gas made in a Karpely generator was used for all process heat not furnished by electrical resistance.

Paste making was a batch operation, enough being made at one time for one day's throughput (3 tons). Coal preparation equipment consisted of a jaw crusher and a pan mill. There was no drying equipment. A screw-type conveyer transported the pulverized coal (minus 200 mesh) to the paste mixers, which were elevated so that their bottom outlets were about 6 feet from the floor. Paste mixing and storage equipment consisted of 2 open top cylindrical vessels with conical bottoms, fabricated from steel plate. They were heated by internal steam coils and provided with vertically mounted motor-driven propeller type stirrers. The paste injector consisted of two single-acting hydraulically operated reciprocating piston type units in parallel, with variable speed stroke. Paste feed to the injector was by gravity.

The hydrogenation system consisted of an indirect gas-fired tubular paste preheater, two converters in series, electrically heated hydrogen preheater, a separator-cooling system and a gas scrubbing unit. Materials of construction and significant dimensions of this equipment will be found on

ENCLOSURE (E)

Figure 2(E). The converters and paste preheater were enclosed in brickwork housings, through which pass the hot gases from the combustion chamber in order to maintain proper operating temperature. The entire hydrogenation system was housed inside the plant building. Protection was provided for the valve operators in the form of a 9 inch thick re-enforced concrete wall (with small glass windows) which separated the pressure vessels from the control room. Valve wheels were fixed to this wall in the operating room, and were connected to the valve stems by means of a shaft and gear arrangement.

Heavy product discharge was manual and intermittent. The heavy oil was separated from solid matter as completely as possible by gravity in the first high pressure separator, the remainder of the oil being removed by a distillation-carbonization operation. Light product carried through the separators by the exit gases was recovered in the oil scrubbing system, employing a creosote oil fraction (boiling range 230-300°C) as the absorbing agent. This unit operated at atmospheric pressure. The light oil was recovered by distillation.

There was very little instrumentation in the plant. All flow controls and product discharge controls were manually operated. There were no mechanical safety devices on moving machinery except for open-type safety valves on the hydrogen compressors. Likewise, the only enclosed motor was on the hydrogen compressor.

The converters and preheater were designed to operate at 200 atmospheres. The remainder of the plant featured extra-heavy-duty equipment, particularly valves, piping, and the paste injector. Such over-design resulted in reasonably infrequent replacement of the parts receiving most wear. However, it was admitted that heavy oil discharge valves suffered severe erosion, requiring change of the working parts about every two weeks. These valves were fairly wide-angle needle type, with stellite needle tip and stainless steel seats. There had been no failure of preheater tubes, but these were changed from time to time because of rusting due to long periods of idleness.

Other features, which simplified operation and thus added to reliability of performance, were incorporated into the plant. The most important of these, from the engineering standpoint were:

1. Omission of heat exchange from the paste injection system.
2. Direct condensation of vapors from converter gases, without heat exchange.
3. Direct preheating of process hydrogen.
4. Omission of the step of recirculating part of the hydrogen to process after partial stripping of the exit gases under pressure.
5. Use of electrolytic hydrogen for process.

The only operating difficulty admitted by the staff, aside from the inadequacy of instrumentation, was the heavy oil discharge valve failure previously mentioned.

Experimentation was confined to hydrogenation of three Japanese coals which laboratory tests had indicated to be most suitable for liquefaction, and consisted in:

1. One month running on Iriyama coal from central HONSHU, a coal lying in rank between lignite and sub-bituminous.

2. Two months on Harutori, a low-rank high-volatile bituminous coal from HOKKAIDO.

3. Two months on Kawakami, a low-rank high-volatile bituminous coal from SAKHALIN.

This work led to the following general conclusions:

1. The three coals tested were readily hydrogenated in the plant at 200 atmospheres pressure.

2. Coals containing as much as 10% ash presented a serious valve problem in discharging heavy product.

3. Zinc chloride was found to be a superior catalyst for hydrogenating low-rank coals. There was no mention of corrosion of HCl.

4. Japanese pressure equipment and machinery showed no particular weakness in performance at 200 atmospheres.

5. No specific improvements of value to the coal hydrogenation industry were developed, either with respect to process or equipment.

The only publication on the operation of this plant is a short paper in the "Journal of the Society of Chemical Industry, Japan", Volume 44 No.10, dated 1941, entitled "On the Hydrogenation of Coal by Semi-Technical Scale Plant".

The data of Table I(E) were submitted as a typical record of operating results.

VII. FISCHER-TROPSCH PROCESS

A. Laboratory Work

Laboratory experiments on the synthesis of hydrocarbons by the Fischer-Tropsch process were begun in 1933. The purpose of the work was to provide Japan with a source of liquid hydrocarbon fuels from raw materials available within the limits of Japan proper. It was the goal of the Institute to develop and promote the full scale exploitation of a complete system of synthetic petroleum manufacture by this method, with particular emphasis placed on catalyst development, converter design, and possibly gas generation.

The key man in the organization was Dr. S. TSUTSUMI, who remained at the Institute from 1933 to 1939. According to present personnel, he personally carried out all the more important work concerning catalyst preparation, catalyst testing, and evaluation of results. When he left the organization in 1939, he took with him all notes and other records concerning his work, leaving nothing to guide his successors in continuation of the program. While at the Institute, he prepared one bulletin describing his work up to 1934 or 1935. This publication has not been translated, except for its title, which is "The Synthesis of Gasoline (Part I)". (The ATIS and ND number of this document will be found in Appendix I of this report).

From the results discussed in this publication, and from the statements of present personnel, the substitution of nickel for cobalt was the object of

ENCLOSURE (E)

much of TSUTSUMI's research. The reason for this was the high cost of cobalt. Good yields were obtained from nickel catalysts over short periods of time, i.e., well above 100 grams per cubic meter of gas input, but the catalysts could not be maintained in an active condition for longer than about a month. Even during this short period they required two high-temperature activations. This performance is not suited to a commercial process.

TSUTSUMI also conducted extensive experimentation on the promoter effect of catalytic materials such as oxides of uranium, thorium and uranium on nickel and cobalt catalysts. His results led to the conclusion that thorium and uranium are most effective for this purpose. Miscellaneous research included studies on the effect of changing the ratio of H_2 to CO in the synthesis gas, the effect of changing the linear gas velocity through the catalyst, the effectiveness of various bulking agents, and studies on the effect of changing the amount of bulking agent. He did no work on iron catalysts.

These experiments were performed at atmospheric pressure, using an electrically-heated single tube converter 20mm inside diameter and 60cm long. There is no record of experiments at intermediate pressures, although some work of this kind was done.

B. <u>Semi-Plant Work</u>

Experiments began on a semi-plant scale in 1936. As a matter of record this was the year in which the MITSUI interests purchased the rights to exploit the Ruhrchemie Fischer-Tropsch process in Japan. It is claimed that the Japanese license was limited to operation at atmospheric pressure, hence the Institute concentrated upon developing a process, operating at pressures above atmospheric. Specifically, 5 atmospheres gauge pressure was arbitrarily chosen for experimentation.

The first converter was a failure, consisting merely of a tube 30cm in diameter and about 2 meters long, without provision for removing the heat generated by the highly exothermic hydrocarbon synthesis. In 1938, operation began on a plant which had been provided with a converter of more appropriate design with respect to heat-control characteristics. Temperature control was effected by circulating water through a system of narrow tubes in parallel, the catalyst being packed in the interstices between the tubes. Design production capacity was 200 kg total crude oil product per day, to be obtained from a throughput of 100 normal cubic meters of synthesis gas per hour with an H_2:CO ratio of 2:1. The catalysts were composed mainly of nickel. Actual composition of the catalyst reported most effective was (in parts by weight) Ni : Co : Cr : Kieselguhr as 40:10:10.5:150. The catalyst charge was said to be one cubic meter bulk volume but actual calculation indicated 3/4 cubic meter to be more nearly correct. Oil production never exceeded 30% of design capacity, according to the records offered as representative of best operating practice. Throughput was likewise about 30% of the design figure.

Performance of catalysts was unsatisfactory with regard to their useful life, although while active, yields as high as 118cc (78 gm) of pentane and heavier hydrocarbons per cubic meter of synthesis gas were obtained. The longest total period of useful activity observed was about a week, this being obtained only by reactivation with hydrogen on the third and fifth days. This type of catalyst had been maintained in an active condition in laboratory tests for about a month. The explanation given for the shorter life in the plant was sulfur poisoning. Spent catalysts were not reworked.

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This plant was operated intermittently from early in 1938 until near the end of 1940. During this time, no changes were made in the plant equipment. Operations ceased when the Mitsui plant at MIIKE began running. This action was explained as partly due to belief that the Miike plant was practically certain of success, and partly because it was realized that modification of the Institute's converter design to give better temperature control would introduce considerable additional expense in its fabrication, and partly because of the unsatisfactory life of the catalysts.

During the time the plant was active, it was estimated that 12 runs of from 1 to 2 weeks duration were made per year for a period of nearly 3 years. The plan followed was to make one run per month.

There was no work at the Institute on refining of the crude oil product or on engine performance of Fischer-Tropsch fractions from any source.

A flow sheet of the plant is shown in Plate I(E). The converter was of the single-pass downflow type, designed to operate at 10 atmospheres gauge pressure, but actually operated at 5 atmospheres. It consisted essentially of a steel cylindrical shell 116cm in diameter and 150cm long, inside which were placed, longitudinally, 860 small steel tubes described as ½ inch "gas pipe". The shell was provided with one integral and one removable head, the latter being at the top. The tubes were connected in parallel by means of an intricate welded header system at top and bottom with pipe connections passing to the outside through removable packing-gland connections in the heads. The entire pipe assembly could be removed and again set in place for the operations of charging and discharging catalyst.

Hot water, at substantially the temperature of the synthesis (180-200°C), was mechanically circulated through the tubes and an external closed condenser system, for controlling catalyst temperature. The catalyst, in pellet form, was loosely but uniformly packed in the interstices between the tubes, which were spaced 35mm between centers. This design is essentially the reverse of the American Downs converter.

The product recovery system comprised:

1. An air-cooled pressure receiver, immediately following the converter, in which water and the heavier hydrocarbon products were collected.

2. A water-cooled shell and tube-type pressure condenser to collect part of the lighter reaction products.

3. A batch-type packed tower pressure scrubber employing a creosote oil fraction boiling in the range 230-300°C for the final stripping of light products from the gases.

4. A continuous steam distillation tower and condensing unit, operating at atmospheric pressure, for stripping light product oil from wash oil.

Exact records of catalyst preparation was not available. From memory, present personnel recalled that all catalysts used in the plant consisted principally of nickel, and the one giving the best results had the approximate weight composition Ni:Co:Cr:Kieselguhr as 40:10:7.5:50. In preparing this catalyst, nitrates of nickel, cobalt, and chromium were dissolved in hot distilled water in the proper ratio to give a final product of the desired composition, the proper amount of kieselguhr added, then, with agitation of the solution, the metals were precipitated by addition of a hot solution of potassium carbonate slightly in excess of the stoichiometric requirement. The precipitate was washed with hot distilled water until no alkalinity was detectable with phenolphthalein indicator. The slurry was then filtered, dried, and the product pelleted. Pellet size was 7mm in diameter and 2.5mm thick at the edge. Pellet faces were convex. Temperatures, time schedules, and solution concentrations during these operations could not be recalled.

Catalysts were all prepared in the laboratory, using glass and stoneware apparatus for the precipitation reactions. Approximately a month was consumed in making a catalyst, requiring the services of 8 persons, working 9 hours daily.

In conditioning for the synthesis, the catalyst was reduced at atmospheric pressure in the converter, with hydrogen. Bayonet-type electric heaters, inserted in sheaths extending from top to bottom inside the converter, supplied the heat required to attain the reduction temperature of 350°C. The reduction schedule was described as follows: Hydrogen was passed over the catalyst while, at the same time, the temperature was increased from atmospheric to 350°C, over a 20-hour period. After 10 hours at 350°C, the temperature was decreased, over an 8-hour period, to 180-190°C. Synthesis gas was then substituted for H_2, and proper operating pressure and flow rate attained at once to start the synthesis.

The method for preparing gas for the synthesis consisted in blending blue water gas with electrolytic hydrogen. The blue gas generator was a small unit which was operated intermittently, gas being prepared and stored in a 30,000 cu. ft. gasholder. Similarly, H_2 was stored in a 10,000 cu. ft. holder. The two were mixed, as required, in another 10,000 cu. ft. holder. There was no storage of compressed gas except an accumulator, about 20 inches I. D. and 42 inches long, immediately following the compressor. All the plant operation was carried out with a synthesis gas of the approximate composition H_2:CO as 2:1.

Because of the sensitivity of the synthesis catalyst to sulfur poisoning, an elaborate but unconventional system for sulfur removal was adopted. Following the blue gas generator was a conventional dry iron-oxide box (to remove all but traces of H_2S), from which the gas passed directly to the water gas holder. Organic sulfur removal occurred after blending and compression for the synthesis. For this step, the gas was passed through a system of five cylindrical steel tubes 30cm in diameter and 2m high, filled with random-packed rectangular pieces of copper gauze (10cm x 20cm, about 10 mesh) coated with a mixture of 90% Ni and 10% Cu. The amount of Ni-Cu mixture in each vessel was about 15 kg. This mixture was prepared by precipitation from the nitrates with sodium carbonate, and was pasted on the gauze while still wet. It was conditioned for use by reduction in the desulfurizers with hydrogen at 350°C. The temperature of operation for desulfurization was 200-250°C.

The five units containing the desulfurizing agent were arranged so that only four were used at any given time, one comprising the first stage and the other three, the second. The fifth was a first-stage spare. A brickwork housing enclosed the units, except for about 6-8 inches at the top and bottom. The housing also served as a combustion furnace chamber, in which stoker coal was burned to supply heat to maintain the required operating temperature. Once fouled, the Ni-Cu mixture could not be regenerated.

The amount of sulfur in the gas entering this unit could not be ascertained, but it was stated that with an active, fresh charge, the sulfur content, after passing through this system, was about 0.02 grain/m^3.

The synthesis plant was without instrumentation to control pressure, gas flow, or recovery operations. Temperature control in the converter was essentially automatic through the action of the condenser in the water circulation system.

The data of Table II(E) was submitted as operating results of one of the best runs.

VIII. LOW-TEMPERATURE CARBONIZATION

Ever since its organization in 1921, the Institute has carried on a continuous program of coal-carbonization studies. The tar has always been recognized as the most important product of the process, but tar production alone cannot carry the expense. It was, therefore, necessary to give attention to the production of a semi-coke end product which would have a ready sale. The coke comprises 65% or more of the weight of the coal charged.

The most attractive potential market for the coke was as a substitute for charcoal as a domestic heating and cooking fuel. Although its characteristics are excellent for burning in domestic furnaces, it was not found applicable to the braziers used in Japanese homes, because of high ignition temperature. It is not usable for metallurigical purposes, and too expensive for boiler use, therefore, a dependable market was never found. Rather recently, some progress has been reported in blending it with coal for coke making. During the war, it was planned to use it to some extent for making water gas and hydrogen as raw materials for synthetic liquid fuel processes.

Carbonization studies at the Institute were carried out both on test-tube scale and in an assay plant having a throughput capacity of about 6 tons per day. A flow sheet of the plant is shown in Figure 2(E) and a drawing of the retorts in Figure 3(E). The retort system, which was designed at the Institute, comprised 6 vertical chambers of rectangular cross section, the carbonizing sections of which are constructed of fireclay tile, externally heated by combustion of producer gas or gas from low-temperature carbonization. Carbonizing temperature is 500°C, the skin temperature on the outer wall of the retort being 700°C.

The retorts are connected in parallel with the recovery system for gases and distilled products, which comprises a water cooler, a Pelouze tar extractor, a Hurdle ammonia scrubber, a gas meter, and gasholder. In this manner, if all 6 retorts are operated simultaneously, total coke and gas production are averaged as though 6 separate tests had been made. Coal is intermittently fed by hand, and coke is carried away continuously by a conveyor.

Three bulletins relating to the carbonization work, have been prepared for distribution, the titles being as follows:

1. "Japanese Coals as Raw Materials for Low-Temperature Carbonization" (out of print).
2. "Report of the Experiment on the Low-Temperature Carbonization of Coal".
3. "The Experiment of the Continuous System for the Low-Temperature Carbonization of Coal"

(ATIS and ND numbers of the last two of these publications are given in Appendix I of this report).

The carbonization group is now emphasizing the utilization of brown coal. The full extent to which this may develop cannot yet be estimated, but it is strongly contended that use must be found for Japan's brown coal, the reserve of which is estimated at 500,000,000 metric tons. The deposits are located principally in northeastern and central HONSHU. This substance resembles

American lignite more than it does the brown coal of Germany. It has a low calorific value, and because of its structure and composition weathers rather severely.

At present, tar from brown coal carbonization is visualized as a petroleum substitute, and the carbonization residue as a substitute for charcoal. It has already been found possible to make a "coalite" with reasonably satisfactory ignition characteristics, at about half the price of charcoal. However, the product so far obtained emits a slight but objectionable odor on combustion.

The data of Table III(E) were submitted as representative yields of tar and gas by low-temperature carbonization of typical Japanese coals.

IX. SUMMARY OF REPORTS DESCRIBING WAR ACTIVITIES

The Institute was under military control from 1944 until the end of the war, and hence was subject to complete reorganization of personnel and activities. However, personnel was increased by only 45 persons (classified as 5 research chemists, 13 assistants and 28 laborers), and hostilities ended to soon for complete conversion of the program to specific war work.

Seven reports were submitted to NavTechJap as covering the complete war program of the Institute. All except one of the investigations described in these reports had its beginning in 1944. The exception is the hydrogenation of Daido coal, which was studied in about 1941. The reports are in Japanese, but with each was submitted an English summary. Following is a digest of the summaries, amplified in some instances by interrogation of Institute personnel. (ATIS and ND numbers will be found in Appendix II of this report).

A. "Hydrogenation of Tatung (Daido) Coal", by M. KUROKAWA and S. ANDO.

The purpose of this investigation was to determine the suitability of this coal as the raw material for establishing a coal hydrogenation plant in China. The Institute's 3-ton-per-day pilot plant was used for the liquid-phase hydrogenation and a 5-liter high-pressure batch-type rotating autoclave for the vapor phase.

The experiment comprised three parts:

1. Coal was hydrogenated in the liquid phase to heavy oil.
2. Heavy oil from (1) was batch-hydrogenated as the first cycle of the vapor stage.
3. Oil heavier than gasoline from (2) was batch-hydrogenated as the second cycle of the vapor stage.

Operating conditions in the liquid phase were 200 atmospheres pressure, a 410°C operating temperature, with a catalyst consisting of $SnCl_2$, equivalent to 1%, by weight, of the paste. Conditions in the vapor phase were 240 atmospheres pressure, a 460°C operating temperature, 1 hour of contact, and a catalyst consisting of 10 parts MoO_3 to 1 part of sulfur, added in an amount equal to 10%, by weight, of the oil charge.

The overall results are given in Table IV(E).

It was concluded that the maximum gasoline production from this coal would be about 35% of the weight of the coal, with a total liquefaction of 60% of the coal.

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B. "The Low-Temperature Carbonization of Coaly Shale" by N. SAITO

The object of this project was to build and operate a low-temperature carbonization plant to treat 20 tons, per day, of coaly shale, such as is found in the western part of HOKKAIDO and in parts of HONSHU and KYUSHU. The product distilled from the shale was to serve as a petroleum substitute for production of aviation gasoline. The plant was built and preliminary operation began August 10, 1945, but was stopped with the cessation of hostilities.

C. "The Carbonization of Pine Wood", by N. SAITO

The purpose of this problem was to study the low-temperature carbonization of pine wood, as a source of tar for conversion to gasoline. A tar yield of 10%, by weight, of the wood charge was obtained in laboratory experiments. However, when the experiment was repeated in the Institute's 6-retort pilot plant, the yield was only 4.38%. The work was not continued long enough to determine whether the laboratory yield could be achieved in plant practice.

D. "The Preparation of Aviation Gasoline from Japanese Pine Root Oil", by T. AMEMIYA

When the gasoline fraction from pine-root oil was subjected to catalytic vapor phase treatment at 400-500°C, using as catalysts such substances as Japanese acid clay, activated acid clay, Kanuma earth and yellow earth, gumming tendency was corrected and a fuel with high octane value was obtained. However, the vapor pressure of the product was low, so it was usable only as blending stock.

Treatment of both the gasoline fraction and the higher boiling components of pine root oil at higher temperatures resulted not only in the production of lower-boiling constituents, but also in excessive decomposition. It was concluded that there is no better process for aviation gasoline production from pine root oil than to treat in a continuous system at 500°C, removing the lighter fractions as they are formed, although their instantaneous concentration is small.

E. "The Catalytic Cracking of Low-Temperature Tar", by M. KUROKAWA, N. ASAOKA, and K. SUGAWARA.

A fraction from low-temperature tar, boiling in the range 200-300°C, was solvent-extracted with phenol containing 20% water. The raffinate was used as a charging stock for catalytic cracking, using pelleted commercial activated clay as the catalyst.

The content of gasoline in the cracked distillate was found to increase with increasing temperature, but the yield on charging stock decreased above 550°C.

F. "The Synthesis of Triptane", by M. KATSUNO

Chemically pure trimethyl butane was prepared in the laboratory to investigate its properties. It was synthesized in the following manner:

Pinacoline and methylmagnesium bromide were subjected to the Grignard reaction, and the alcohol thus produced dehydrated to 2 + 3 + 3 methylbutene -1, which was hydrogenated to 2, 2, 3-trimethylbutane.

ENCLOSURE (E)

As the industrial method of preparation, alkylation of isobutane and propylene was proposed. Only a few preliminary experiments were carried out, using phosphoric acid and $AlCl_3$ as catalysts. The problem was discontinued before the products could be examined.

G. "The Explosive Combustion of Coal Dust in Air", by T. INATOME

The ultimate object of this investigation was the development of explosives whose ingredients are powdered coal and air. Three series of preliminary experiments were performed in the laboratory.

1. Inside a 19mm I.D. a silica tube was compressed a hollow cylindrical plug of coal dust. The hole through the plug was 6mm in diameter, the length of the plug, 55mm. The silica tube, containing the coal dust was suddenly introduced into a tube furnace heated to 800-1000°C, and oxygen was passed through the hole in the plug. Carbonization, combustion of volatile matter, and combustion of fixed carbon occurred in the order mentioned, and at a rate which was slow and irregular, because of the slow rate of heating of the pellet.

2. A tube containing the hollow plug described above was placed in a cold zone (below 100°C) outside the tube furnace, but coaxial with it and near enough to the hot zone to be strongly affected by the radiation from it. Oxygen was passed through the hole in the plug, as before. In this experiment, radiation from the hot zone caused ignition of the plug at the end nearest the furnace, and combustion proceeded until the plug was consumed, but the reaction rate was slow.

3. If oxygen and coal dust were mixed in the stoichimetric proportions for complete combustion before passing into the tube furnace, the rate of reaction was of the order of the speed of an explosion.

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Table I(E)
HYDROGENATION OF HARUTORI COAL IN THE SEMI-PLANT

Type of Coal: High volatile bituminous.
Proximate Analysis: (%)

Moisture	5.44
Ash	13.3
Volatile Matter	42.56
Fixed Carbon	38.7

Ultimate Analysis (Dry Basis): (%)

Ash	14.07
C	62.59
H	4.87
O	17.23
S	0.42
N	1.07

Heating Value 6250 cal/gm

Weight ratio coal: vehicle	1:1
Catalyst	Nickel Oxide
Rate of paste input	157 kg/hr
Hydrogen input	146 m^3/hr (N.T.P.)
Mean reaction temperature	410°C
Mean reaction pressure	200 atmospheres
Duration of run	about 2 months
Degree of coal liquefaction	86.2%
[1]Heavy oil production	788.3 kg/metric ton paste (60.08% distilling up to 300°C)
[2]Light Oil production	39.9 kg/metric ton paste
[3]Volatile oil production	24.6 kg/metric ton paste
[4]Residue	81.5 kg/metric ton paste
Gas	27.8 kg/metric ton paste
Loss	48.0 kg/metric ton paste
H_2 consumed	10.1 kg/metric ton paste

Note

(1) Heavy oil : product boiling above 200°C
(2) Light oil : product boiling up to 200°C, condensed by air and water cooling in recovery equipment preceding oil scrubbing
(3) Volatile oil : low boiling product by oil scrubbing of exit gases
(4) Residue : unliquefied carbonaceous material and ash

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Table II(E)
RESULTS OF TEST RUN OF FISCHER-TROPSCH SEMI-PLANT

Catalyst	Ni:Co:Cr:Kieselguhr, 40:10:7.5:150
Working pressure	5 atm. gauge
Temperature	$195^{\circ}C$
Vol. inlet gas	931 m^3
Duration of run	30 hrs
Average rate of gas flow	31 m^3/hr
Oil yield from condensers	61.83 lit. (sp. gr. 0.7583 (20°C)Olefines 5%(vol.)
Oil yield from scrubber	28.04 lit. (sp. gr. 0.7248 (20 C)Oilfines 2%(vol.)
Total oil yield	89.87 lit.
Total yield/m^3 inlet gas	117.5cc (inlet gas corrected for components other than H_2 and CO)
Total water	161.12 lit.
Vol. exit gas	298 m^3
Contraction	68%

Gas Analysis

	Inlet Gas	Exit Gas
CO_2	2.670%	12.0%
O_2		
CO	27.4	10.0
H2	54.6	19.5
CH_4	0.7	12.3
N_2	14.7	46.2

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Table III (E)
YIELDS OF CARBONIZATION PRODUCTS FROM JAPANESE COALS

Name of Coal	Type of Coal	Proximate Analysis					
		H_2O	Ash	Vol. Matter	Fixed C	Heating Value (Cal/gm)	Tar Yield*
Horonai	Non-coking bituminous	3.41	10.94	40.77	45.33	7,035	15.38
Okinoyama	Sub-bituminous	10.79	14.03	49.93	25.95	5,622	7.78
Kidomo	Brown Coal	27.67	14.71	34.70	22.92	3,667	4.00

Name of Coal	Tar Analysis (wt %)					Sp.Gr.	Heating Value (Cal/gm)
	Org. Acid	Phenols	Bases	Neutral Oil	Ether Insoluble		
Horonai	2.53	18.18	3.33	75.39	0.57	0.9656	9,249
Okinoyama	10.92	19.49	1.85	66.93	0.81	0.9668	9,398
Kidomo	11.46	20.85	0.34	53.23	14.12	0.9811	8.730

Name of Coal	Gas Yield (m^3/ Metric Ton)	Analysis of Gas						
		CO_2	Illuminants	O_2	CO	H_2	CH_4	H_2O
Horonai	700	6.1	3.7	1.1	8.9	21.0	48.6	10.4
Okinoyama	1,070	21.3	3.8	0.8	10.2	21.2	38.6	4.1
Kidomo	726	3.3	1.2	1.2	15.8	11.2	24.3	2.5

* On basis of coal charged (wt %)

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Table IV(E)
HYDROGENATION OF DAIDO COAL

	Input (kg)		Product (kg)	
1st Stage	Coal H_2	1,000 22.4	Heavy Oil Light Oil Light Hydrocarbons	550 90.6 18.6
1st Cycle 2nd Stage	Heavy Oil H_2	550 31.4	Middle Oil Refined Gasoline Light Hydrocarbons	112.3 297 93.2
2nd Cycle 2nd Stage	Middle Oil H_2	112.3 6.4	Middle Oil Refined Gasoline Light Hydrocarbons	23 54.8 18.4

ENCLOSURE (E)

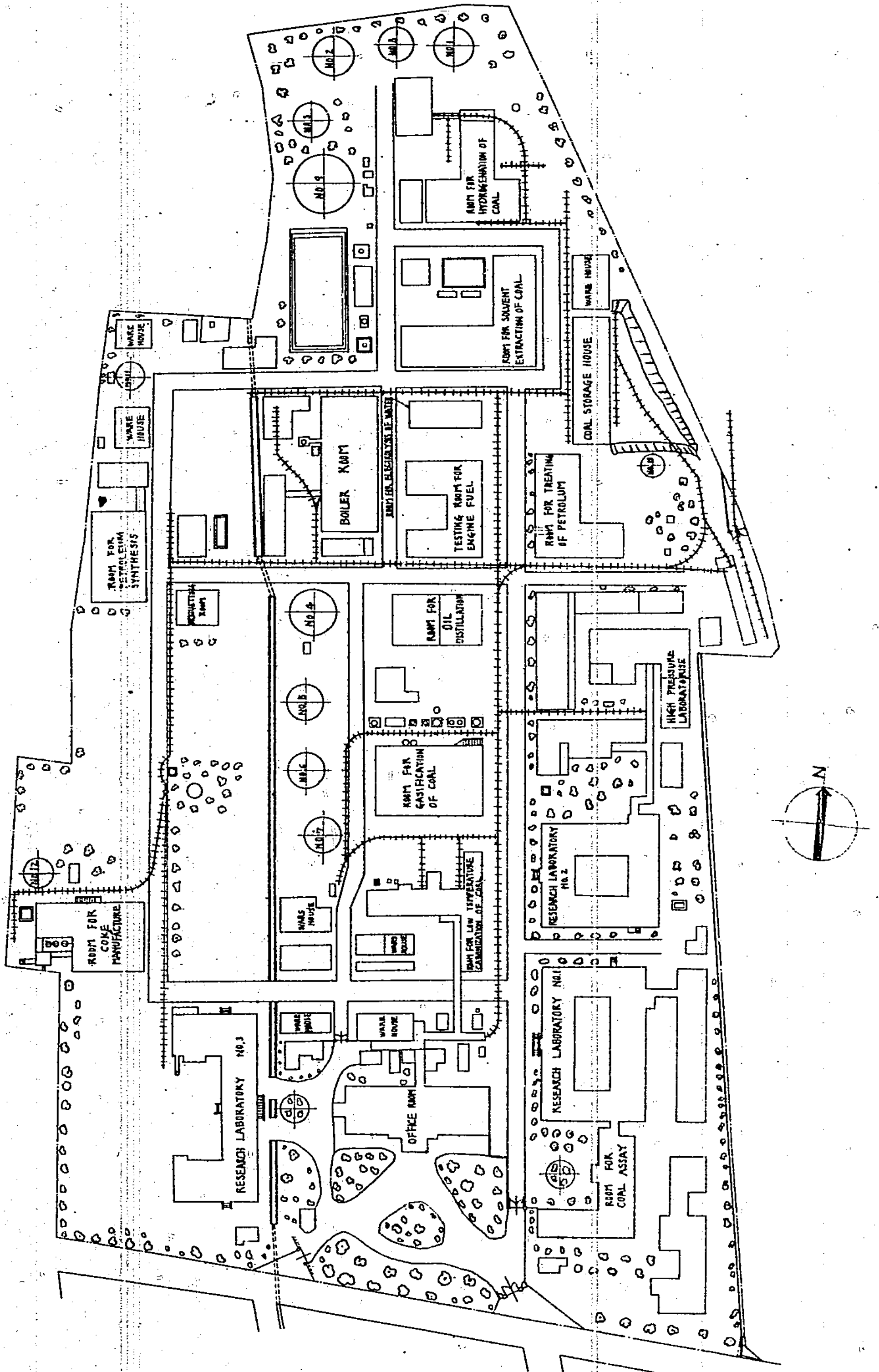


Figure 1(E)
THE IMPERIAL FUEL RESEARCH INSTITUTE
KAWAGUCHI, Saitama, Pref., Honshu, Japan

ENCLOSURE (E)

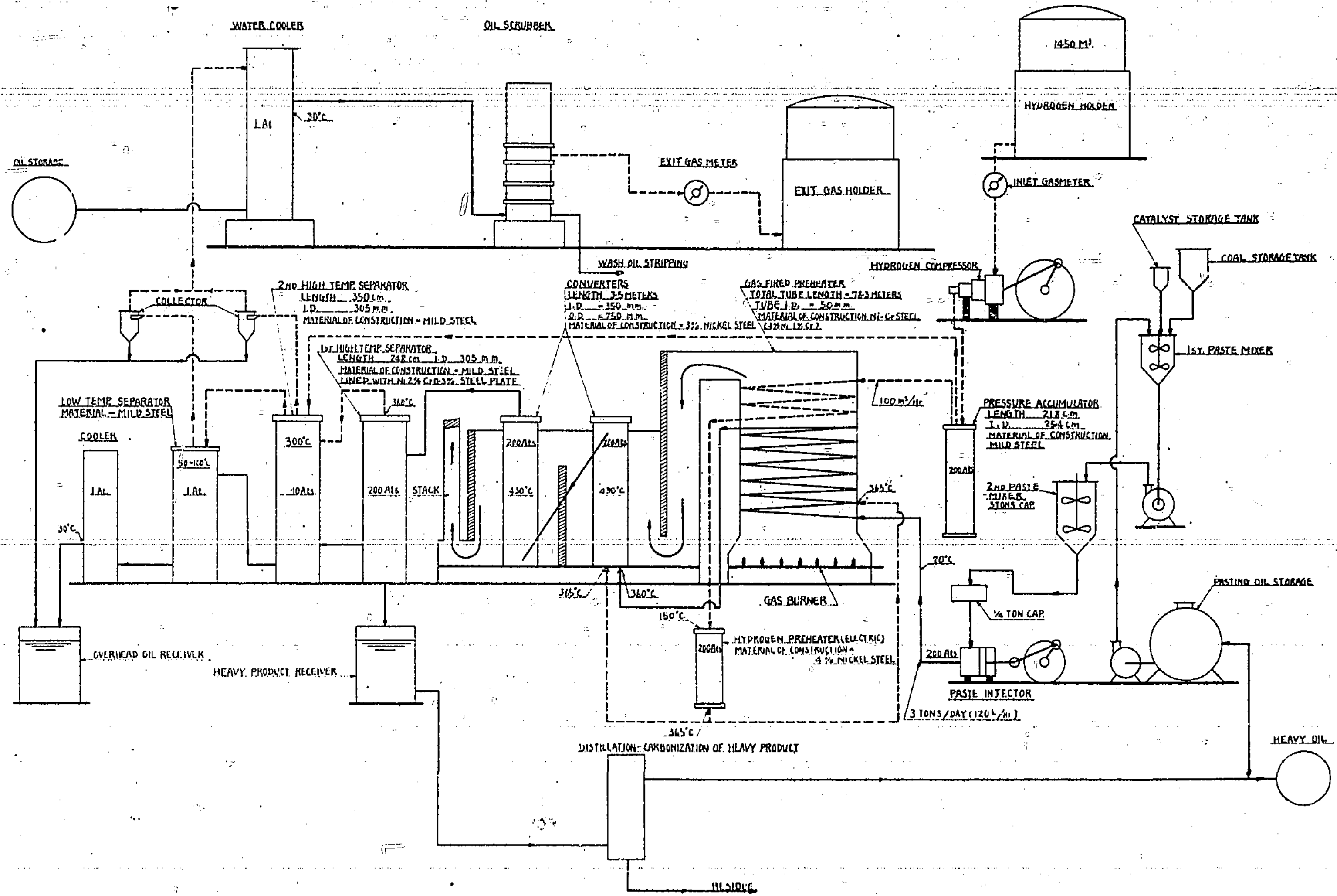


Figure 2(E)
FLOW SHEET OF IMPERIAL FUEL RESEARCH INSTITUTE
PILOT PLANT FOR HYDROGENATION OF COAL
KAWAGUCHI, Saitama, Japan

ENCLOSURE (E)

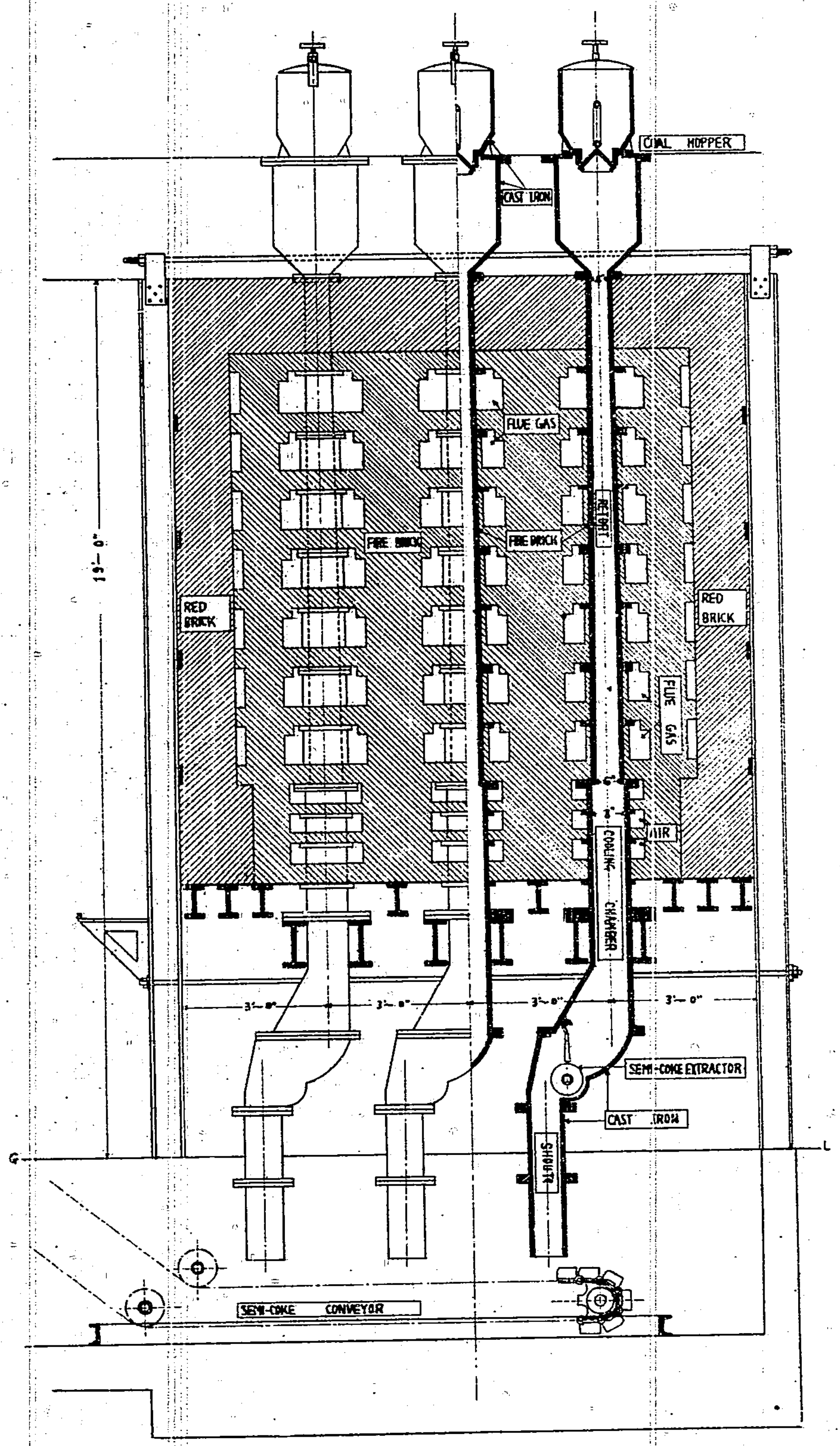


Figure 3(E)
ELEVATION
OF LOW
TEMPERATURE
CARBONIZATION
RETORT SYSTEM
Imperial Fuel
Research Institute,
KAWAGUCHI,
Saitama Pref.,
Japan

RETORT BENCH
12 x 13 x 19
NO. OF RETORTS
Six
OUTPUT
Six Tons Per Day
DIMENSIONS OF RETORTS
Top- 4 x 29½
Bottom- 6 x 33½
Height- 11
WORKING TEMPERATURE
500°C Inside Retort
700°C Outside Retort
FUEL
Producer Gas or Low
Temp. Carbonization Ga

ENCLOSURE (E)

APPENDIX I
JAPANESE DOCUMENTS

Bulletins of the Imperial Fuel Research Institute Related to Synthetic Fuel Investigation, Forwarded Through ATIS to the Washington Document Center

NavTechJap Document No.	ATIS No.	Title and Author
ND26-0023.1	4594	Studies on the Liquefaction of Coal (Part V) (Action of Catalysts on the Coal Paste) by M. KUROKAWA.
ND26-0023.2	4594	The Preparation of Benzol from High Temperature Tar by Hydrogenation, by T. NIIMURA, H. NOMURA and N. TAKASE.
ND26-0023.3	4594	Studies on the Liquefaction of Coal (Part IV) (The Preparation of Hydrogen by the Water Gas Reaction) by M. KUROKAWA and K. TAKENAKA.
ND26-0023.4	4594	Studies on the Liquefaction of Coal (Part III) (Test Results by Various Catalysts) by M. KUROKAWA, K. HIROTA, K. FUJIWARA and S. ASAOKA.
ND26-0023.5	4594	The Hydrogenation of Phenols (Part II) (On the Preparation of Hydrocarbons from Low-Temperature Tar Acids) by A. ANDO.
ND26-0023.6	4594	The Hydrogenation of Heavy Oils, by S. ANDO.
ND26-0023.7	4594	The Hydrogenation of Low-Temperature Tar, by S. ANDO.
ND26-0023.8	4594	Studies on the Liquefaction of Coal (Part II) (Test Results of Japanese Coals) by S. UCHIDA.
ND26-0023.9	4594	Hydrogenation of Phenols (Part I) by S. ANDO.
ND26-0023.10	4594	Studies on the Liquefaction of Coal (Part I) (Recovery of Hydrogen from Waste Gases) by K. TAKENAKA.
ND26-0024.1	4595	The Experiment on the Tully Gas Manufacture, by Y. BAN, R. KOMURA and N. SAITO.
ND26-0024.2	4595	The Synthesis of Gasoline (Part I) by S. TSUTSUMI.
ND26-0024.3	4595	The Preparation of Water Gas from Methane, by S. TSUTSUMI.
ND26-0025.1	4596	The Experiment on the Low-Temperature Carbonization of Coal, by Y. BAN, N. SAITO and S. ISHIKAWA.
ND26-0025.2	4596	The Experiment on the Continuous System of the Low-Temperature Carbonization of Coal, by Y. BAN, N. SAITO and R. KOMURA.

ENCLOSURE (E)

APPENDIX II
JAPANESE DOCUMENTS

Reports on War Activities of the Imperial Fuel Research Institute Forwarded Through ATIS to the Washington Document Center

NavTechJap Document No.	ATIS No.	Title and Author
ND26-0023.11	4594	The Catalytic Cracking of Low Temperature Tar. By K. SUGARAWA.
ND26-0023.12	4594	The Hydrogenation of Tatung (Daido) Coal. By M. KUROKAWA and S. ANDO.
ND26-0025.3	4596	The Low-Temperature Carbonization of Coaly Shale. By N. SAITO.
ND26-0025.4	4596	The Carbonization of Pine Wood. By N. SAITO.
ND26-0020	4591	The Preparation of Aviation Gasoline from Japanese Pine Root Oil. By T. AMEMIYA.
ND26-0021	4592	The Explosive Combustion of Coal Dust Fuel. By T. INATOME.
ND26-0022	4593	The Synthesis of Triptane. By M. KATSUNO.

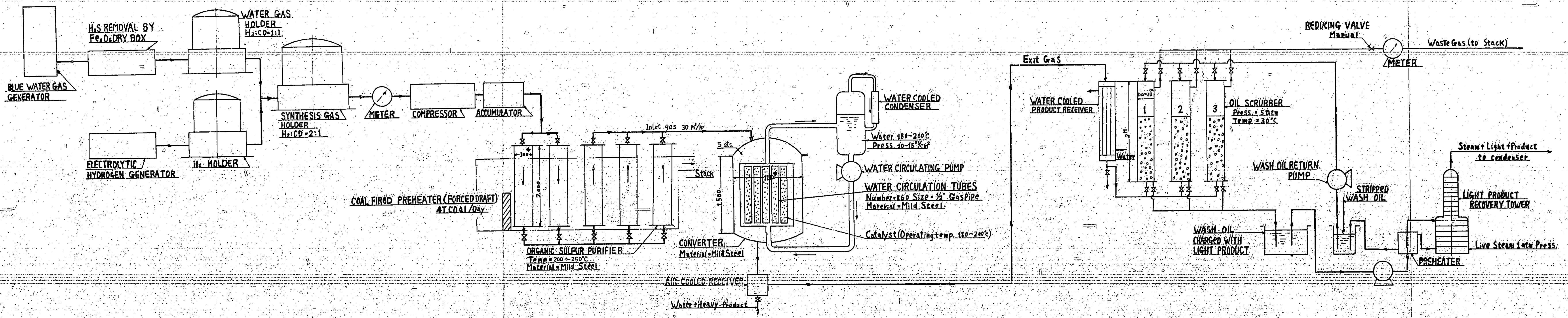
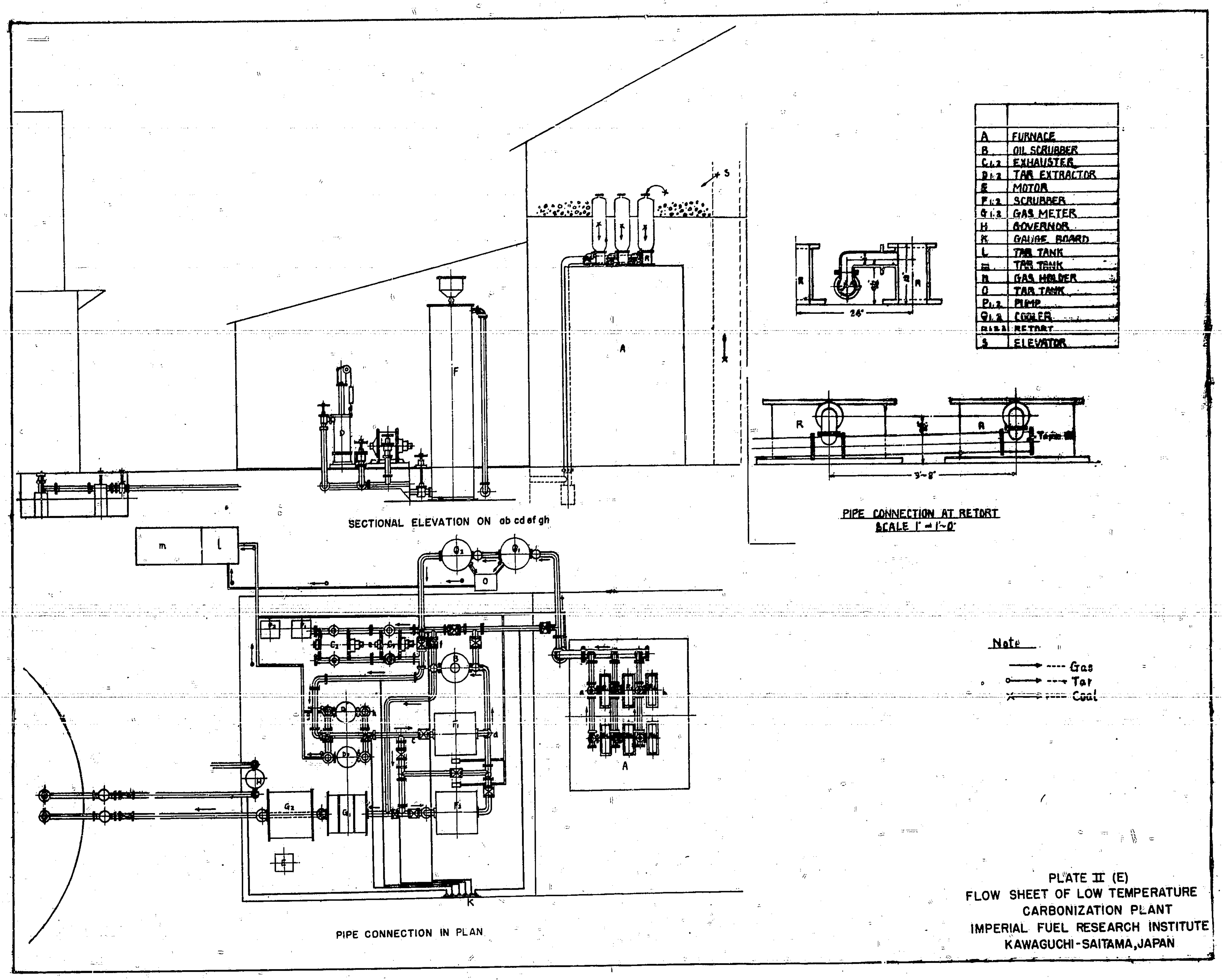


PLATE I (E)
FLOW DIAGRAM OF FISCHER
TROPSCH PILOT PLANT
IMPERIAL FUEL RESEARCH INSTITUTE
SAITAMA-KAWAGUCHI, JAPAN



A	FURNACE
B	OIL SCRUBBER
$C_{1,2}$	EXHAUSTER
$D_{1,2}$	TAR EXTRACTOR
E	MOTOR
$F_{1,2}$	SCRUBBER
$G_{1,2}$	GAS METER
H	GOVERNOR
K	GAUGE BOARD
L	TAR TANK
m	TAR TANK
n	GAS HOLDER
O	TAR TANK
$P_{1,2}$	PUMP
$Q_{1,2}$	COOLER
$R_{1,2,3}$	RETORT
S	ELEVATOR

PLATE II (E)
FLOW SHEET OF LOW TEMPERATURE
CARBONIZATION PLANT
IMPERIAL FUEL RESEARCH INSTITUTE
KAWAGUCHI-SAITAMA, JAPAN

ENCLOSURE (F)

ENCLOSURE (F)

REPORT ON THE COAL HYDROGENATION PLANT AT FUSHUN, MANCHURIA

ENCLOSURE (F)

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ENCLOSURE (F)

I. INTRODUCTION

This report records and summarizes technical data on the South Manchurian Railway Co.'s coal hydrogenation plant at FUSHUN, Manchuria, obtained by the Petroleum Section of NavTechJap on 11 and 17 January, 1946. In this report, South Manchurian Railway Co. will be designated by the abbreviation S.M.R.

This plant was not inspected by NavTechJap personnel, since NavTechJap's request, via official channels, to visit the Fushun plant was disapproved in view of the unsettled military conditions prevailing in that area. The information presented was obtained by interview in TOKYO with Mr. T. MIYAMA, who was Technical Director of the Fushun plant from 1937 to 1942, and is now residing in TOKYO as Technical Director of Teikoku Nenryo (Teinen). He has been connected with Teinen since 1942.

The material in this report is based on Mr. MIYAMA's memory, and on memoranda from his personal notes. He stated that he no longer had any official records of Fushun, since those in his possession were burned when his home in TOKYO was destroyed in a fire-bomb raid.

II. HISTORY

Intensive experimentation directed toward establishing the Fushun coal hydrogenation plant began about 1928. At that time, an informal co-operative agreement was made between S.M.R. and the Japanese Imperial Navy's Laboratory at TOKUYAMA, to the effect that both organizations would share research data on coal hydrogenation, with erection of a full-scale plant at FUSHUN as the goal. S.M.R.'s work was done at the Company's Central Research Laboratory at DIAREN, under the direction of Dr. R. ABE, who later became assistant to Mr. MIYAMA at FUSHUN.

Co-operation on this undertaking presumably continued throughout what may be termed, the development period, which ended in 1936. At that time, definite commitments were made toward erection of a plant, the design of which would combine the best features of the Navy's research and the work at DAIREN. The Navy stipulated that all machinery and process equipment must be made in Japan. Accordingly, pressure vessels for converters and separators were ordered from the Kure Navy Yard. The largest of these vessels, which were to become the converters, were 7.3 meters long by 95cm inside diameter. It is of interest that these vessels, according to Mr. MIYAMA, were the largest of this type which could be made in Japan at that time. Neither annealing furnaces nor ingots were available for the manufacture of larger pieces.

The Fushun plant was erected between 1936 and 1939. The Navy-type converter, which was to be 7.3 meters long and equipped with a propeller-type stirrer, was not installed because of objections offered by S.M.R. technical advisers. In its place, two of the 7.3 meter vessels were joined end-to-end by bolting, thus doubling the size. The Navy catalyst ($ZnCl_2$) was likewise rejected in favor of S.M.R.'s precipitated FeS.

The plant comprised a single converter, liquid-phase system, designed to run on Oyama coal. Preliminary operation began in April, 1939. In November of that year, a second converter was added. Liquid phase hydrogenation was continued until February, 1940, when the addition of a separate vapor phase reactor system (installed at the direction of the Navy) was completed. From this time until July, 1942, the plant operating schedule was divided between liquid-phase coal hydrogenation, and vapor-phase hydrogenation of fractions from low-temperature tar and from the liquid-phase coal process. From July, 1942 until the end of the war, coal hydrogenation was abandoned, at the direction of the

Navy, and full attention was given to the manufacture of aviation gasoline by hydrocracking of gas oil and kerosene.

Throughput capacity of the liquid phase plant was about 10,000 metric tons of coal per year. Mr. MIYAMA estimates that a total of about 15,000 metric tons of product was made during the entire period of the plant's operation, the greater part of which was heavy oil, a primary product from the liquid-phase operation.

III. DESCRIPTION OF PLANT AND PROCESS

A. Liquid Phase System

Plate I(F) is a flow diagram of the liquid phase system for coal hydrogenation. This diagram was prepared by Mr. MIYAMA and his associates for NavTechJap.

The converter originally proposed by the Navy was not used. This converter was to be 7.3 m long, with an I.D. of 95cm and a free volume of 4.5 m^3. Its outside diameter could not be ascertained. It was to be provided with a propeller-type stirring device, designed to rotate at 200 r.p.m. Each propeller was to have two blades, and there was to be pitch reversal between adjacent propellers. The supporting shaft was to pass through both converter heads, which were to be equipped with external packing glands. Results at TOKUYAMA indicated that agitation, such as would be provided by this device, would increase throughput by about 40%.

The technical staff of S.M.R. foresaw a serious leakage problem with every type of packing gland suggested; the staff also believed the converter size should be doubled. Accordingly, the converter which was installed had no stirring apparatus, and the desired size was obtained by bolting together two of the short sections end-to-end at the body flanges. Material of construction of the converters could not be determined.

S.M.R. technologists also objected to the use of the $ZnCl_2$ catalyst recommended by the Navy. Their own experiences indicated that the use of this catalyst would result in severe corrosion of equipment. They also believed zinc to be too expensive for this purpose, since the amount required was 1% of the weight of the coal processed, and recovery from the residue was not economically feasible. They had found a less expensive catalyst, precipitated FeS, to be effective at the same concentration employed for zinc. It was agreed to use the S.M.R. catalyst, and Mr. MIYAMA stated that, to his knowledge, no other catalyst was ever employed in the liquid-phase plant. As a matter of record, it was also stated that no form of iron oxide was found to be as effective as ferrous sulfide.

The system for hydrogen manufacture comprised a blue water gas generator, sulfur purification equipment, a water gas shift plant, and a carbon dioxide removal system. The gas generator used high-temperature coke as raw material, producing a gas having the approximate composition H_2, 50%; CO, 40%; CO_2, 5%; N_2, 5%. The desulfurizer consisted of a conventional dry iron-oxide box. Although this provided no means for organic sulfur removal, Mr. MIYAMA stated that, after the water shift and scrubbing, the total sulfur content was about 0.02 gm/m^3.

ENCLOSURE (F)

The shift catalyst comprised a mixture of 95% Fe and 5% Cr, prepared by precipitation from a solution of ferrous and chromic sulfates. This catalyst operated at 540°C. Mr. MIYAMA could not recall the space velocity of reactants over the catalyst, or whether a bulking agent or carrier was used in its preparation. Carbon dioxide was removed by a water wash at 12 atmospheres of pressure.

Ohyama was the only coal processed during the period of Mr. MIYAMA's connection with the plant. He could not recall the analysis of this coal, but stated that it is a pit mine product from FUSHUN, containing about 42% volatile matter and averaging 8-10% ash. He described it as "a very high quality brown coal, approaching bituminous." Possibly it would be classified as sub-bituminous. An analysis of Ohyama coal, obtained from other sources, is presented in Table I(F)

The preliminary steps of coal preparation consisted in grinding the coal to 4 mesh and smaller in a roll crusher, after which, de-ashing was effected in a Dyster system. Ash was thereby reduced to 3-4% in the material charged to the hydrogenation plant.

Paste preparation was operated as a continuous process. The vehicle consisted of about 7% low-temperature tar and 93% heavy oil from coal hydrogenation and was stored at 80°C for feeding to the tube mill mixer. Coal and catalyst were fed to the mill in the wet condition. The coal was charged as the 4 mesh material from the crusher, and, during the mixing operation, was ground to about 200 mesh.

For making a hypothetical 250-ton batch of paste, the following materials would be required (metric tons-dry basis):

Coal	100
Low temperature tar	10
Heavy oil from coal hydrogenation	125
Catalyst	1
Water (adhering to coal and catalyst)	14
	250

According to Mr. MIYAMA's verbal statement, paste input to the converter was 60 tons per day. This is not in agreement with the material flow as indicated on Plate I(F), which shows "normal" input to be 4 tons per hour or 96 tons per day. It should also be noted that only one converter is shown on the flow sheet, whereas Mr. MIYAMA had stated that two were in operation after 1939.

Hydrogenation conditions for the liquid-phase system were 200 atmospheres pressure and 430°C. The only serious operating difficulty admitted was severe erosion of the valve throttling the discharge of heavy oil, containing ash, from the high temperature separator. A serviceable arrangement, requiring change about once in two months, was found to be a valve with needle tip and seat made of tungsten carbide. The stem of this valve was rotated continuously at about 60 r.p.m.

B. Vapor-Phase System

Figure 1(F) is a flow diagram of the plant modified to operate on vapor-

ENCLOSURE (F)

phase hydrogenation. This system was designed to process about 40 kl of liquid per day at 200 atmospheres pressure over a fixed catalyst. Two converters were in series, the reaction temperature of the first being 430°C and the second, 440°C. The preferred catalyst was a pelleted mixture of 40% MoS_3 and 60% acid clay. Charging stock to the vapor-phase plant was either a fraction from low-temperature tar, boiling between 180° and 240°C, or a fraction of similar boiling range obtained from liquid-phase coal hydrogenation. The operating plan for coal hydrogenation work, after installation of the vapor-phase unit, was to run the liquid-phase plant 3 months, storing the product, then shut down and operate 1½ months on vapor phase, using the stored product as charging stock.

The overall yield of products obtained from 250 tons of paste, by combining liquid and vapor-phase operation, was said to be as follows (metric tons):

Aviation gasoline	22.9 kl = 17.4
Motor gasoline	22.1 kl = 17.7
Cresols and phenol	3.2
Gasol ($C_3 + C_4$)	3.5
Pitch coke (from centrifuge residue, contains 50% ash)	20.0
Recycle oil	60.0*
Residual (heavy) oil	65.0*
Gas and loss	Remainder

*Returned to paste making.

This represents about 35% by weight, conversion of coal to gasoline, in terms of raw coal charged.

It was maintained by Mr. MIYAMA that, although the Fushun plant was of full scale commercial size, with nominal capacity for processing about 10,000 metric tons of coal per year, it had been regarded as an experimental plant. An experimental operating program may, therefore, partly explain the low total production, which he estimated to be 15,000 metric tons. Most of this product was the heavy oil obtained from the liquid-phase hydrogenation of coal.

Table I(F)
ANALYSIS OF OYAMA COAL

Proximate					Ultimate				
H_2O	Ash	Volatile Matter	Fixed C	Heating value cal/gm	C	H	O	S	N
5.5	7.0	41.1	46.4	7200	73.7	5.7	12.0	0.5	1.2

ENCLOSURE (F)

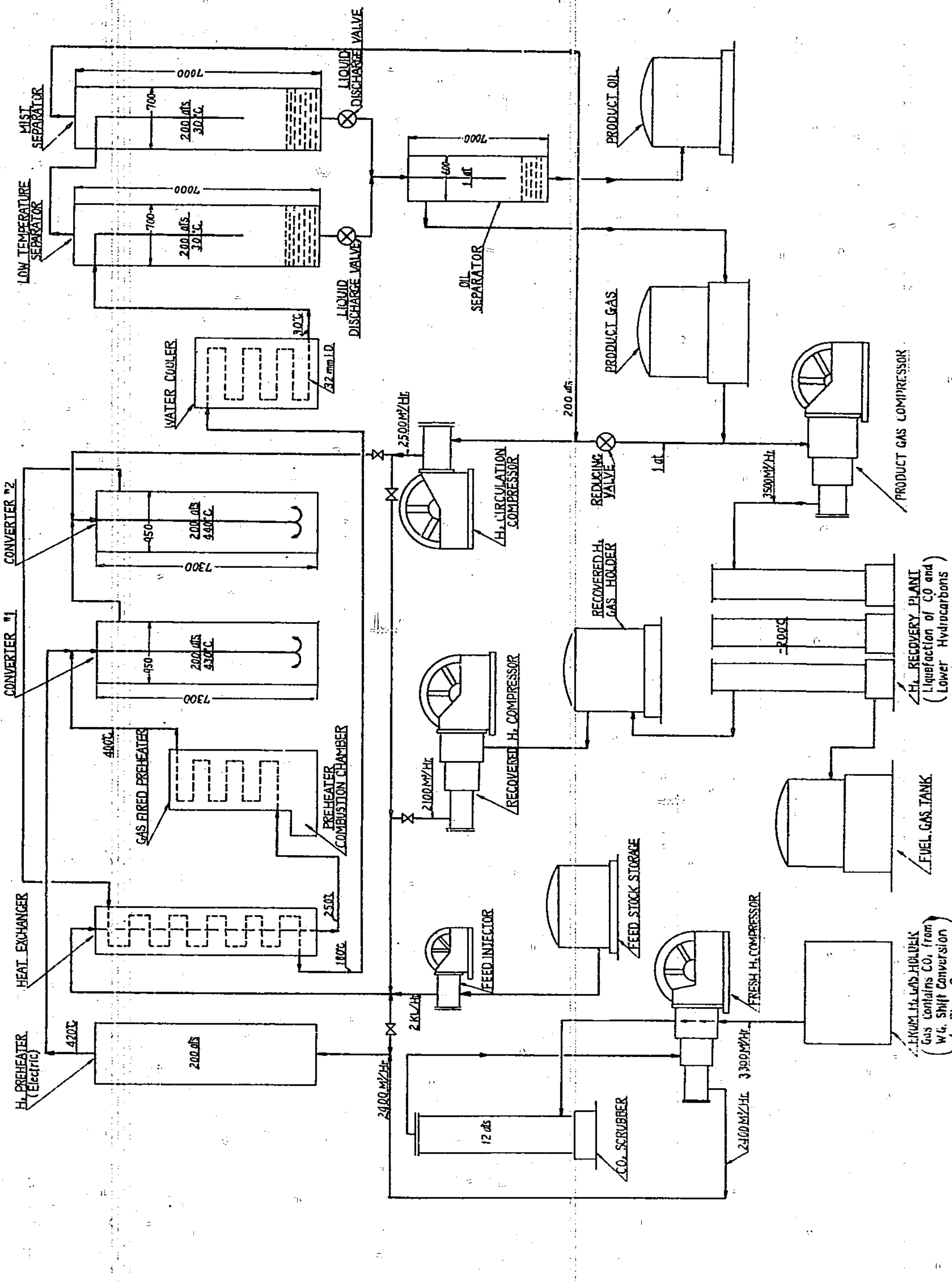
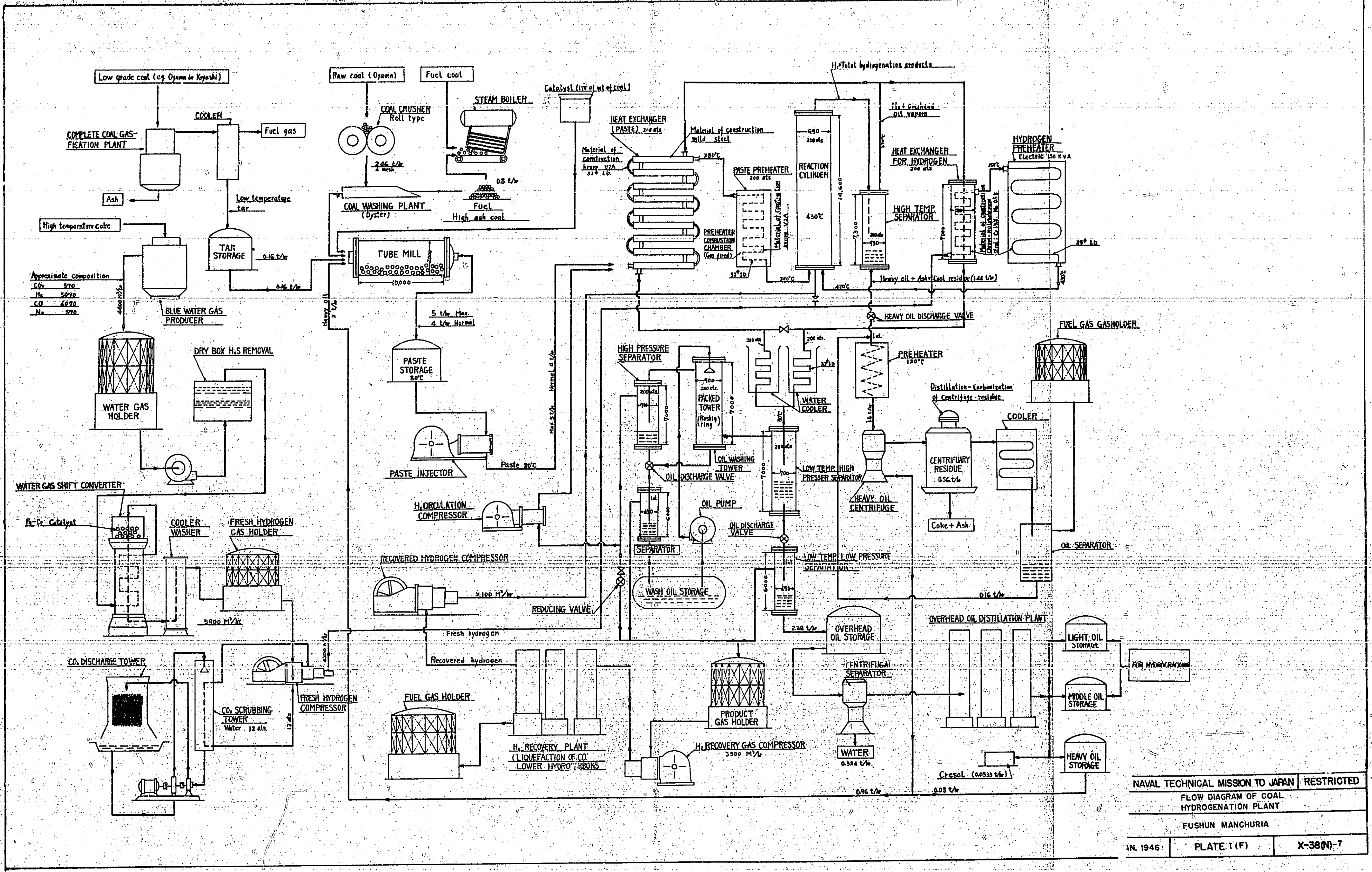


Figure 1(F)
FLOW DIAGRAM OF HYDRO-CRACKING PLANT



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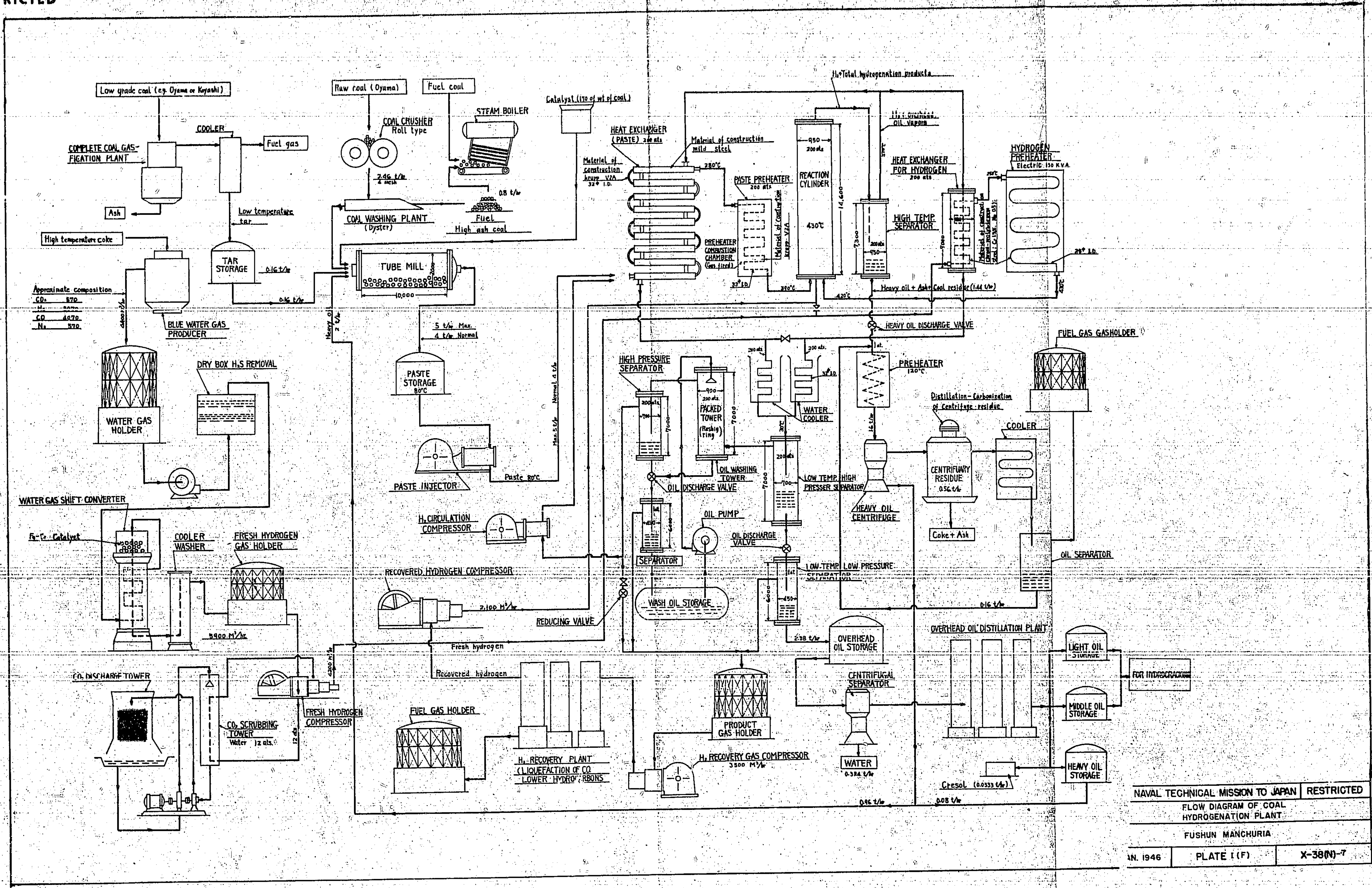
FLOW DIAGRAM OF COAL
HYDROGENATION PLANT

FUSHUN MANCHURIA

JAN. 1946 | PLATE I (F) | X-38(N)-7



NAVAL TECHNICAL MISSION TO JAPAN | RESTRICTED

FLOW DIAGRAM OF COAL
HYDROGENATION PLANT

FUSHUN MANCHURIA

AN. 1946 | PLATE I (F) | X-38(N)-7

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ENCLOSURE (G)

ENCLOSURE (G)

REPORT ON
MIIKE SYNTHETIC OIL COMPANY
OMUTA, KYUSHU

ENCLOSURE (G)

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ENCLOSURE (G)

SUMMARY

This report records and summarizes technical data on the Miike Synthetic Oil Company at OMUTA, Kyushu, obtained by the Petroleum Section of NavTechJap during the period 3-9 October 1945.

The Miike plant utilizes the conventional low-pressure Fischer-Tropsch process, with cobalt-thorium catalyst, for production of oil from Miike coal. The process was licensed from Ruhrchemie and most equipment was constructed by the Koppers Co.

The plant produces gasol (liquefied propane and butane), motor gasoline, diesel fuel, and several grades of paraffin wax. All products were distributed to the Army, Navy or civil government. A plant to produce lubricating oil by aluminum chloride polymerization of paraffin oil, was under construction.

Plant capacity was rated at 30,000 metric tons of total synthetic product per year, but actual production during the peak year 1943 was only 16,000 tons. This was primarily due to decreased production of synthesis gas, the result of water gas generator operating difficulties with the high sulfur, low melting point ash Miike coke. The low production was also due to a low yield of oil per unit of synthesis gas, apparently due to low catalyst activity.

The plant suffered no serious damage from air raids, but due to two explosive bomb hits, one on the main coke conveyor and one on the main synthesis gas line at the desulfurization unit, the entire plant had been shut down since 7 August 1945.

Details on history, ownership and organization of the concern, process flow sheets, plant layout, product quality and output are presented herewith. Also attached are documents pertaining to research work on synthetic lubricating oil, cracking of pine root oil, and iron synthesis catalyst, and copies of original correspondence with German firms.

ENCLOSURE (G)

I. INTRODUCTION

The Miike Synthetic Oil Company is located in the city of OMUTA, Fukuoka Prefecture, Kyushu, Japan. The center of the plant is located approximately at 33°-01'-14" N, 130°-27'-50" E.

The following Japanese personnel were interviewed and assisted in supplying the information presented herewith:

Mr. Takanaga MITSUI, President
Mr. Masao TAKEI, Head of Chemical Dept.
Mr. Heima NAGAHAMA, Head of Mechanical Dept.

II. HISTORY AND ORGANIZATION

Construction of the plant was started in November 1936 by a special construction department in the Mitsui Mining Company. Oil production was started in May 1940. With separation of the chemical department from the Mitsui Mining Company, the plant was transferred in April, 1941, to the newly established Mitsui Chemical Industrial Company. In October 1943, the Independent Miike Synthetic Oil Co. was founded by the joint interests of Mitsui and the TEIKOKU NENRYO KOGYO (Imperial Fuel Industry) Corporation, with a capitalization of 50,000,000 Yen. In October 1944, the following firms were amalgamated to form the NIPPON JINZO SEKIYU (Synthetic Oil) Co., Ltd., with a capitalization of 150,000,000 Yen:

The Miike Synthetic Oil Co. (Capital 50,000,000 Yen)
The Hokkaido Synthetic Oil Co. (Capital, 70,000,000 Yen)
The Amagasaki Synthetic Oil Co. (Capital, 30,000,000 Yen)

Of the total capitalization, Mitsui has about 20% and the Imperial Fuel Industrial Corp., an amount greater than 50%. Headquarters of the NIPPON Synthetic Oil Co. are located in TOKYO at 6, Nishi-Ginza, Kyobashiku. This parent concern was established to manufacture and refine synthetic fuel and its derivatives. The top management of this concern is as follows:

Chairman of Board	Mr. Yoshi MISHUKU
President	Mr. Takanaga MITSUI
Managing Director	Mr. Masumi YAMAGUCHI
Directors	Mr. Ryo MITSUI Mr. Tosaki MATSUMOTO Mr. Toshitada KII Mr. Masana KAWAGUCHI Mr. Heima NAGAHAMA Mr. Ryoichi NISHIKAWA Mr. Takashi EGUCHI Mr. Masao TAKEI Mr. Rokuro MIKI Mr. Shuji NISHITERU Mr. Masajiro UCHIDA Mr. Gunji IJICHI
Inspectors	Mr. Kaneyoshi SAKAI Mr. Tamesuke OKAMOTO Mr. Norito HIRASAWA

ENCLOSURE (G)

The following outlines the personnel organization of the Synthetic Oil Plant at Miike:

President Mr. T. MITSUI

Mechanical Division Mr. H. HAGAHAMA, Chief

a. Machinery Dept. Mr. I. HIDAKA
b. Building & Repair Dept. Mr. K. SAIGO
c. Planning Dept. Mr. T. MIYAMAYE.
d. Electrical Dept. Mr. Y. KUBOTA
e. Orderly Dept. Mr. T. UCHIDA

Chemical Division Mr. M. TAKEI, Chief

a. Gas Dept. Mr. A. NAKAGAME
b. Synthetic Dept. Mr. M. SHIBUYA
c. Refining Dept. Mr. M. ANDO
d. Catalyst Mfg. Dept. Mr. S. KOJIMA
e. Research Analytical Dept. Mr. NAKAJIMA

Business Division Mr. J. KONDO

a. Accounting Dept. Mr. J. AOKI
b. Sales Purch. Dept. Mr. AWAZU
c. General Dept. Mr. M. HIRASHIMA
d. Personnel Dept. Mr. M. YOSHITAKE
e. Labor Welfare Dept. Mr. H. KAKURA

The total number of employees at Miike is approximately 1400 and the average daily wage of plant laborers is 2½ Yen.

III. DESCRIPTION OF PROCESS

A. General

The Miike Synthetic Oil Co. operates a conventional low-pressure Fischer-Tropsch process, utilizing a cobalt-thorium catalyst. Synthetic gas, with H_2:CO ratio maintained at 2:1, is obtained by blending water gas and re-formed coke oven gas. Coke oven gas, and coke for the water gas generators, are obtained by high-temperature carbonization of Miike coal in Koppers ovens. Organic and inorganic sulphur are removed from the synthesis gas by use of the iron oxide catalyst, "Luxamasse". Catalysts for sulphur removal and oil synthesis are manufactured in a catalyst plant on the factory grounds. The synthesis reaction is carried on in low-pressure reactors of conventional Ruhrchemie design. The heavier synthesis oil is separated by direct condensation with water, and lighter components are picked by adsorption on activated carbon. Distillation of these products yields liquefied propane-butane, motor gasoline, diesel fuel, and paraffin wax. An outline of the over-all process flow is given in Plate I(G).

B. Coke Oven Plant

The coke oven plant was designed, and the equipment manufactured, by the Koppers Co. The plant consists of two batteries of 25 ovens each, and was designed to handle 750 tons of Miike coal per day. Actually, only about 650 tons per day are charged due to the limited coke demand of the water gas generators.

ENCLOSURE (G)

Typical analyses of Miike coal and coke are as follows:

	Coal	Coke		
Water	8.1%	7.8%		
Ash	12.4	19.5		
Volatiles	40.6	2.0		
Sulphur	2.4	2.2		
Fixed Carbon	47.4	78.5		
M.P. of Ash	1060°C	1060°C		
Caking Index	28			
Shatter Test			above 50mm	38.1%
			above 40mm	48.4
			above 25mm	63.8
			above 15mm	78.4
			below 15mm	21.6

The coke oven by-products plant contains conventional equipment for production of coal tar and crude benzol, which are shipped to the neighboring Miike Dyestuffs Works, and also ammonium sulphate, which is marketed. Coke oven gas is charged to the Koppers gas re-forming plant. The coke is screened, and particles greater than 25mm in size are charged to the Koppers water gas generators. Coke breeze is charged to five small Koppers producer gas units, yielding about 400 m3/day, which is used for firing the coke ovens.

A process flow chart for the various units of the gas department is given in Plate II(G).

C. Water Gas Plant

The water gas plant consists of five Koppers generators, each with a rated capacity of 100 tons of coke per day. The plant was designed to operate with four generators on stream, and one on standby, producing 444,000 m3/day of water gas. In actual practice, it was usually possible to maintain only three on stream, due to operating difficulties resulting from a lower quality of coke than was expected. The high sulphur content of the coke resulted in severe corrosion; for example, within a period of four years, a 14mm steel wall in the gas scrubber was reduced to 1.5mm. Considerable operating time also was lost due to clinker formation, and breakage of mechanical grates.

Due to the low melting point of the ash, it was necessary to reduce the operating temperature from the 1200°C design optimum to 1100°C, resulting in lower gas production and the rejection of considerable unburned carbon in the ash (about 15%). Actual gas production was only about 1000 cubic meters per ton of coke, compared with the expected 1335. The lower temperature in the reaction zone also resulted in a lower content of CO in the water gas and a higher content of inerts, especially CO_2. This restricted the amount of re-formed gas of high hydrogen content which could be mixed and still maintain a H_2:CO ratio of 2:1 in the synthesis gas. As a result of these difficulties, production of total synthesis gas amounted to only 600,000 m3/day compared with design maximum of 900,000.

No unusual design features or modifications appeared to be incorporated in in this plant.

D. Gas Re-forming Plant

The gas re-forming plant was designed, and the equipment constructed, by the Koppers Co. There are two sets of Cowpers stoves and auxiliary equipment. Design capacity of the plant is 456,000 m^3/day. In practice, a mixture of coke oven gas, residual gas from the synthesis, and CO_2 obtained from the neighboring Oriental High Pressure Plant, are re-formed with steam. The CO_2 is added to increase the percentage of CO in re-formed gas to compensate for the reduced percentage of CO in the water gas. Actual re-formed gas production is about 360,000 m^3/day, of which, 60,000 m^3/day is sent to the Oriental High Pressure Plant.

Water gas and re-formed gas are blended to maintain a H_2:CO ratio of approximately 2:1. In practice, about 300,000 m^3/day of water gas are blended with 300,000 m^3/day of cracked gas, yielding a synthesis gas mixture of the following composition:

	Actual	Koppers Design
H_2	55.8%	60%
CO	27.3	30
CO_2	7.2	5
CH_4	2.5	1
N_2	7.2	4
	100.0%	100%

E. Desulfurization

The Klonne desulfurization system is employed, and consists of a "grossreinigung" section for removal of inorganic sulfur, and a "feinreinigung" section to handle organic sulfur. Raw synthesis gas contains approximately 6-10 gm/m^3 of total sulfur. After "grossreinigung", the sulfur content is reduced to 0.1 gm/m^3, and after "feinreinigung", to 4 mg/m^3.

The inorganic removal system consists of two banks of 4 towers each. One tower in each series is ordinarily down for regeneration. Each tower is filled with 600 tons of catalyst, distributed over 16 trays, which has the following composition:

Iron Oxide (Aso Oda)	95%
Soda Ash	5%

The catalyst is manufactured in the Miike plant, but is apparently not as efficient as the German "Luxmasse", requiring an appreciably longer time to regenerate. To shorten the regeneration time, some air is added continuously to the synthesis gas feed. The catalyst is replaced after its sulfur content has risen to 45% by weight.

After leaving the inorganic purifiers, the gas is passed through a two-stage organic sulfur removal plant. The gas is heated to 280°C, and passed through 4 towers in series, each filled with catalyst of the following composition.

Iron Oxide (Aso Oda)	75%
Soda Ash	25%

Spent catalyst is regenerated by air blowing. A process flow chart for the desulfurization section is given Figure 1(G).

F. Oil Synthesis

Oil synthesis is carried on in reaction chambers of Ruhrchemie design. The reaction occurs at 3-5 lbs/in^2 and 180-200°C. Originally, 40 reactors were installed, but this number was increased to 56, of which 30 are used in the first reaction stage, 18 in the second stage, and 8 off-stream. Each chamber consists of 550 closely-spaced vertical steel plates, arranged perpendicular to a large bundle of water cooling tubes, 630 in number. About 4½ tons of catalyst is contained in the space between the plates, on the outside of the tubes. A process flow chart for the synthesis section is given in Plate III(G).

The yield expected from the two-stage reaction, according to the Koppers design calculations, was 116 grams of total product per cubic meter of synthesis gas. The actual yield is substantially below this, amounting to 70-85 gm/m^3. Reasons given for this lower yield were, that the synthesis gas composition suffers considerable variation and has a higher content of inerts than design, the catalyst activity is lower, (possibly due to the fact that the hydrogen used for reactivation is not pure enough), and also, that water tube leakage reduced the capacity. It is also conceivable that Japanese catalyst-manufacturing technique is not on a par with that of the Germans.

The catalyst is replaced about every 120 days, however, every 20 days, activity is increased by passing hydrogen gas over it at a rate of 800-1000 m^3/hr, at a temperature of 205-210°C, for 24 hours. The operation is stopped when exit gases contain less than 1% of methane. The schedule of treatment is as follows:

Treatment	Reaction Temp. Start	Reaction Temp. Stop	Days
Fresh Catalyst	180°C	190°C	0-20
#1	180	190	21-40
#2	183	193	41-60
#3	185	195	61-80
#4	187	200	81-100
#5	190	200	101-120

The procedure for replacing old catalyst is as follows: Synthesis gas is displaced with CO_2. The temperature of the catalyst chamber is maintained at 170-180°C, and the catalyst is washed with 35 kls of wash oil (boiling range 180-220°C). The wash period is 15-17 hours. After washing, the temperature of the chamber is raised to 205-210°C, and the catalyst is dried with hydrogen gas. Temperature is dropped gradually to 100°C and hydrogen is displaced with CO_2. The chamber is opened and the spent catalyst discharged into a receiving vessel at the bottom of the chamber. Fresh reduced catalyst is then introduced. Both discharging and charging operations are conducted in a current of CO_2, to protect the catalyst from oxidation. Fresh catalyst is brought on stream at a temperature of 180°C.

G. Oil Recovery

The heavier oil is recovered from the reaction exit gas by direct condensation with water, and then, by passage through charcoal adsorbers to recover the lighter gasoline components. Two recovery stages are employed, one after the first synthesis stage and the other after the second stage. Each recovery stage consists of a packed condenser, tower, wherein reaction gases are passed counter-current in direct contact with cold, recirculated water. Oil condensed by this operation is separated and sent to the distillation plant. The overhead gas from the condenser tower is passed through an absorber containing about 15 tons of activated carbon. The exit gas from the first absorption stage is sent to the second synthesis stage, and the exit gas from the second absorption stage ("rest" gas), is recycled to the gas re-former unit, or utilized as fuel gas. The light hydrocarbons absorbed on the carbon are periodically stripped off with steam, condensed, and sent to a "gasol" storage tank.

The raw gasol is compressed to 4-5kg/cm^2 and passed into a packed absorber tower, counter-current to circulated oil. The lean exit gas is sent to fuel, and the rich absorber oil is charged to a stabilizer, where finished gasol is taken overhead. This product consists mainly of butanes and is marketed in steel bottles for use as motor fuel. Since the capacity of the absorption plant is 500 m3/hr, and only about 3600 m^3/day are received from the synthetic plant, the absorption plant is only operated about 6-7 hours per day.

H. Oil Distillation

The condensed oil from the synthetic plant is charged to a pipe still of Wilke design, and separated into a light benzine overhead cut, which is charged to the gasoline stabilization plant, diesel oil fractions, and a paraffin oil fraction.

Condensed light gasoline, from the activated carbon units and from the condensed oil distillation plant, is charged to a Wilke stabilization column, wherein stabilized motor gasoline is produced, together with a gasol overhead which is mixed with the product from the gasol absorber. No chemical treatment is given to either the gasol, gasoline, or diesel oil.

I. Paraffin Plant

The paraffin plant was installed to recover paraffin from the catalyst wash oil. The plant produces recovered wash oil, diesel oil, and three grades of wax.

J. Catalyst Manufacturing Plant

Complete facilities are installed for manufacture of fresh synthesis catalyst, and for the recovery of cobalt and thorium from spent catalyst. All cobalt used in the manufacture was obtained before the war from Katanga, Africa, via Ruhrchemie. Thorium was obtained from U. S. sources. No supplies of these metals have been shipped to Japan since the start of the war. Design capacity of the plant is 4½ tons of non-reduced catalyst per day. Normal production, however, is about 3 tons per day. Facilities for reducing the catalyst are available, and reduced catalyst is shipped in closed metal containers in 1 atmosphere of CO_2. Mr. MITSUI advised that this plant was the only cobalt manufacturing unit in Japan. It was stated that no innovations or departures from the original Ruhrchemie manufacturing technique had been introduced in this plant.

A flow chart for the catalyst manufacturing plant is given in Plate IV(G).

Further details on the plant layout are given in detail drawings listed in Appendix IV.

K. Miscellaneous

Plans were purchased in 1939 from the Universal Oil Products Co. for a Dubbs-Kogasin cracking unit and a non-selective gas polymerization unit. Construction work had not yet started on the polymerization unit. Work was in progress on the cracking unit, but was being held up due to lack of furnace tubes and hot oil pumps. This unit was stated to have a capacity of 2kls per hour. At the direction of the government, it was planned to utilize the cracking unit to lightly crack paraffin oil to make charge stock for an $AlCl_3$ lubricating oil plant.

Construction work also was in progress on the lubricating oil polymerization reactors and clay filtration units. In the polymerization section it was planned to mix 3-5% of $AlCl_3$ with the cracked paraffin oil and react at 60-90°C for 8-12 hours. The reaction mix was to be drawn off, settled, filtered through activated clay, and vacuum distilled. It is understood that the NIPPON Oil Co. near YOKOHAMA has a similar process in production.

L. Plant Layout

Plate V(G) gives the layout of the entire plant, showing location of all major units and buildings. Also indicated on this layout, is the bomb damage suffered during three air raids on the plant. The plant was not seriously damaged as a result of these raids, although the rupturing of the main synthesis gas line at the "feinreinigung" plant and also the main belt conveyor at the coke plant due to explosive bomb hits on 7 August, 1945, resulted in complete stoppage of oil production. The damage was still being repaired at the time of this inspection.

IV. PRODUCTION

The plant production capacity, according to Koppers design calculations, was as follows:

Basis	Vol. of Synthesis Gas - (m^3/day)	Annual Production Total Product
Design Maximum	900,000	38,100 met. tons
Design Normal	770,000	32,600
"Rated" Capacity		30,000

Actual production was considerably less than this, due to the lower volume and quality of synthesis gas produced. Low synthesis gas production was a result of operating difficulties in the water gas plant caused by a poorer quality of Miike coke than was expected. The conversion of gas to oil, in the synthesis step, was also much lower than expected.

Actual annual production figures are given in Table I(G) and II(G). It will be noted that the peak monthly production rate, in March 1944, was about 1500 tons, corresponding to an annual production of 18,000 tons. Actual production for the peak year of 1943 was roughly 16,000 tons.

During the period 1943-45, inclusive, about 25% of the motor gasoline output went to the Army and the remainder went to the Civil Government. About 18% of the diesel oil went to the Army and the balance to the Navy.

An inventory of products in storage at the Miike Plant as of 8 October 1945, follows:

ENCLOSURE (G)

Stock	Amount
Motor Gasoline	4.0 kl
Diesel Oil	
Light No. 1	1.3 kl
Light No. 3	110.8 kl
Heavy Oil	85.8 kl
Paraffin Oil	4587.9 kl
Solid Paraffin	7.0 tons

Paraffin oil was being accumulated in storage to serve as feed stock for the lubricating oil plant under construction.

V. QUALITY OF PRODUCTS

Actual inspections of the several types of products made at Miike are given in Table III(G). These inspections are well in line with Fischer-Tropsch cobalt catalyst data reported from other sources. In addition to the products listed, Miike produced paraffin wax in the following grades:

Paraffin No. 4	Melting point higher than 50°C
Paraffin No. 6	Melting point higher than 60
Paraffin No. 8	Melting point higher than 70

Samples of all Miike products and catalysts were obtained and shipped to the Ordnance Investigating Laboratory, Indian Head, Md., for forwarding to the Naval Research Laboratory, Anacostia, Md. NavTechJap serial numbers assigned to this shipment are JE-26-0001 to 0006 inclusive.

VI. RESEARCH WORK

The Miike plant has only a small research group containing five people. Most attention was devoted to the study of plant operating problems. Some basic research work on oil synthesis was carried on at the Meguro Laboratory in TOKYO. At Miike, most attention was concentrated on a pilot plant study of lubricating oil production, by $AlCl_3$ polymerization of lightly cracked paraffin oil, and the production of gasoline from pine root oil. Investigation of the latter process was undertaken upon orders from the Army.

Documents pertaining to these projects, together with miscellaneous reports from Miike and other laboratories, were obtained and are listed in Appendix II(G). Several papers on iron synthesis catalyst and studies of paraffin oxidation products are of special interest.

VII. PATENTS

Appendix I contains a list of all Japanese patents held by the Miike Company. Copies of the same were not available at Miike.

VIII. NEGOTIATIONS WITH GERMANS

Selected copies of correspondence between Mitsui Bussan, (Mitsui Trading Co.) and German firms during the years 1936-37, together with an index and abstract of the same, were obtained and are listed in Appendix III. Correspondence for other years is held in the Tokyo Company Headquarters. This correspondence mainly concerns licensing agreements with Ruhrchemie, and negotiations with Heinrich Koppers, regarding design and construction of equipment.

ENCLOSURE (G)

Table I(G)
ACTUAL PRODUCTION FIGURES

	June-Dec. 1940	1941	1942	1943	1944	Jan.-July 1945
Coal Charged (tons)	136,706	227,179	208,203	234,807	218,781	101,913
Water Gas (1000 m^3)	23,745	24,368	52,793	86,628	78,478	26,143
Cracked Gas (1000 m^3)	17,685	104,411	78,926	103,503	82,617	33,877
Synthesis Gas (1000 m^3)	29,444	103,670	136,123	198,024	163,890	57,370
Synthetic Oil (kl)	3,787	7,787	10,063	15,258	14,323	3,079
No. of Chambers Operated	2,036	5,625	6,231	13,170	9,077	2,532
No. of Working Days	204	322	293	350	293	91

Table II(G)
ACTUAL PRODUCTION OF FINISHED PRODUCTS

	April-Dec. 1940-1942	1942	1943	1944	Jan.-July 1945
Motor Gasoline (kl)	5,556	6,743	10,142	5,938	1,038
Light Diesel Oil (kl)	3,772	2,559	3,815	3,472	662
Diesel Oil (kl)				343	16
Liquefied Petroleum Gases (tons)	128	278	468	226	48
Paraffin Oil (kl)	204	1,366	1,817	1,086	119
Paraffin Wax (tons)			82	56	10
Ammonium Sulphate (tons)	1,708	1,856	1,749	1,162	235
Carbon Black (tons)			959	946	172
Coke (tons)	152,859	150,811	155,997	138,321	35,132
Tar (tons)	13,573	13,189	12,635	12,812	3,394

ENCLOSURE (G)

Table III(G)
TYPICAL INSPECTIONS OF OIL PRODUCTS

Test	Condensed Oil	Active Carbon Oil	Motor Gaso.	Diesel Oil	Paraffin Oil	Washing Oil
ASTM Distillation						
I.B.P.	136.9	24.7	36.9	170.7		127.4
10%	168.6	37.2	56.2	195.0	290.1	158.8
50%	239.8	77.1	97.3	243.2	349.7	190.3
90%	313.3	139.5	145.4	286.1	387.2	204.4
97%	333.2	159.1	158.6	307.3	399.1	210.6
E.P.	350.6	173.5	171.2	316.5	413.3	226.2
Specific Gravity	0.7658	0.6729	0.7079	0.7685	0.7980	0.7456
Flash Point, °C				58.8		
Solid Point, °C				-3.9	22.2	
Octane No.			About 40			
Cetane No.				About 85		
Visc. Red, at 30°C				28.3		
Acid Value	0.06					
Vapor Press. kg/cm^2		0.78	0.52			
Carbon Residue				0.03		
Ash, %				0.001		

ENCLOSURE (G)

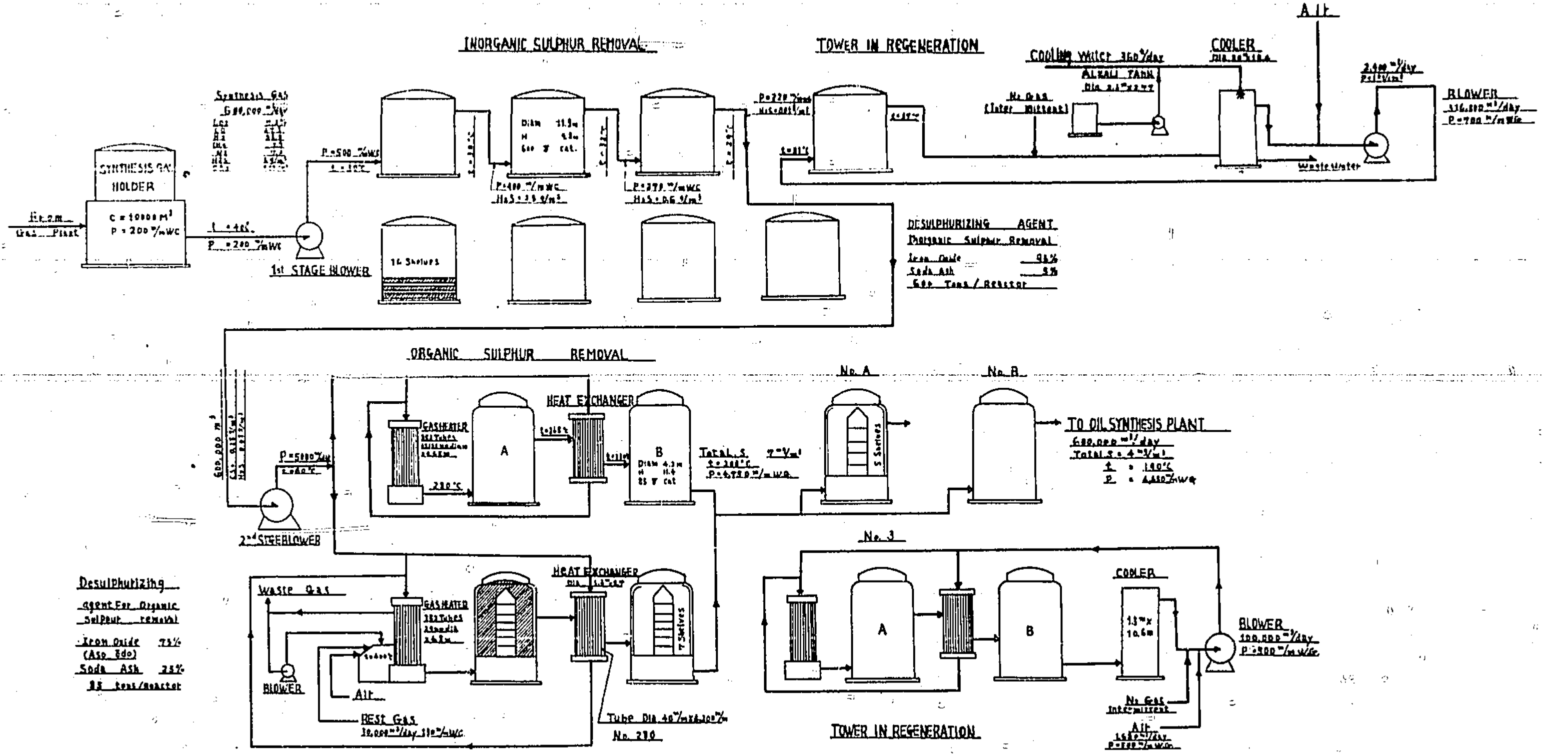


Figure 1(G)

DESULPHURIZATION PLANT

MIIKE SYNTHETIC OIL CO.

ENCLOSURE (G)

APPENDIX I
LIST OF PATENTS

Patents Held by Miike Synthetic Oil Co.

Patent No.	Title and Inventor
128,550 133,888	"The Preparation of Sulfur Purifier of Gas" by Y.NIKAIDO
139,563	"Thermostat Apparatus in Gas Reaction Cmamber Using Catalyst" by S. KOIZUMI
157,995	"Synthetic Oil Apparatus" by Y. NIKAIDO
161,655	"Liquefied Gas Charging Method" by H. YANAI
163,776	"Treatment Preliminary to Fractional Rectification of Hydrocarbons" by H. YANAI
287,840	"A New Design for Catalyst Tube of Gas Reaction Chamber" by T. KII

Patents Pending in Showa 18 (1943)

3,299	"The Preparation of Gas for Oil Synthesis" Unknown
11,102	"Double Distillation Apparatus" by H.YANAI
12,406	"Absorption Pipette for Gas Analysis" by M. YASUDA
13,312 (12 July '43)	"Method of Grease Making from Oxidized Products of Paraffin Hydrocarbons" by KIYOHISA
14,186	"Method of Soap Making by Oxidation of Paraffin Hydrocarbons" by KIYOHISA

ENCLOSURE (G)

APPENDIX II
LIST OF RESEARCH DOCUMENTS OBTAINED FROM MIIKE SYNTHETIC OIL CO.

ATIS No. 4587

NavTechJap Document No.	Title	Date
	LUBRICATING OILS	
ND26-0016.1	Report concerning synthetic oil produced from Gishin coal.	9 November 1939
ND26-0016.2	Description of lubricating oil plant including flow chart.	no date
ND26-0016.3	The process of manufacturing grease from oxidation products of paraffin hydrocarbons.	24 July 1943
ND26-0016.4	(copy of above)	
ND26-0016.5	Stability of lubricating oils produced by polymerization of olefins.	15 November 1943
ND26-0016.6	Report on attempt to improve the synthetic polymerized oil, whose index of viscosity is too low for use in aircraft engines, by making a cut at the lower boiling point.	3 August 1944
ND26-0016.7	Comparison of properties of various lubricating oils.	April 1937
ND26-0016.8	Research on polymerization of synthetic lubricating oils using $AlCl_3$ catalyst.	no date
ND26-0016.9	Research on the manufacture of olefins by normal pressure cracking.	15 October 1943
ND26-0016.10	Translation into Japanese of final Fischer Method contract.	no date
	ATIS No. 4588	
	CATALYSTS	
ND26-0017.1	Study on lowering of reaction temperature of gasoline synthesis using iron catalyst.	December 1939
ND26-0017.2	Data on iron catalysts.	June 1944
ND26-0017.3	Report on raw iron catalysts used in the production of synthetic gasoline.	December 1938
ND26-0017.4	Report on synthesis catalyst production at Holten.	March 1942

ENCLOSURE (G)

ATIS No. 4589

NavTechJap Document No.	Title PINE OIL	Date
ND26-0018.1	Report of laboratory and pilot plant results in processing pine root oil for production of aviation gasoline.	1945
ND26-0018.2	(copy of above)	

ATIS No. 4590

MISCELLANEOUS

NavTechJap Document No.	Title	Date
ND26-0019.1	Results of cracking a mixture of coke oven gas and rest gas (containing CO_2).	October 1942
ND26-0019.2	Research on alkylization of synthetic gasoline produced with an iron catalyst (or gasoline produced by cracking).	February 1945
ND26-0019.3	A discussion of metal-organic compounds, chiefly Al, Zn, Fe, salts of fatty acids. (TN: compounds formed during Fischer process.)	December 1937
ND26-0019.4	"Research on Antioxidants of Gasoline" by K. MORIKAWA.	1944
ND26-0019.5	Desulfurization and oxidation with inorganic desulfurization agent.	February 1943
ND26-0019.6	Studies in the use of rest gas as the reduction gas in the hydrogen generator in the Iron Contact Process.	June 1943
ND26-0019.7	Analysis of Manchurian coal.	no date
ND26-0 19.8	Heat decomposition of coke oven gas with Cowper equipment.	December 1942
ND26-0019.9	Tables of fuel specifications.	May 1944
ND26-0019.10	Specifications for fuels used by Army and Navy.	no date
ND26-0019.11	The process of manufacturing soap by oxidation of paraffin hydrocarbons.	August 1943
ND26-0019.12	(copy of above)	
ND26-0019.13	(copy of above)	

ENCLOSURE (G)

ATIS No. 4590

NavTechJap Document No.	Title MISCELLANEOUS	Date
ND26-0019.14	The process of manufacturing grease from oxidation products of paraffin.	July 1943
ND26-0019.15	Comparison of two batteries; one operated on producer gas and one operated on coal gas.	March 1941
ND26-0019.16	Research (Oil Synthetic Plant)	October 1945
ND26-0019.17	The Manufacture of Catalyst.	October 1945
ND26-0019.18	The Fischer Method of petroleum synthesis.	July 1938
ND26-0019.19	Paraffin with high melting point from synthesis process.	April 1943

ENCLOSURE (G)

APPENDIX III

LIST OF SELECTED CORRESPONDENCE BETWEEN GERMANY AND MITSUI BUSSAN

ATIS No. 4575

NavTechJap Document No.	Description	Date
ND26-0004.1	Telegrams from Deutsche Bussan advising on progress of negotiations for Fischer process, interest of other countries in the process, development of Fischer plants in Germany, etc.	2/6-12/36
ND26-0004.2	Confirmation by Mitsui Bussan Co. of telegram received from Deutsche Bussan. (Context in 1)	2/10/36
ND26-0004.3	Confirmation by Mitsui Bussan Co. of telegram received from Deutsche Bussan. (Context in 1)	2/13/36
ND26-0004.4	Confirmation by Mitsui Bussan Co. of telegram received from Deutsche Bussan regarding negotiations for general license for Fischer process.	2/18/36
ND26-0004.5	Telegram from Essen announcing signing of contract for Fischer process and giving various details.	2/20-21/36
ND26-0004.6	Deutsche Bussan Purchase Report on license for Fischer process made to the account of the Mitsui Bussan Co. Ltd.	2/20/36
ND26-0004.7	Letter regarding proposed contract for Fischer process sent from Ruhrchemie to Deutsche Bussan. contains power of attorney for Mitsui Bussan Co's agent in Germany, and Proposed contract.	2/20/36
ND26-0004.8	Confirmation of telegram sent by Deutsche Bussan describing new Fischer water gas unit.	3/3/36
ND26-0004.9	Telegram from Berlin representative recommending second payment as Fischer process investigated and thought to be a success in Japan.	2/28/36
ND26-0004.10	Telegram to Berlin representative regarding proposed Hokkaido Fischer plant and suitable personnel for the new set up.	3/5/36
ND26-0004.11	Telegram from Berlin representative recommending contract for exclusive license for Fischer process in view of its undoubted success in Japan and so that Mitsui will be in strong position to control proposed new combine.	4/14/36

ENCLOSURE (G)

ATIS No. 4575

NavTechJap Document No.	Description	Date
ND26-0004.12	Letter from Heinrich Koppers to Deutsche Bussan regarding tests on Japanese coal to be used in production of synthetic gas, and a proposal to build benzine synthesis plant for them.	5/20/36
ND26-0004.13	Letter from Heinrich Koppers to Deutsche Bussan clarifying their proposal to supply diagrams, blueprints, and technical information for the construction of a benzine synthesis plant for the Japanese.	6/18/36
ND26-0004.14	Letter from Fried. Krupp to Deutsche Bussan regarding offer to deliver works blue prints and provide a foreman for the construction of contact ovens for a Fischer Benzine Synthesis Plant.	7/20/36
ND26-0004.15	Letter from Krupp defining terms under which a foreman will be sent to Japan to supervise building of contact ovens.	7/20/36
ND26-0004.16	Telegram from Deutsche Bussan regarding report on comparison of German plants observed and agreement of Krupp to send an engineer to supervise construciton of contact ovens.	7/27/36
ND26-0004.17	Letter from Heinrich Koppers to Deutsche Bussan regarding their offer to contract for the building of the synthetic plant.	7/27/36
ND26-0004.18	Letter from Gutehoffnungshutte to Deutsche Bussan regarding offer to supply certain machines and tools for construction of contact ovens for Fischer Benzine Synthesis Plant.	8/4/36
ND26-0004.19	Letter from Ruhrchemie to Deutsche Bussan giving list of material sent.	8/5/36
ND26-0004.20	Contract between Mitsui Bussan and Ruhrchemie for the Fischer Process.	11/27/36
ND26-0004.21	Proposed option contract between Ruhrchemie and Mitsui Bussan regarding the use of the Schmieroel Process, also final copy of contract regarding Schmieroel Process.	11/27/36
ND26-0004.22	Specifications of Catalyst Fabrick Design.	12/17/36
ND26-0004.23	Letter from Koppers giving the basic calculations of benzine synthesis by the Fischer-Tropsch method for Mitsui Bussan.	12/18/36

ENCLOSURE (G)

ATIS No. 4575

NavTechJap Document No.	Description	Date
ND26-0004.24	Letter from Vergasungs-Industrie to Deutsche Bussan concerning the production of synthesis gas from Fushun coal for the petrol synthesis according to the Fischer-Tropsch method. Letter contains offer to construct synthesis gas plant.	9/15/37
ND26-0004.25	Telegram from Berlin representative to Mitsui Bussan regarding shipment of various equipment.	12/31/37
ND26-0004.26	Telegram from Mitsui Bussan to Berlin requesting that certain drawings be sent.	12/31/37
ND26-0004.27	Letter from Deutsche Bussan to Mitsui Bussan regarding progress of negotiations for getting patent rights for producing synthetic fatty acid.	1/5/38
ND26-0004.28	Letter from administrative head of Miike Factory to main office requesting return of certain documents in order to have complete file for Allied inspection.	9/27/45
ND26-0004.29	Portion of telegram (sender and addressee not given) regarding advisability of investing in new company in Japan to manufacture anhydrous alcohol with the Scholler patent. Telegram of the 29th states Scholler better than Bergins for manufacture of alcohol.	7/25-29/?
ND26-0004.30	Portion of telegram (sender and addressee not given) regarding information on the Fischer process and terms of agent's authorization for prepayment.	no date
ND26-0004.31	Report on the meeting of the German Society for Oil Investigation held in Berlin. Report consists of notes on talks given at the meeting concerning: methods to increase German mineral oil production; outline of German industrial and economical policy in respect to motor fuel production and consumption; difficulties and advantages of the Fischer Hydrogenation Process.	9/28/?

ENCLOSURE (G)

APPENDIX IV
LIST OF MISCELLANEOUS DETAIL DRAWINGS OBTAINED FROM MIIKE SYNTHETIC OIL CO.

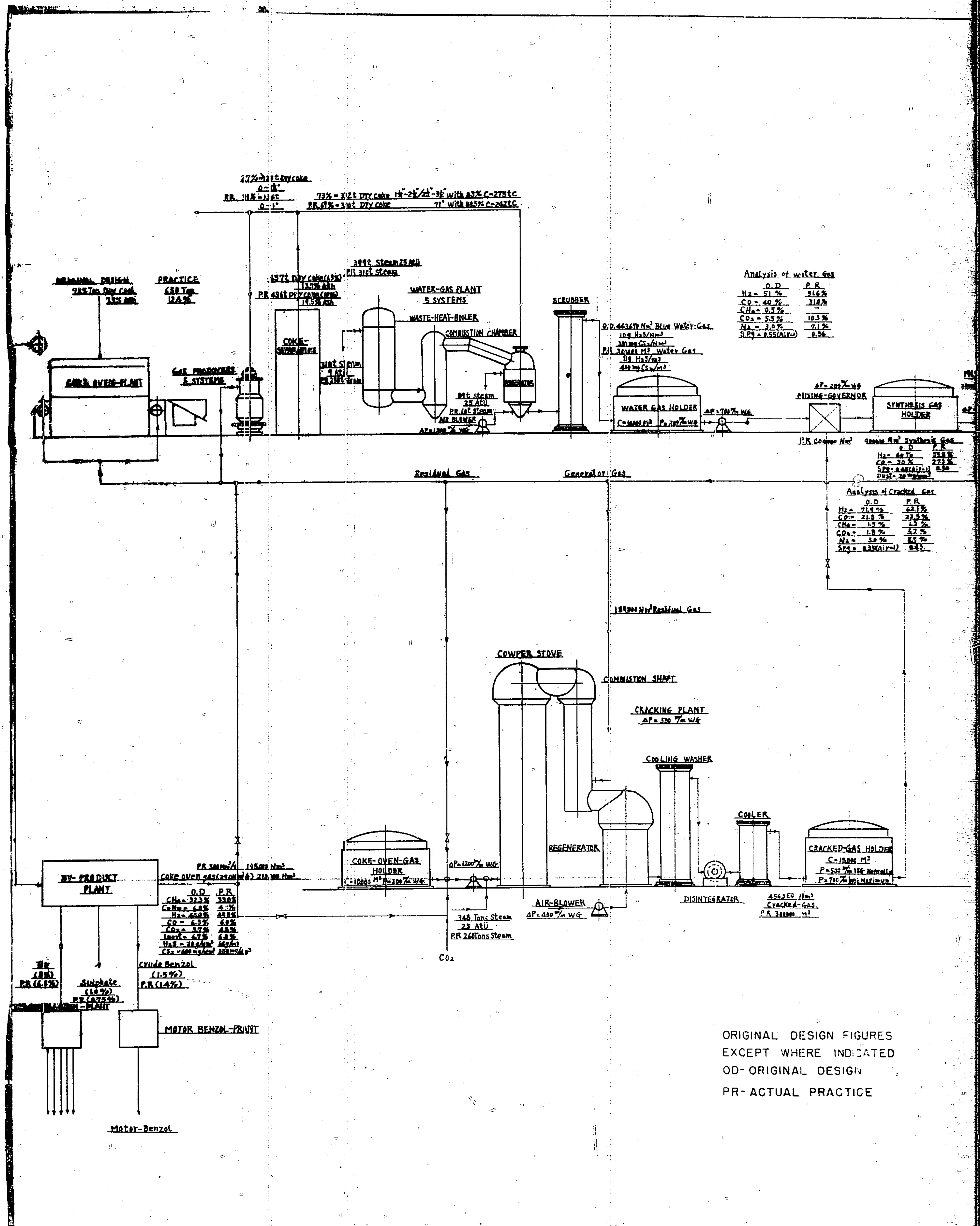
ATIS No. 4586

NavTechJap Document No.	Subject
ND26-0015.1	Flow Sheet of Fischer-Tropsch Benzine Synthetic Process.
ND26-0015.2	General Arrangement.
ND26-0015.3	Coke Oven for Synthetic Plant.
ND26-0015.4	Flow Sheet of H_2SO_4. Mother Liquor and Ammonia Plant.
ND26-0015.5	Flow Sheet of Tar Plant.
ND26-0015.6	Flow Sheet of Benzol Absorption and Crude Benzol Distillation Plant.
ND26-0015.7	General Arrangement of By-Product Plant.
ND26-0015.8	General Arrangement of Producer Gas Plant.
ND26-0015.9	Arrangement for Producer Gas Generator of Producer Plant.
ND26-0015.10	Arrangement of Apparatus of Water Gas Plant.
ND26-0015.11	Gas Producer Washer and Ignition Chamber Arrangement.
ND26-0015.12	General Arrangement of Cracking Plant.
ND26-0015.13	800IΦ Revolving Gas Piping from Torbo Blower to Grob Reiniger.
ND26-0015.14	Arrangement of Organic Desulphurizing Apparatus.
ND26-0015.15	General Arrangement of Apparatus of Organic De-Sulphurizing Plant.
ND26-0015.16	General Arrangement of Synthesis Plant.
ND26-0015.17	Construction of New Type Contact Furnace of Synthesis Plant.
ND26-0015.18	Flow Sheet of Condensation Plant.
ND26-0015.19	Layout of a Benzine Absorption Plant of the Carbo Union Process (Sheet 1)
ND26-0015.20	(Sheet 2)
ND26-0015.21	(Sheet 3)

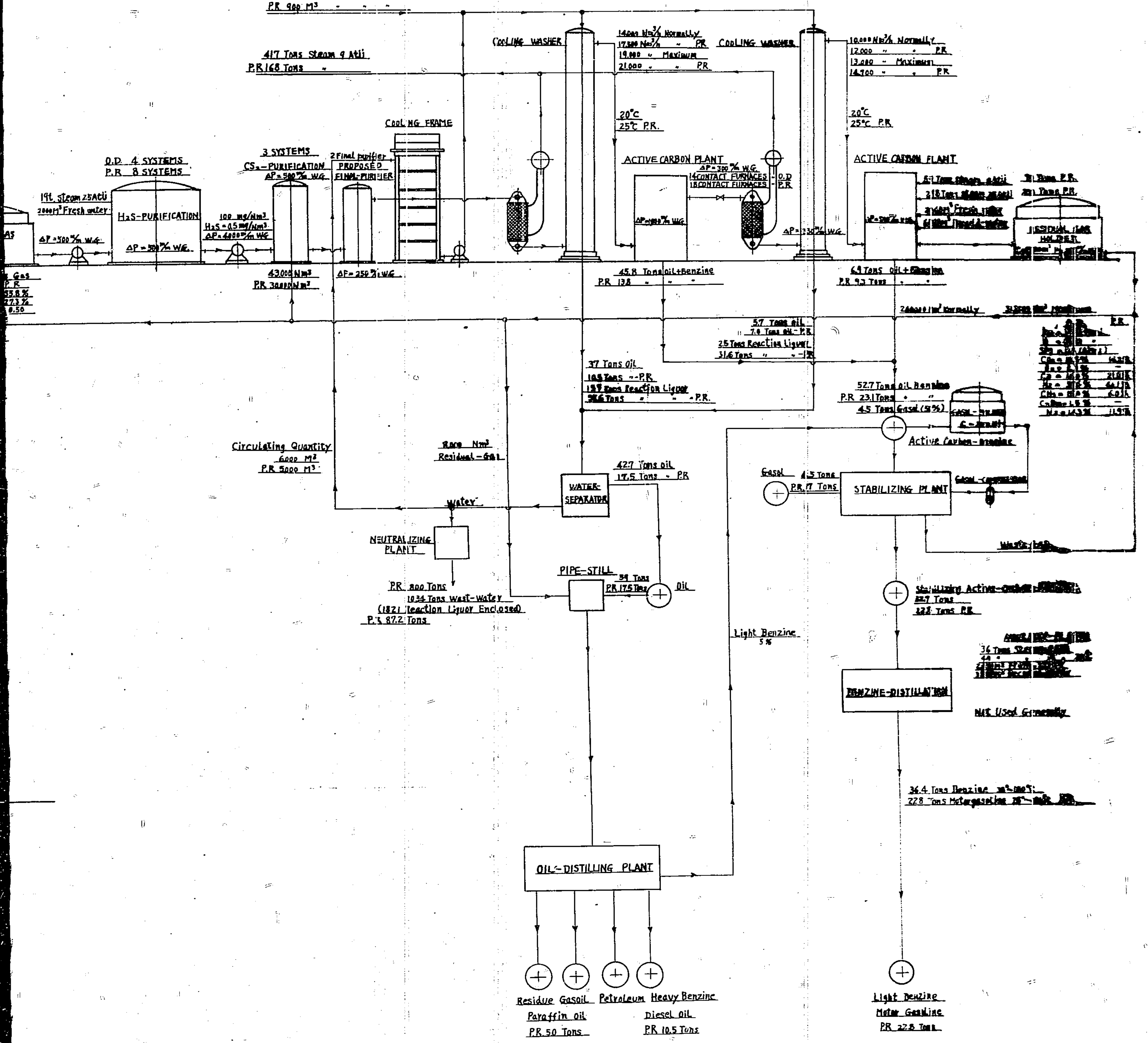
ENCLOSURE (G)

ATIS No. 4586

NavTechJap Document No.	Subject
ND26-0015.22	(Sheet 4)
ND26-0015.23	Distillation Plant.
ND26-0015.24	Arrangement of Paraffin Purifying Apparatus.
ND26-0015.25	Arrangement of Lubricant Plant.
ND26-0015.26	General Flow Sheet of Extension Plan of Catalyst Plant.
ND26-0015.27	General Arrangement of Apparatus for Extension of Catalyst Plant.
ND26-0015.28	Flow Sheet of Reduction Plant of Catalyser.
ND26-0015.29	Machine Arrangement of the Reduction Plant of Catalyst.
ND26-0015.30	General Arrangement of Luxemass Plant.

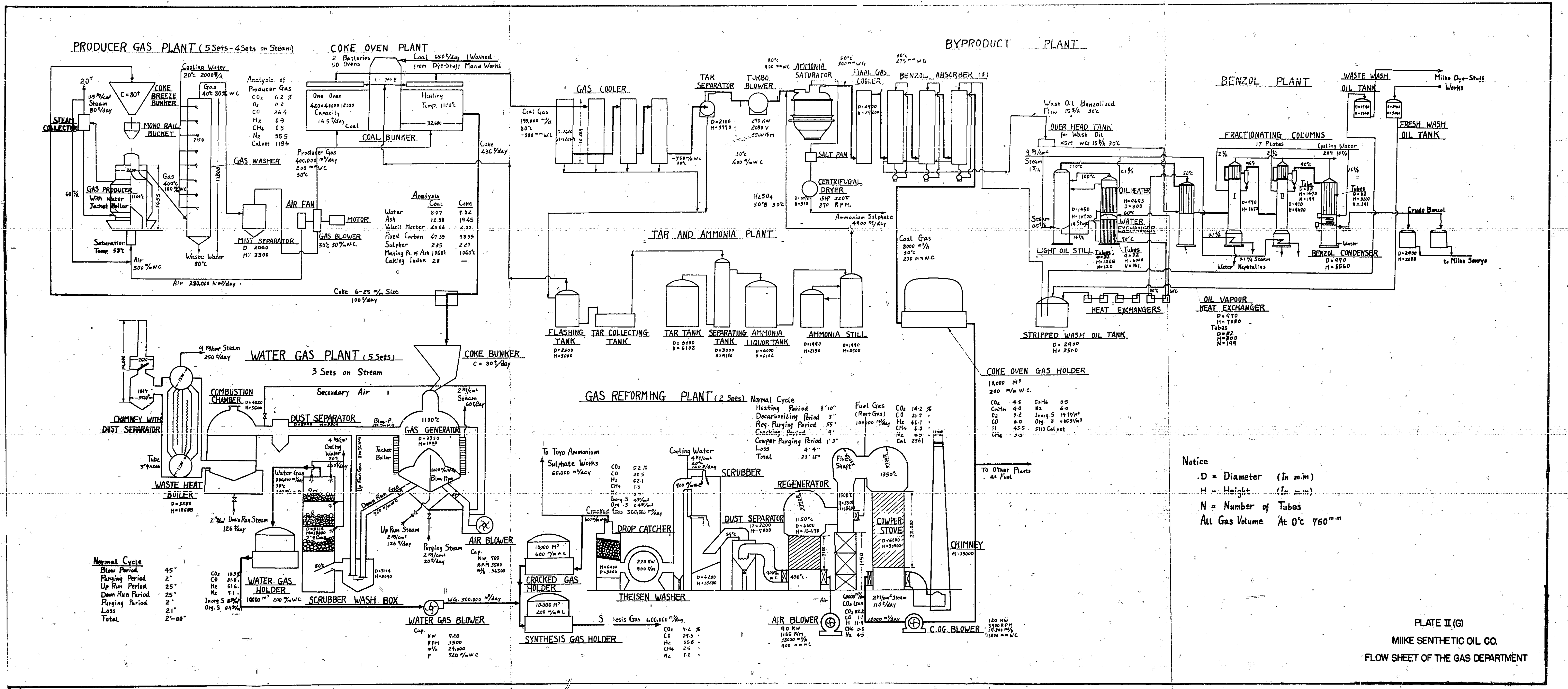


ORIGINAL DESIGN FIGURES
EXCEPT WHERE INDICATED
OD- ORIGINAL DESIGN
PR- ACTUAL PRACTICE



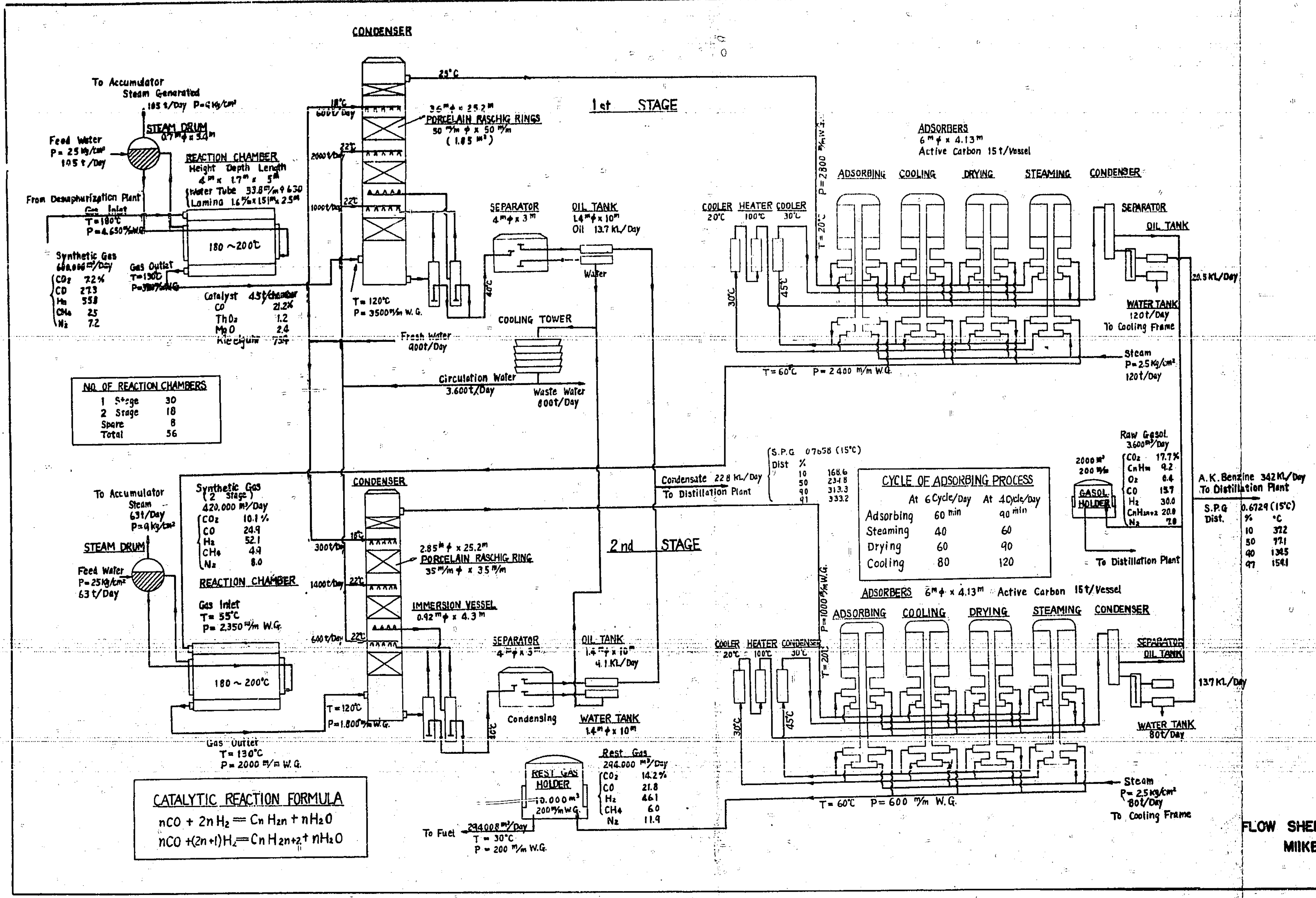
QUANTITIES PER 24 HOURS

PLATE I (G)
GENERAL FLOW SHEET
MIIKE SYNTETIC OIL CO.



Notice
- D = Diameter (In m.m)
- H = Height (In m.m)
- N = Number of Tubes
- All Gas Volume At 0°c 760 m.m

PLATE II (G)
MIIKE SENTHETIC OIL CO.
FLOW SHEET OF THE GAS DEPARTMENT



NO. OF REACTION CHAMBERS

1 Stage	30
2 Stage	18
Spare	8
Total	56

CYCLE OF ADSORBING PROCESS

	At 6 Cycle/Day	At 4 Cycle/Day
Adsorbing	60 min	90 min
Steaming	40	60
Drying	60	90
Cooling	80	120

CATALYTIC REACTION FORMULA

$$nCO + 2nH_2 = C_nH_{2n} + nH_2O$$

$$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O$$

PLATE III (G)

FLOW SHEET OF SYNTHESIS SECTION

MIIKE SYNTHETIC OIL CO.

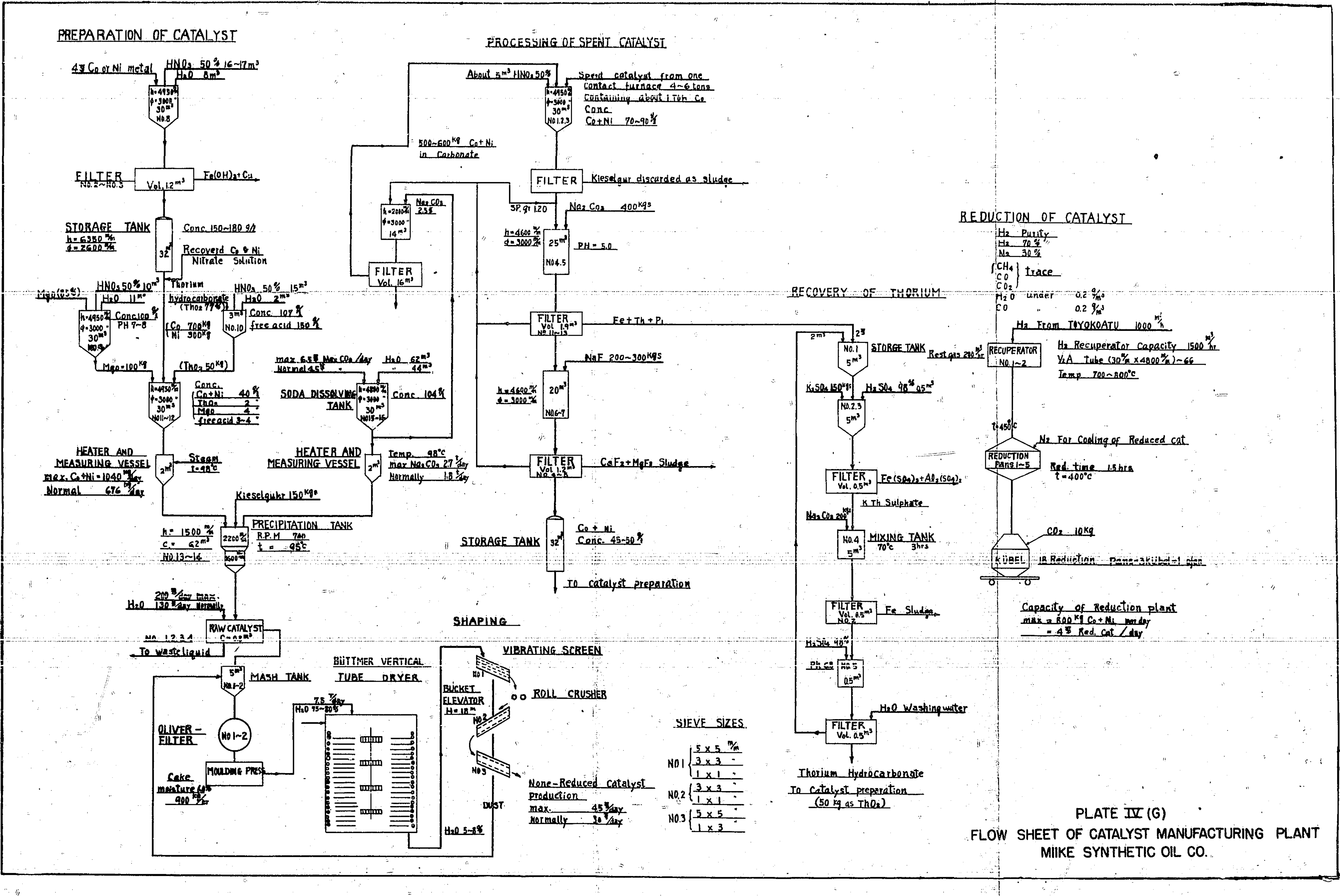
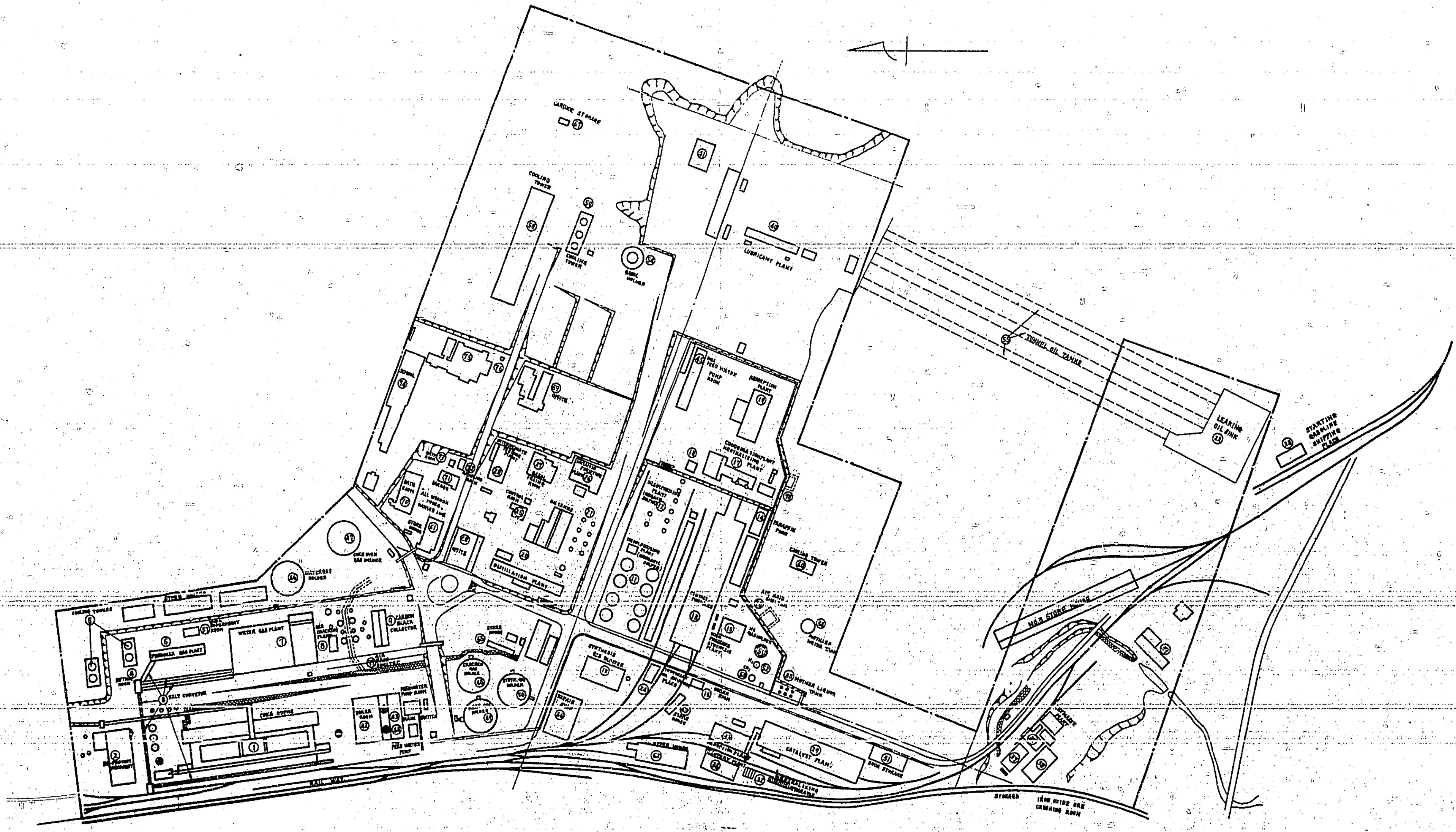


PLATE IV (G)

FLOW SHEET OF CATALYST MANUFACTURING PLANT
MIIKE SYNTHETIC OIL CO.

(Ser. No. 084, Enc. G).



U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
PLANT LAYOUT MAP		
MIKE SYNTHETIL OIL CO.		
DEC.24,1945	PLATE V G	X-38(N)-7

ENCLOSURE (H)

ENCLOSURE (H)

REPORT ON

NISSAN EKITAI NENRYO CO., LTD.

WAKAMATSU PLANT

ENCLOSURE (H)

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ENCLOSURE (B)

I. INTRODUCTION

The Wakamatsu low-temperature coal carbonization plant, of the NISSAN EKITAI NENRYO K. K., was inspected by the Petroleum Section of the U. S. Naval Technical Mission to Japan, during the period 24-25 October, 1945. This report records and summarizes the technical information obtained during this visit. Japanese personnel connected with the plant, who assisted in supplying this information, were as follows:

Mr. N. YAMADA	Director of Plant.
Mr. S. KUNII	Head of Carbonization and Refining Departments.
Mr. T. FUJIO	Head of Mechanical Dept.
Mr. T. MONDEN	Office Manager.

II. HISTORY AND ORGANIZATION

The company was founded on 25 February 1939, with an initial capitalization of 10,000,000 Yen, and construction was started on a plant at WAKAMATSU, to produce oil from coal mined nearby in the Orio district of NORTH KYUSHU. The design of the low-temperature carbonization plant was based on the patents of the Lurgi-Gesellschaft, Frankfurt-am-Main. Complete licensing rights for this process had been purchased by the Teikoku Nenryo Co., Ltd., who in turn, sub-licensed to the Nissan Ekitai Nenryo Company. The first units of the Wakamatsu plant were completed in March 1941, and consisted of a Lurgi low-temperature retort of 300 tons/day coal charge capacity plus tar separating and light oil distilling equipment. Production of gasoline, fuel oil and semi-coke was started. Additional refining equipment, including tar distillation, light oil treating, and de-waxing units, were completed by the middle of 1942, and from that time on, the plant produced motor gasoline, diesel oil, fuel oil, pitch, semi-coke (coalite) and raw wax.

Three German engineers from Lurgi-Gesellschaft assisted in the construction and acceptance tests of the first units. Mr. Finkbeiner arrived in September, 1940, Mr. Erb in December, 1940 and Mr. Bruggeman in March, 1941. All three departed in June, 1941.

In September, 1941, the Japanese Government ordered an extension of the plant, and work was started on the construction of three additional low-temperature retorts plus auxiliary equipment. For this extension, the capitalization of the company was increased to 15,000,000 Yen on 22 December 1941, and a special "accomodation" loan of 15,000,000 Yen additional was obtained from the Teikoku Nenryo Company. The first additional unit was completed in May, 1943, the second in May, 1944, and the third in November, 1944. In connection with this extension, the company also undertook installation of additional tar distilling and dewaxing units, also gasoline and phenol distillation equipment. This equipment was still in the process of construction in October, 1945. To finance this construction, the capitalization was increased, on 15 November 1944, to 25,000,000 Yen.

The plant maintained steady production with two or three units continuously on stream until the fire-bomb raid of 8 August 1945. Although damage was relatively light, destruction of the central tar oil pumping room necessitated a shut down of the entire plant. It was anticipated that production would be started again in November, although the supply of coal was becoming critical due to labor difficulties at the mines.

In the initial establishment of the company, it was planned to install a pilot plant for the hydrogenation of tar oils, and reaction vessels had been ordered from the Krupp Corp. in Germany. These vessels were not delivered and other items required were never ordered, due to increasing difficulties in procuring construction materials.

The main offices of the company are located in TOKYO, and at present, of the total capitalization of 25,000,000 Yen (20,000,000 paid up), the Teikoku Nenryo Company owns 50 per cent and the balance is largely held by the Nippon Kogyo Co., Ltd. (Nippon Mining Co.) The top management of Nissan Ekitai Nenryo Co. is as follows:

President:	Mr. M. FURUKAWA
Directors:	Mr. J. TANAKA Mr. N. YAMADA Mr. E. SUZUKI Mr. T. YAMADA Mr. S. UCHIDA
Inspectors:	Mr. S. NATSUBORI Mr. R. KUMADA
Counsellors:	Mr. M. FUJITA Mr. M. TAKASHIMA

The management of the Wakamatsu plant is as follows:

Mr. N. YAMADA	Plant Director
Mr. S. KUNII	Head of Low-Temp. Carb. and Tar Oil Refining Depts.
Mr. T. FUJII	Head of Mechanical Dept.
Mr. T. MONDEN	Office Manager

Before the end of the war, the plant had a total of about 700 employees.

The Nissan Ekitai Nenryo Company has no other plants in or outside of Japan.

III. DESCRIPTION OF PROCESS

A layout map for the Wakamatsu Plant is given by Plate I(H), and an over-all flow diagram is given by Plate II(H).

The coal charged to the low-temperature carbonization units is obtained from mines in the Orio district, and was stated to be a coal with low sulphur content (0.5%), poor coking qualities, and well suited for gasification. A flow sheet of the Lurgi-design low temperature-carbonization plant is given by Plate III(H). Coal is conveyed to the coal bunkers at the top of the retort and passes downward through the drying zone at about 250°C and the carbonization zone at 600°C. The coke (coalite) is cooled by cold circulated fuel gas, introduced at the bottom of the retort. Heat for carbonization and drying is supplied by circulating gas from each of these zones through external "verbrennungsofen's". Hot carbonization gas, withdrawn from the top of the carbonization zone, is passed successively through the pre-cooler, Cottrell precipitator, coolers, and gasoline absorber. A flow diagram for the latter unit is given by Plate IV(H).

Tar from the pre-cooler and Cottrell is sent to batch tar stills (total charge capacity 10 tons oil per 24 hours) and fractionated into pitch and heavy oil. The heavy oil is dewaxed by cooling to -5°C and filtering. The dewaxed oil is used either in bunker or semi-diesel fuels, and the raw wax is sold for use in lubricating oil manufacture.

ENCLOSURE (H)

Both the crude middle oil from the coolers and gasoline from the absorption plant are washed with 10% caustic, to remove phenols and cresols, which are recovered and sold. The neutral middle oil can be used in diesel oil or fractionated for production of solvent naphthas. The caustic washed gasoline is treated with 60° Be. sulphuric acid, then with 4% caustic, and finally washed with water.

IV. PRODUCTION

Capacity of each of the four Lurgi retorts is 300 tons of coal per 24 hours. Table I(H) summarizes actual quantities of coal charged during the period from the start of operations on 16 April 1941, to 8 August 1945, when production was stopped as the result of a fire-bomb raid on that date. The consumption of NaOH and H_2SO_4 is given by Table II(H). Actual output of products is given by Table III(H). The yield of oil obtained is about 90% of that shown by the Fischer-Hempel carbonization test. No major operating difficulties were encountered, although actual retort throughputs varied with the coking properties of the coal.

Typical inspections on the several products are given in Table IV(H). No significant difference existed between design and actual product yields and quality.

In general, the plant appeared to be well-managed, and the maintenance of equipment was good.

V. RESEARCH AND DEVELOPMENT

The research department was very small, consisting of only three chemists plus assistants, and it was primarily concerned with tests necessary in controlling plant operations. The following Japanese patents regarding low-temperature carbonization are held by the company:

Patent No.	Date of Patent	Inventor	Title of Patent
No. 67614	25 Feb., 1926	O. Hubman	Process of drying fuels and its equipment.
No. 73611	28 Sept.,1927	G. Munschel	Process of drying fuels and its equipment.
No. 82931	4 Nov., 1929	O. Hubman	Equipment for low-temperature carbonization of fuels by internal heating.

ENCLOSURE (H)

Table I(H)
ACTUAL COAL CHARGED TO WAKAMATSU PLANT

		Metric Tons			
	1941	1942	1943	1944	1945
Jan.		7,162	10,230	15,245	20,794
Feb.		7,015	3,630	16,002	14,801
Mar.		7,669	7,797	16,120	19,602
Apr.	2,978	6,656	11,109	15,417	20,149
May	7,781	108	8,017	19,063	13,427
June	5,906	8,219	13,690	16,693	18,441
July	7,662	10,602	18,612	17,956	11,308
Aug.	6,815	8,957	17,817	18,388	2,136
Sept.	7,457	9,569	15,390	17,536	0
Oct.	6,849	8,145	10,831	18,454	0
Nov.	6,740	5,404	10,463	19,102	
Dec.	7,221	9,073	12,019	22,010	
Total	59,409	88,579	139,610	211,976	120,444

ENCLOSURE (B)

Table II(E)
ACTUAL CONSUMPTION OF SODIUM HYDROXIDE AND SULPHURIC ACID
(Metric tons)

	1943		1944		1945	
	NaOH	H_2SO_4	NaOH	H_2SO_4	NaOH	H_2SO_4
Jan.	-	-	3	4	15	38
Feb.	-	-	56	83	9	19
Mar.	-	-	76	100	24	29
Apr.	-	-	41	52	29	29
May	-	-	27	44	28	44
June	-	-	40	72	28	51
July	-	-	33	57	44	54
Aug.	-	-	39	71	6	13
Sept.	-	-	41	75	0	0
Oct.	37	64	43	72	0	0
Nov.	40	66	20	32	-	--
Dec.	30	44	21	35	-	--
Total	107	174	440	697	183	277

ENCLOSURE (H)

Table III(H)
ACTUAL PRODUCTION AT WAKAMATSU PLANT

		Semi-cokes (tons)	Gasoline (kl)	Fuel oil (kl)
1941	Apr.	1,856	0	286
	May	4,740	0	717
	June	3,721	31	636
	July	4,814	139	700
	Aug.	4,496	145	758
	Sept.	4,792	151	769
	Oct.	4,318	115	607
	Nov.	4,246	107	566
	Dec.	4,549	168	734
	Total	37,532	856	5,773
1942	Jan.	4,513	132	645
	Feb.	4,420	132	934
	Mar.	4,832	148	701
	Apr.	3,919	141	626
	May	68	0	68
	June	5,178	148	753
	July	6,892	157	992
	Aug.	5,822	161	824
	Sept.	6,220	168	862
	Oct.	5,294	134	738
	Nov.	3,518	85	505
	Dec.	5,898	125	909
	Total	56,574	1,531	8,557

Note: Semi-diesel, pitch, and crude wax were not produced.

ENCLOSURE (H)

Table III(H) (cont'd)
ACTUAL PRODUCTION AT WAKAMATSU PLANT

		Semi-cokes (tons)	Gasoline (kl)	Semi-diesel (kl)	Fuel oil (kl)	Pitch (tons)	Crude wax (tons)
1943	Jan.	6,419	126	-	968	-	-
	Feb.	2,285	42	-	327	-	-
	Mar.	4,859	86	-	736	-	-
	Apr.	7,030	137	-	1,173	-	-
	May	6,936	154	-	1,076	-	-
	June	9,326	161	-	1,385	-	-
	July	11,997	150	-	1,749	-	-
	Aug.	11,458	157	-	1,708	-	-
	Sept.	10,556	341	-	1,529	-	-
	Oct.	7,268	191	507	1,010	147	-
	Nov.	6,721	143	172	657	101	16
	Dec.	7,711	209	76	560	28	8
	Total	92,566	1,897	755	12,878	276	24

		Semi-cokes (tons)	Gasoline (kl)	Semi-Diesel (kl)	Fuel Oil (kl)	Pitch (tons)	Cresol (tons)	Crude wax (tons)
1944	Jan.	9,486	73	83	1,152	40	75	7
	Feb.	10,307	81	0	1,059	35	25	0
	Mar.	10,378	160	187	1,076	10	23	0
	Apr.	9,923	0	182	983	0	14	0
	May	12,290	89	170	1,607	0	18	0
	June	10,753	152	170	1,307	0	17	0
	July	11,517	553	259	1,378	0	25	0
	Aug.	11,867	272	200	1,429	0	37	0
	Sept.	11,301	372	69	1,610	0	56	0
	Oct.	10,985	272	281	1,471	0	69	0
	Nov.	11,371	75	78	1,490	57	0	0
	Dec.	15,550	150	180	1,717	60	0	0
	Total	135,728	2,249	1,859	16,279	202	359	7
1945	Jan.	12,796	131	61	1,847	43	0	0
	Feb.	9,090	123	56	1,246	8	7	0
	Mar.	12,057	176	413	1,301	20	0	12
	Apr.	12,399	124	466	1,433	70	22	24
	May	8,229	0	414	679	25	0	0
	June	11,340	104	266	1,195	102	0	0
	July	6,915	204	350	410	95	0	0
	Aug.	1,303	87	62	79	33	0	0
	Sept.	0	0	0	0	0	0	0
	Oct.	0	0	0	0	0	0	0
	Total	74,129	949	2,038	8,190	396	29	36

ENCLOSURE (H)

Table IV(H)
PROPERTIES OF PRODUCTS

		Liquid Fuels (°C)		
		Semi-diesel Oil	Fuel Oil	Motor Gasoline
Distillation	Dew point	76	98	72
	5%	222	238	108
	10%	233	256	114
	20%	248	293	126
	30%	257	332	135
	40%	270	349	142
	50%	282	370	151
	60%		372	160
	70%	318		168
	80%	350		179
	90%			194
	97%			216
Composition	Acidic oil (%)	19.0	36.5	
	Basic oil (%)	2.0	0.5	
	Neutral oil (%)	79.0	63.0	
Red. Visc. (50°C secs)		36	174	
Flash Point (°C)		87	118	
Specific Gravity		0.941 (15°C)	0.967 (50°C)	795 (15° C)
Solidifying Point (°C)		13	31	
Spont. Ign. Point (°C)		285		

ENCLOSURE (H)

Table IV(H) (Cont.)
PROPERTIES OF PRODUCTS

Pitch

Solidifying point.................above 150°C

Volatile matter.......................54.86%

Fixed carbon..........................44.88%

Ash.....................................0.26%

Cresols

Distillation

Dew point	76°C	
5%	199	(H_2O 3.8%)
10%	205	
20%	207	
30%	209	
40%	211	
50%	215	
70%	225	
90%	268	

Coke

Volatile matter..........................9.4%

Fixed carbon............................67.5%

Ash.....................................22.5%

Sulfur...................................0.4%

Calorific value..................6,000 Cals

Melting point of Ash..............1,500°C

ENCLOSURE (H)

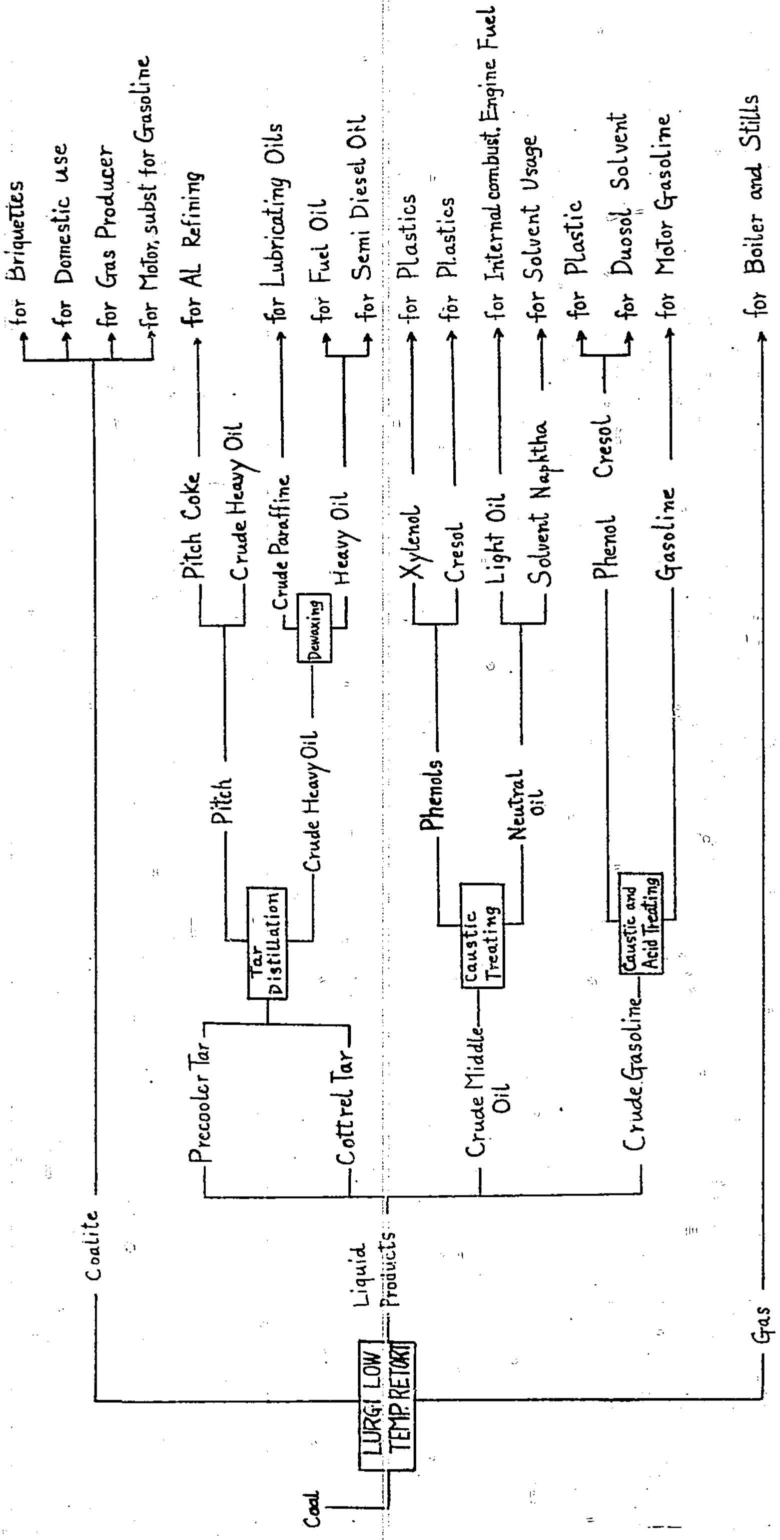
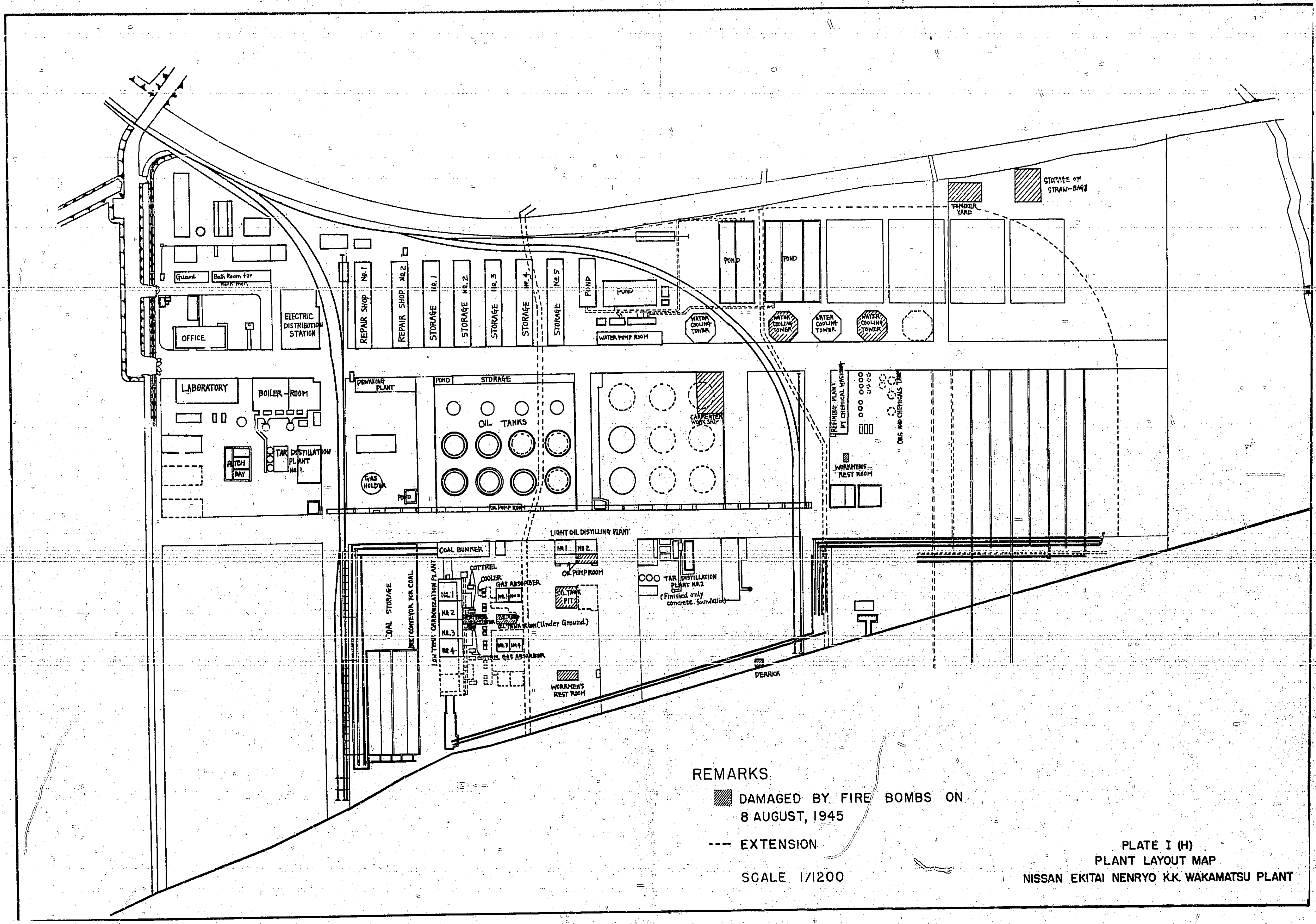


Figure 1(H)
OVER-ALL FLOW SHEET



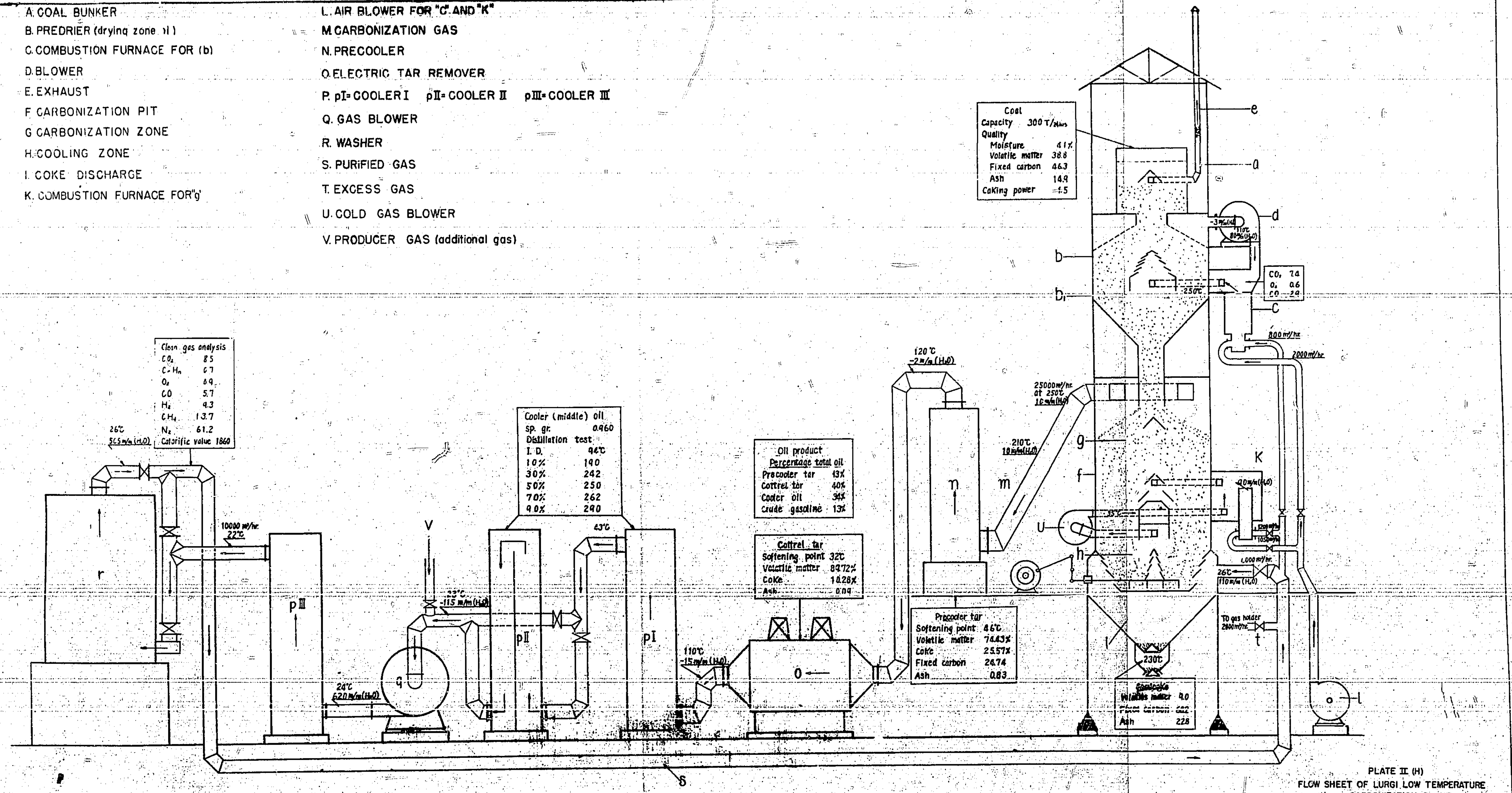
REMARKS

▨ DAMAGED BY FIRE BOMBS ON 8 AUGUST, 1945

--- EXTENSION

SCALE 1/1200

PLATE I (H)
PLANT LAYOUT MAP
NISSAN EKITAI NENRYO K.K. WAKAMATSU PLANT



Coal	
Capacity	300 T/24hrs
Quality	
Moisture	4.1%
Volatile matter	38.8
Fixed carbon	46.3
Ash	14.9
Caking power	4.5

CO_2	7.4
O_2	0.6
CO	2.9

Clean gas analysis	
CO_2	8.5
C_mH_n	6.7
O_2	6.9
CO	5.7
H_2	4.3
CH_4	13.7
N_2	61.2
Calorific value	1860

Cooler (middle) oil	
sp. gr.	0.960
Distillation test	
I. D.	94°C
10%	190
30%	242
50%	250
70%	262
90%	290

Oil product Percentage total oil	
Precooler tar	13%
Cottrel tar	40%
Cooler oil	34%
Crude gasoline	13%

Cottrel tar	
Softening point	32°C
Volatile matter	89.72%
Coke	10.28%
Ash	0.09

Precooler tar	
Softening point	46°C
Volatile matter	74.43%
Coke	25.57%
Fixed carbon	24.74
Ash	0.83

Semicoke	
Volatile matter	9.0
Fixed carbon	[illegible]
Ash	22.8

PLATE II (H)
FLOW SHEET OF LURGI LOW TEMPERATURE CARBONIZATION PLANT
NISSAN EKITAI NENRYO K.K. WAKAMATSU PLANT

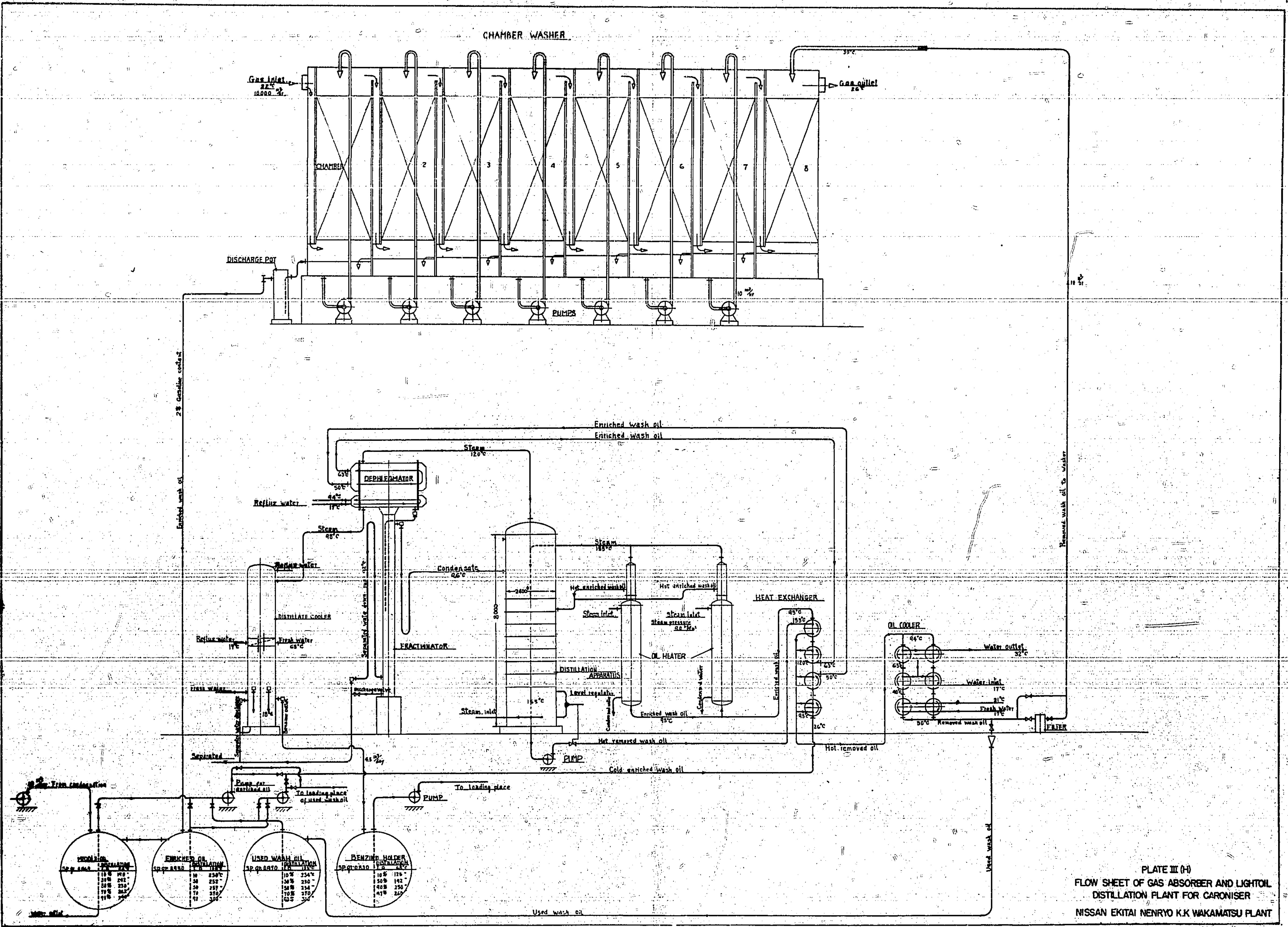


PLATE III (H)
FLOW SHEET OF GAS ABSORBER AND LIGHTOIL DISTILLATION PLANT FOR CARONISER
NISSAN EKITAI NENRYO K.K WAKAMATSU PLANT

ENCLOSURE (I)

ENCLOSURE (I)

HISTORY OF THE SYNTHETIC OIL INDUSTRY IN JAPAN

by

ASST.-CHIEF ENGINEER N. SHONO

TEIKOKU NENRYO KOGYO, K.K.

ENCLOSURE (I)

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ENCLOSURE (I)

I. GENERAL DESCRIPTION

The Japanese Government began consideration of a liquid fuel policy in 1923, but little was done until 1933 when a practical liquid fuel program was established. With regard to synthetic oil in this program, it was decided to aid and develop the low-temperature coal carbonization industry, and to increase the production of shale oil at FUSHUN in Manchuria.

In 1934, the Government established subsidies for low-temperature carbonization of coal, but this industry still did not become active. In July, 1936, the government established a new program, to be made effective in 1937. In this policy they included the following items concerning synthetic oil, intended to assist the petroleum substitutes fuel industry:

1. Institution of laws and regulations to encourage the petroleum substitutes industry.

2. Institution of payments for losses in coal-liquefaction, Fischer-Tropsch synthesis, and low-temperature carbonization of coal industries.

3. Carrying into effect any other measures to aid security and promotion of this industry.

A seven-year synthetic oil plan was drafted to incorporate these items and the Synthetic Oil Production Industry Law and Imperial Fuel Development Company Law were instituted in August, 1937 to accomplish this plan. The Synthetic Oil Production Industry Law was enforced from January, 1938 and the Imperial Fuel Development Company Law from September, 1937.

II. SEVEN-YEAR PLAN FOR SYNTHETIC OIL

This plan was drafted to produce annually 1,000,000 kiloliters each of gasoline and fuel oil from synthetic oil by 1943 in Japan and Manchuria. The quantities produced were expected to supply half of the civilian demands in 1943, and, of this amount, 500,000 kiloliters were expected to be produced in Manchuria. Manufacturing processes were, (1) direct coal liquefaction, (2) Fischer-Tropsch Synthesis and (3) low-temperature carbonization of coal. Raw materials were coal, lignite, and natural gas. The program of plant erection was as follows: 10 units for hydrogenation of coal (capacity of each unit, 100,000 kiloliters per year), 11 Fischer-Tropsch units (capacity of each unit, 500,000 kiloliters per year), and 66 low-temperature carbonization units (capacity of each unit, 100,000 tons of coal per year). The total requirement of funds was expected to be 750,000,000 yen, distributed as follows: 360,000,000 yen for hydrogenation, 121,000,000 yen for Fischer-Tropsch 115,500,000 yen for low-temperature carbonization, and for the expense of coal field developments, 15 yen per ton of output. 50,000,000 yen of the 750,000,000 had already been invested in plants of this type.

III. SYNTHETIC OIL PRODUCTION INDUSTRY LAW

This law was enforced since January, 1938, in Japan proper, Korea, Sakhalin and Formosa. The main object of this law was to protect and help the synthetic oil industry to become firmly established as quickly as possible.

At first, the plants to which this law was applied were as follows: (1) Hydrogenation plants, whose raw materials were coal, lignite, and tar, and whose producing capacities were over 10,000 kiloliters per year. (2) Petroleum synthesis (Fischer-Tropsch) plants, whose producing capacities were over 10,000 kiloliters per year.

ENCLOSURE (I)

(3) Low-temperature carbonization plants, processing either coal or lignite, and which processed more than 100,000 tons of coal per year. In 1941 the government abolished this limit for raw materials and products and amended its policy so as to include any plant which produced fuel oil, lubricants or any crude oil whose main components were hydrocarbons, from any raw materials except natural petroleum. All plants were included which had a capacity of more than 1,000 kiloliters per year production of aviation gasoline blending stock and lubricants. For any other oil products the minimum capacity remained at 10,000 kiloliters per year.

These companies were to be exempted from income tax, profit tax, local tax, and import duty for necessary machines or appliances. The privilege of applying the land expropriation law for plant erection was given to these companies. At first, this law provided that the government would deliver a bonus for synthetic oil produced, but in 1942 this practice was abolished. From that time onward, the government substituted the policy of establishing prices which insured manufacturers of synthetic products a fair profit only.

IV. IMPERIAL FUEL DEVELOPMENT COMPANY LAW

This law was passed in August, 1937, and went into effect in September. It was revised in 1940, 1941, and 1942. The Imperial Fuel Development Company, Ltd. was established in January, 1938 to administer this law, some of whose provisions were as follows:

Art. 1. The Imperial Fuel Development Company shall make it their object to transact all business which will promote synthetic oil production.

Art. 2. The Imperial Fuel Development Company shall have a capitalization of 100,000,000 yen, half of which is supplied by the government. The company can increase the capitalization when approved by the government. (Capitalization was increased to 250,000,000 yen by the end of the war.)

Art. 10. The president and vice-president shall be appointed by the government and their term of office shall be five years.

Art. 12. The Imperial Fuel Development Company shall finance synthetic oil enterprises. They may manufacture or sell synthetic oils, etc., or manage other business necessary for promoting synthetic oil production, when permitted by the government.

Art. 13. The Imperial Fuel Development Company can issue debentures up to an amount equal to five times their paid-up capital.

Art. 15. The government guarantees the return of the face value of shares and the payment of interest.

Art. 20. The Government supervises the business of the Imperial Fuel Development Company.

Art. 30. The Imperial Fuel Development Company shall not be obliged to pay dividends on shares held by the government unless the amount of their annual profit reaches six per cent of the value of paid-up shares not held by the government. Should the annual profit of the Imperial Fuel Development Company fail to reach four per cent of the value of paid-up shares (excluding government holdings) in the first three years of their existence, and six per cent in the following seven years, the government shall subsidize the difference so that

ENCLOSURE (I)

dividends may reach the above-mentioned percentage.

Art. 32. The Imperial Fuel Development Company shall be exempted from corporation and business taxation in the first year of their existence and in the following ten years.

V. GOVERNMENT SUBSIDIES

In Table I(I), the column headed "Estimated Subsidy" refers to the amount of money the government estimated would be paid out in subsidies if the proposed synthetic fuel program produced in accordance with expectations. The column headed "Actual Amount Paid" is self-explanatory. Ten yen per ton of tar was paid in Japan proper, and two yen per ton of coal processed in Sakhalin. This agreement continued in effect until 1937.

At the end of each year, after the Synthetic Oil Production Law went into effect in 1938, the government determined the amount paid out in subsidies to synthetic oil manufacturers in Japan proper. In Table II(I), all synthetic oil produced has been divided into 2 categories (1) gasoline and (2) all other synthetic products combined. The unit of production to which the subsidy applies is not specified.

The practice of subsidizing production was abolished in 1942 when the government initiated the policy or fixing the prices of synthetic oil products. At these fixed prices (which included suitable profit), the Sekiyu Kyohan Company, Ltd. bought the products from synthetic oil companies and pooled them with natural petroleum products bought from refining companies. The purchase price was based on production cost. The production cost of synthetic oil and the price at which the pooled material was distributed is presented in Table III(I).

The annual Government susidies paid through the Imperial Fuel Development Company were as follows (yen):

1937	148,094
1938	878,387
1939	1,938,000
1940	2,625,057
1941	4,086,052
1942	4,050,650
1943	7,497,335
1944	8,519,288

VI. CONSTRUCTION AND PRODUCTION

In 1937, when the government began the seven year synthetic oil plan, there were five plants in operation, one on shale oil, and four on low-temperature carbonization. Three plants were under construction in Japan and Manchuria, two of these being for coal hydrogenation, and one for the Fischer-Tropsch synthesis. The next year, 1938, six additional plants were placed under construction, and in 1939, six more. The seven-year plan for synthetic oil did not progress successfully, however. At the end of 1940, the government planned to limit the synthetic oil expansion program to plants already established. However, after 1941, progress in erection was very slow because of material shortages and therefore production of synthetic oil could not meet the government objective. In 1942, Japan obtained petroleum from the East Indies, but the government declared that the synthetic oil industry should be continued under the same policy and completed as rapidly as possible. Actually, erection of plants was very slow and production was very small. Thus, the Japanese synthetic oil production was not successful at the end of the war. Almost no aviation gasoline was produced from synthetic oil. Production since 1937 was as follows (Kl -'lubricant from rubber is not included):

1937	4,950	excludes Korea & Manchuria
1938	7,400	excludes Korea & Manchuria
1939	17,934	excludes Korea & Manchuria
1940	33,254	excludes Manchuria
1941	52,056	excludes Manchuria
1942	75,984	excludes Manchuria
1943	106,146	excludes Manchuria
1944	113,166	excludes Manchuria
1945	29,351	excludes Manchuria

In 1945, seven synthetic oil plants in Japan were bombed, three of which received heavy damage. All seven plants ceased production and had not been able to resume operation by the end of the war. After the war, production of synthetic oil was limited by coal shortages.

In December, 1945, the government abolished the synthetic oil production industry law and declared that they would not help such an expensive industry in the future. The government decided that the Ube Works and Takikawa Works would in the future produce sulfate of ammonia with synthetic oil produced as a by-product. Two plants, the Miike Works and the Wakamatsu Works, would produce synthetic oil only. The present oil capacity of these plants is as shown in Table IV(I).

ENCLOSURE (I)

Table I(I)
GOVERNMENT SUBSIDIES (YEN)

	Estimated Subsidy	Actual Amount Paid
1934	449,500	
1935	505,300	165,556
1936	552,000	287,092
1937	517,300	455,102

Table II(I)
SYNTHETIC OIL PRODUCED (YEN)

	Process	Gasoline	Other Oil
1938	Hydrogenation		
	Fischer-Tropsch		
	Low-Temp. Carbonization	43.88	17.20
1939	Hydrogenation	77.00	34.00
	Fischer-Tropsch	66.00	47.00
	Low-Temp. Carbonization	47.00	18.00
1940	Hydrogenation	72.00	24.00
	Fischer-Tropsch	60.00	50.00
	Low-Temp. Carbonization	39.00	13.00
1941	Hydrogenation	72.00	24.00
	Fischer-Tropsch	60.00	50.00
	Low-Temp. Carbonization	39.00	13.00

ENCLOSURE (I)

Table III(I)
PRODUCTION COSTS & RETAIL PRICE OF SYNTHETIC OIL

Type of Product	Process	Production Cost of Synthetic Oil (Yen/kl)	Official Retail Prices (Yen/kl)
Aviation Gasoline	Hydro.	600	444
Motor Gasoline		400	307
Gas Oil A - 1	Hydro & L.T.C.	230	152
Gas Oil A - 2		220	141
Gas Oil B - 1	**Fischer-Tropsch**	340	177
Gas Oil B - 2		330	167
Gas Oil B - 3		320	157
Semi-diesel Oil	L.T.C.	180	88
Bunker Fuel Oil		100	84

Table IV(I)
SYNTHETIC OIL CAPACITIES

Name of Works	Name of Company	Process	Capacity kg/year
Miike	Nippon Jinzo Sekiyu	Fischer-Tropsch	13,000
Wakamatsu	Nissan Ekitai Nenryo	L.T.C.	21,000
Takikawa	Nippon Jinzo Sekiyu	Fischer-Tropsch	14,000*
Chisso	Ube Kosan	L.T.C.	10,000
Wanishi	Nippon Seitetsu	L.T.C.	1,500
Ube	Teikoku Nenryo Kogyo	L.T.C.	0**
	Total		59,500

* Capacity will decrease to 6,000 kl/year when sulphate of ammonia is produced.

** After one year, plants shall be restablished and shall have capacity 15,000 kiloliters per year.

RESTRICTED

ENCLOSURE (J)

ENCLOSURE (J)

REPORT ON

TEIKOKU NENRYO K. K. UBE WORKS

ENCLOSURE (J)

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LIST OF TABLES AND ILLUSTRATIONS

ENCLOSURE (J)

I. INTRODUCTION

This report records and summarizes technical information obtained by the Petroleum Section of NavTechJap during an inspection of the Ube Works of Teikoku Nenryo K. K. on 28 October 1945. The following Japanese personnel were interviewed and assisted in supplying the information presented herewith:

Mr. K. IWAMOTO, Plant Manager
Mr. ITO, Head of General Affairs Dept.
Mr. UWABA, Head of Production Dept.
Mr. IKI, Gas Engineer
Mr. TAWARDA, Business Manager

II. HISTORY AND ORGANIZATION

The Ube Works was founded in August, 1939, with a capitalization of 50,000,000 yen invested by the Teikoku Nenryo and the Ube Kosan K. K., and was called the Ube Yuka Kogyo K. K. (Ube Synthetic Oil Co.). In October, 1944, the company was taken over by Teikoku Nenryo and designated as its Dai-Ichi Jigyosho (First Plant). At the outset, it was planned to produce annually 40,000 kl. of gasoline by low-temperature carbonization of Ube brown coal and by hydrogenation of the light tar oil, and also synthetic ammonia.

Construction of the Koppers low-temperature ovens was started in February, 1942, together with auxiliary coal handling and oil recovery and refining apparatus. In October, 1941, the decision was made to install ten Lurgi retorts to produce 90,000 kl. tar, per year of low temperature and the first of these was completed in October, 1943.

Construction of a plant to make lubricating oil from rubber was started in February, 1943, and operation began in October of the same year. The methanol plant was also started in 1943.

The plant suffered very severe damage in four bombing raids, July 2nd, 15th, 23rd and August 5th, 1945, which stopped operations completely. Prior to these raids, two Koppers ovens and four Lurgi ovens were operating; but six Lurgi ovens, the hydrogen manufacturing plant, the oil hydrogenation plant, the ammonia synthesis unit, and the methanol plant had not yet been completed.

In spite of the extensive damage, plans were being laid to repair and convert the plant to manufacture synthetic ammonia to the extent of 150,000 tons per year.

The total number of plant employees before the bombing was 350 staff officials and 1,200 workmen.

III. DESCRIPTION OF PLANT EQUIPMENT

A layout map of the Ube Works, which also shows the extent of air raid damage is given by Plate I(J) and an over-all process flowsheet by Figure 1(J). Process flowsheets for the Koppers low-temperature carbonization ovens and oil recovery system, the methanol plant, and the oil hydrogenation unit are given by Plates II(J), III(J), and IV(J), respectively. Data relative to the designers and constructors of the several units are summarized in Table I(J).

The process, utilized for manufacturing lubricating oils from rubber was as follows: Shredded natural rubber was mixed with calcined natural clay from Sendai Province, and with light oil recycled from the process, in the following proportions:

ENCLOSURE (J)

Rubber	100 kg
Clay	100 kg
Light Oil	230 kl

This mix was charged to batch retorts 6 meters long and 2 meters in diameter, and heated by direct firing and steam coils for a period of 24 hours to 300°C maximum. The mix was filtered to remove clay and sludge, and batch-distilled to produce light oil and machine oil of the desired viscosity.

IV. PRODUCTION OUTPUT AND QUALITY

Data on actual throughputs at the Ube Works, for the period April, 1944-June, 1945, are summarized in Table II(J). Data for other years was not available, due to destruction of records by fire.

Typical inspections of refined products are given in Table III(J).

Table I(J)
DATA ON EQUIPMENT AT UBE WORKS

Unit	Designer	Constructor	Catalyst
Koppers Ovens	Heinrich Koppers, A. U.	Kubota, I. W. Mitsubishi Kakoki, K. K.	
Lurgi Ovens	Lurgi, A. U.	Hitachi Kosen K. K.	
Oil Hydrogenation	Third Naval Fuel Depot, TOKUYAMA	Kobe Gaiko, K. K.	Navy Ofuna
Hydrogen Manufacture	Kobe Seiko, K. K.	Kobe Gaiko, K. K.	
Lubricating Oil from Rubber	Toa Nenryo, K. K.	Hitachi Kosen, K. K.	
Ube Methanol synthesis	Teikoku Nenryo, K. K.	Osaka, K. K.	Navy Ofuna
Ammonia Synthesis		Nebuhara	Fauser

ENCLOSURE (J)

Table II(J)
ACTUAL PRODUCTION, - UBE WORKS

		April, 1944 March, 1945	April, 1945 June, 1945
Coal Charged	Koppers	178,930 tons	
	Lurgi	143,090 tons	
	Total	322,020 tons	
Products	Motor Gasoline	2831 kl	543 kl
	Light Oil	1423 kl	186 kl
	Heavy Oil No. 1	207 kl	1157 kl
	Heavy Oil No. 2	13825 kl	2920 kl
	Machine Oil	1720 kl	16 kl
	Motor Oil	kl	3 kl
	Total	20,006 kl	4,825 kl
	Cresols	598 tons	89 tons

Table III(J)
TYPICAL INSPECTION OF REFINED PRODUCTS
UBE WORKS - JUNE, 1945

		Motor Gasoline	Light Oil
Sp. Gravity (d_4^{15})		.812	0.910
	IBP	64°C	231°C
Distillation (^{o}C)	10%	95°C	
	50%	141°C	253°C
	90%	205°C	284°C
	97%	223°C	
	FBP		310°C
Sulfur (wt %)		0.9	
Reaction		neutral	
Ignition point			78°C
Appearance			yellowish-red and clear

Table III(J) (cont.)
TYPICAL INSPECTION OF REFINED PRODUCTS
UBE WORKS - JUNE, 1945

		Heavy Oil		Lube Oil	
		No. 1	No. 2	Machine	Mobile
Reaction		neutral	neutral		
Ignition point		80°C	129°C	110°C	130°C
Viscosity	at 50°C, secs., Red. #1	45	259		
	at 30°C, secs.			151	
	at 80°C, secs.			75	210
	at 100°C, secs.			41	51
Freezing point		15°C	33°C	below 0°C	below 5%
Carbon Residue		0.665%	4.6%		0.8%
Ash		0%	0.08%		
Water		0.3%	0.9%		
Sulfur		0.9%			
Tar acids		23%	25%		
Specific gravity at 50°C			0.964%		

ENCLOSURE (J)

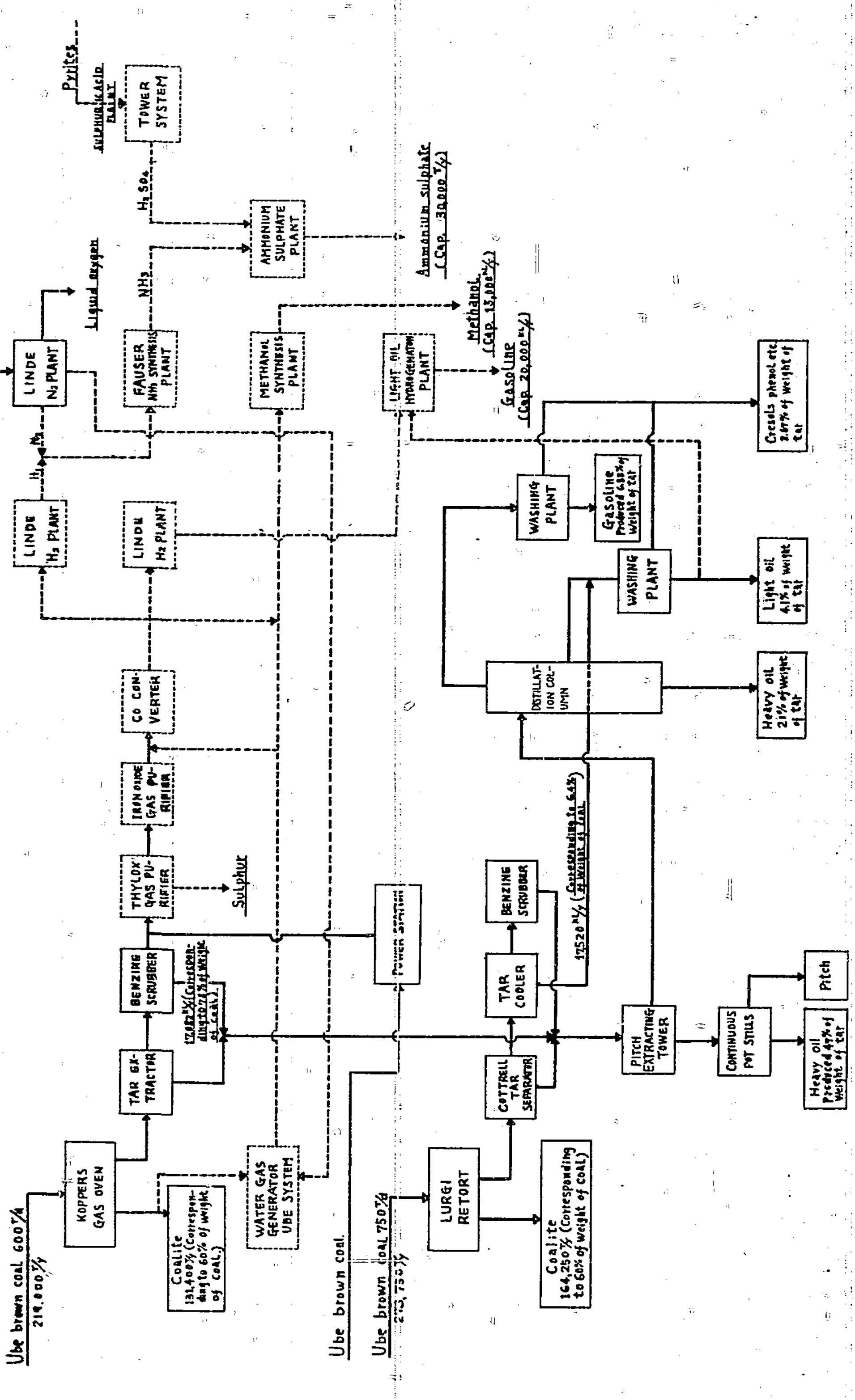
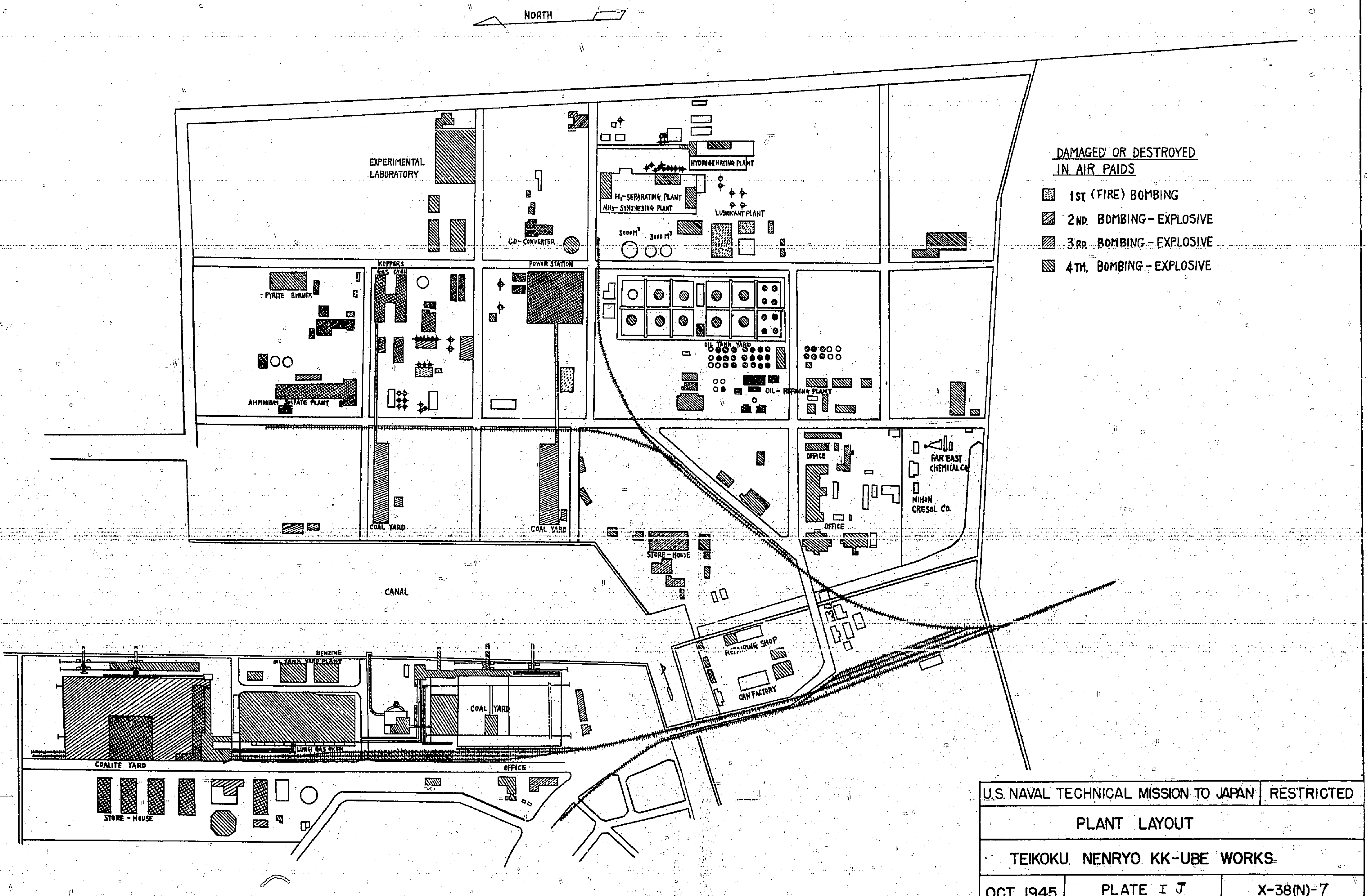


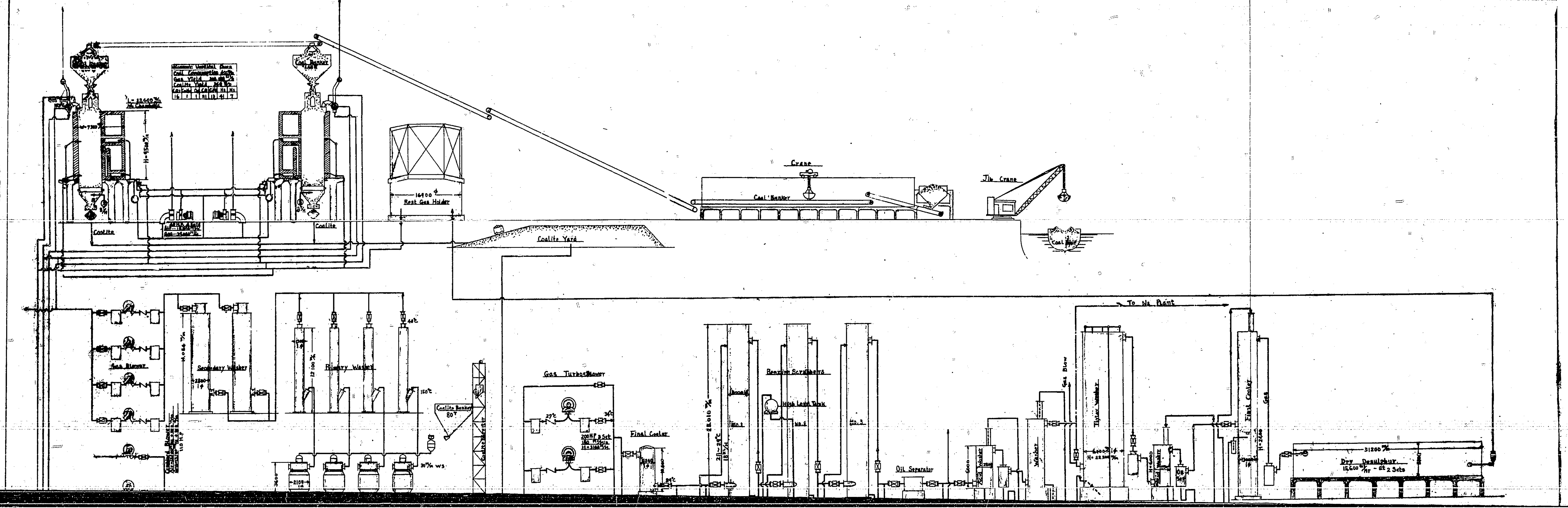
Figure 1(J)

FLOW SHEET OF OPERATIONS

Teikoku-Nenryo K.K.-Ube Works



U.S. NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
PLANT LAYOUT		
TEIKOKU NENRYO KK-UBE WORKS		
OCT. 1945	PLATE I J	X-38(N)-7


Coal Bunker
Coal Consumption
Gas Yield
Coalite Yield
16 1 1 21 13 41 7
L = 13640 m/m
W = 7300
H = 9500 m/m
Coalite
Coalite
Rest Gas Holder
16400 φ
Crane
Coal Bunker
Jib Crane
Coalite Yard
Gas Blower
Secondary Washer
14,054 m/m
2880 1φ
Primary Washer
12 100 m/m
40°C
150°C
Coalite Bunker
80T
30 m/m WS
3600
2100
Gas Turbo Blower
27°C
34°C
200 HP 3 Set
H = 3100 m/m
Final Cooler
24°C
Benzine Scrubbers
28,010 m/m
21~29°C
High Level Tank
No. 1
No. 2
No. 3
Oil Separator
Washer
Gas Blow
To N2 Plant
Tyler Washer
6000 m/m 1φ
H = 22,500 m/m
H = 6000
Oil Sep
Final Cooler
Gas
H = 2100
31200 m/m
Dry Desulphur
15,600 m³/hr - at 2 Sets

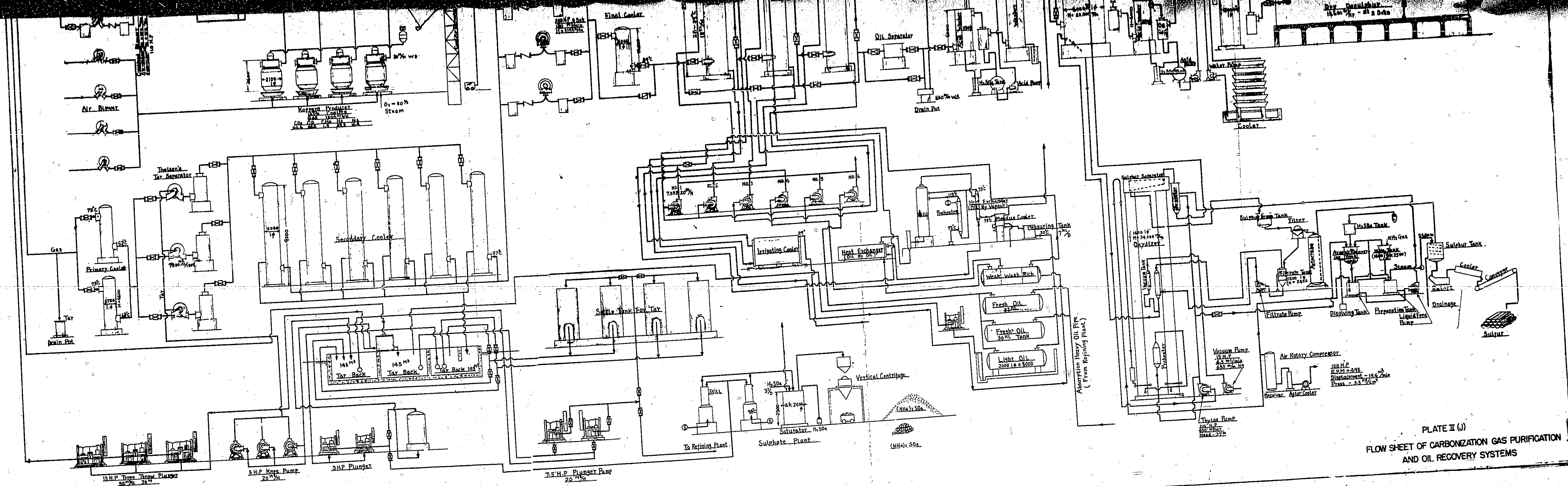
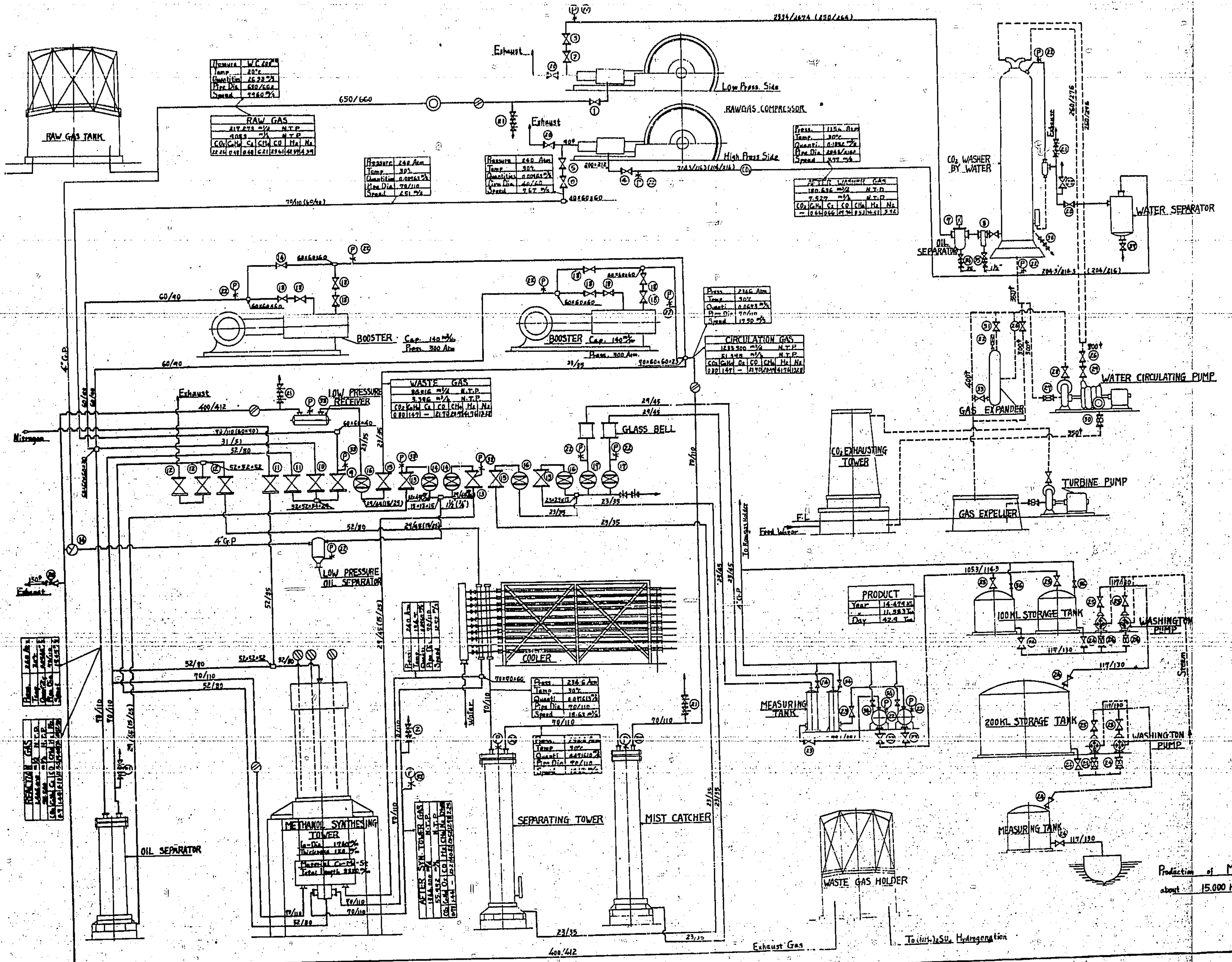


PLATE II (J)

FLOW SHEET OF CARBONIZATION GAS PURIFICATION AND OIL RECOVERY SYSTEMS

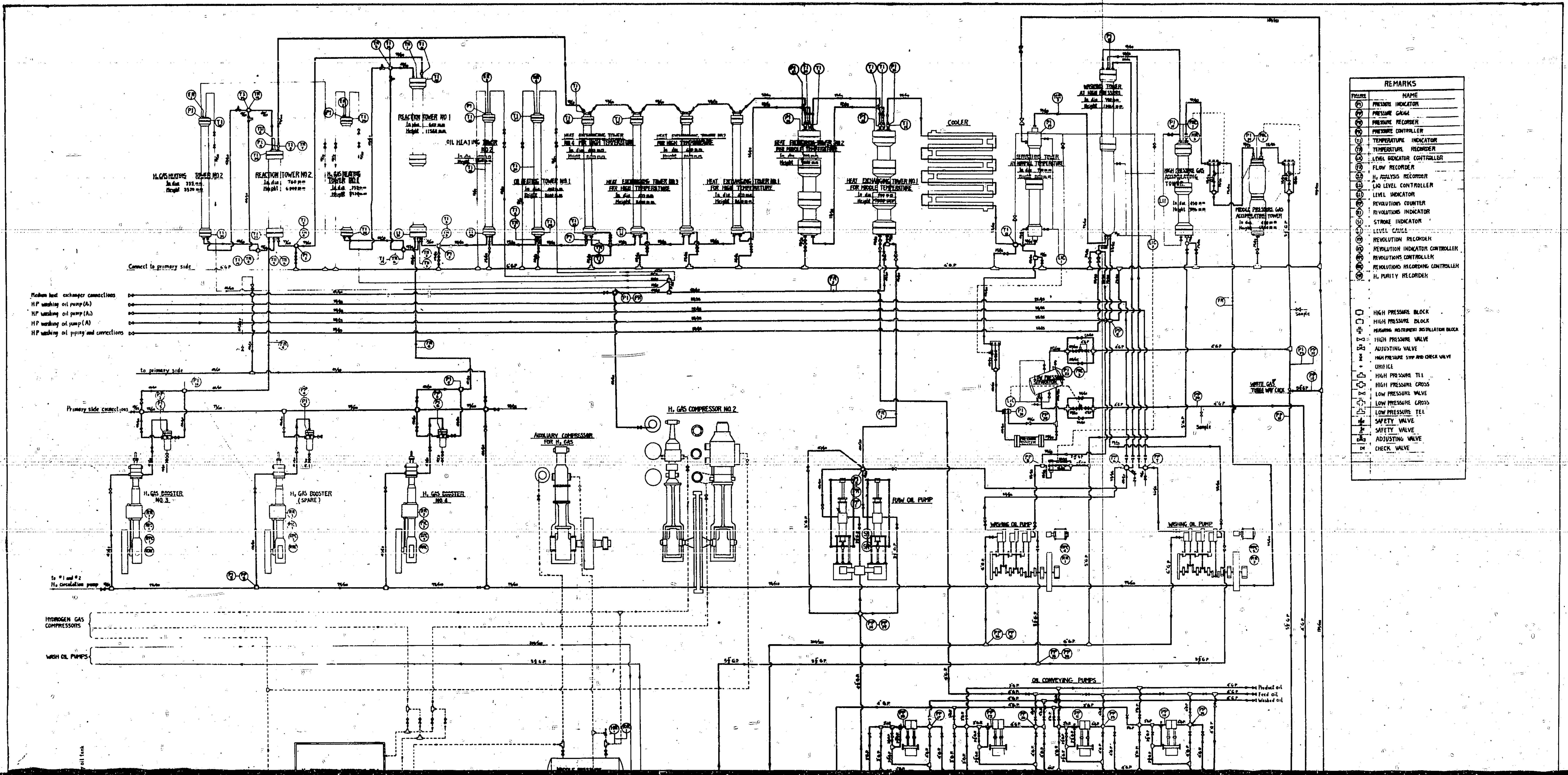


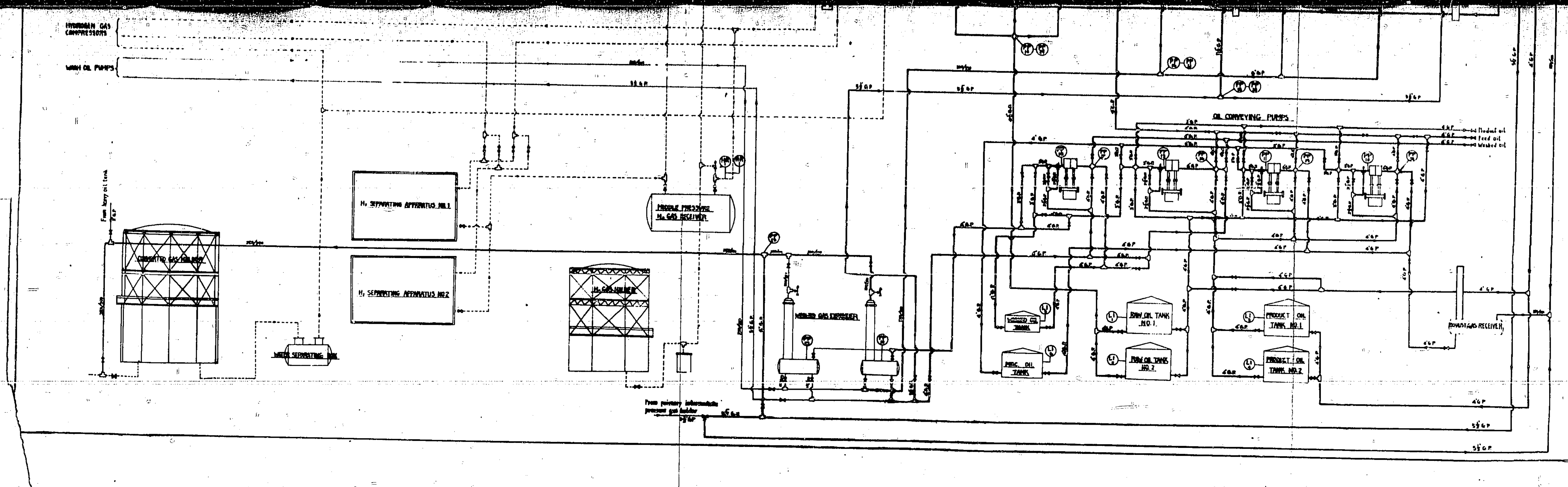
Production of Methanol
about 15,000 KL/Year

No	Valve	Quantity	Dimension mm	Remarks
1	Cast Iron Stop Valve	1	650°	
2	Cast Steel 〃	1	250	
3	〃 Check Valve	1	250	
4	〃 Stop Valve	1	200	
5	Forged Steel 〃	1	60	MSY 18-1
6	〃 Check Valve	1	60	MSY 18-2
7	Cast Steel Safety Valve	1	100	
8	〃 Check Valve	1	200	
9	Forged Steel 〃	1	36	MSY 18-11
10	〃 Stop Valve	1	36	MSY 18-3
11	〃 〃	2	60	MSY 18-6
12	Special Steel 〃	3	60	
13	Forged Steel 〃	2	15	MSY 18-5
14	〃 Reduction Valve	2	15	MSY 18-6
15	〃 Stop Valve	3	26	MSY 18-7
16	〃 Reduction Valve	3	26	MSY 18-8
17	〃 〃	2	15	MSY 18-6
18	〃 Stop Valve	10	60	MSY 18-4
19	Cast Steel Three Way Cock	1	100	
20	〃 Stop Valve	4		
21	Mild Steel Needle Valve	12	9	MSY 18-9
22	Cast Steel Stop Valve	13	6	MSY 18-10
23	〃	4	80	
24	〃 Sluice Valve	4	110	
24	〃 Stop Valve	6	110	
25	〃 〃	6	80	
26	〃 〃	2	300	
27	〃 Sluice Valve	1	300	
28	〃 Stop Valve	1	400	
29	〃 Check Valve	1	300	
30	Cast Iron Sluice Valve	1	350	
31	Cast Steel Spherical Valve	1	160	
32	〃 Safety Valve	7	50	
33	〃 Stop Valve	1	400	
34	Cast Iron 〃	6	35	
35	〃	2	1½	
36	〃	4	50	
37	Cast Steel 〃	1	50	
38	Forged Steel 〃	7	6	MSY 18-10

Designation	Name
─▷◁─	Stop Valve
─▷⊠◁─	Sluice Valve
─▷◁─	Check Valve
─⊠─	Safety Valve
─⊗─	Reduction Valve
─▷|◁─	Needle Valve
→▷◁─	Exhaust Valve
─×─	Pressure Guage Valve
─□─	High Pressure Block
─▷◁─▷◁─	Sample Valve
─Ⓨ─	Three Way Cock
─○─	Bell Type, Lap Type Oxygen Alarm
─⊘─	Flow Indicator
─Ⓒ─	CO₂ Analyser
◖──	Resistence Thermometer
◷──	Pressure Gauge
⊘──	Thermo Couple Thermometer
─▭─	Level Gauge

U.S. NAVAL TECHNICAL MISSION TO JAPAN | REST
FLOW SHEET OF METHANOL SYSTEM
TEIKOKU NENRYO K.K. UBE WORKS
JULY 10, 1946 | PLATE III J | X-38(N).


H₂ GAS HEATING TOWER NO 2
In dia 352 mm
Height 3570 mm
REACTION TOWER NO 2
In dia 760 mm
Height 6000 mm
H₂ GAS HEATING TOWER NO 1
REACTION TOWER NO 1
In dia 660 mm
Height 11560 mm
OIL HEATING TOWER NO 2
OIL HEATING TOWER NO 1
HEAT EXCHANGING TOWER NO 4 FOR HIGH TEMPERATURE
HEAT EXCHANGING TOWER NO 3 FOR HIGH TEMPERATURE
HEAT EXCHANGING TOWER NO 2 FOR HIGH TEMPERATURE
HEAT EXCHANGING TOWER NO 1 FOR HIGH TEMPERATURE
HEAT EXCHANGING TOWER NO 2 FOR MIDDLE TEMPERATURE
HEAT EXCHANGING TOWER NO 1 FOR MIDDLE TEMPERATURE
In dia
Height
COOLER
SEPARATING TOWER AT NORMAL TEMPERATURE
WASHING TOWER AT HIGH PRESSURE
HIGH PRESSURE GAS ACCUMULATING TOWER
In dia 450 mm
Height
MIDDLE PRESSURE GAS ACCUMULATING TOWER
Connect to primary side
Medium heat exchanger connections
HP washing oil pump (A₁)
HP washing oil pump (A₂)
HP washing oil pump (A)
HP washing oil piping and connections
to primary side
Primary side connections
H₂ GAS BOOSTER NO 3
H₂ GAS BOOSTER (SPARE)
H₂ GAS BOOSTER NO 4
AUXILIARY COMPRESSOR FOR H₂ GAS
H₂ GAS COMPRESSOR NO 2
to #1 and #2 H₂ circulation pump
HYDROGEN GAS COMPRESSORS
WASH OIL PUMPS
oil tank
LOW PRESSURE SEPARATOR
RAW OIL PUMP
WASHING OIL PUMP
WASHING OIL PUMP
WASTE GAS THREE WAY COCK
Sample
Sample
OIL CONVEYING PUMPS
Product oil
Feed oil
Washed oil
REMARKS
FIGURE
NAME
PI PRESSURE INDICATOR
PP PRESSURE GAUGE
PR PRESSURE RECORDER
PC PRESSURE CONTROLLER
TI TEMPERATURE INDICATOR
TR TEMPERATURE RECORDER
LIC LEVEL INDICATOR CONTROLLER
FR FLOW RECORDER
H₂ ANALYSIS RECORDER
LLC LIQ LEVEL CONTROLLER
LI LEVEL INDICATOR
RC REVOLUTIONS COUNTER
RI REVOLUTIONS INDICATOR
SI STROKE INDICATOR
LG LEVEL GAUGE
RR REVOLUTION RECORDER
RIC REVOLUTION INDICATOR CONTROLLER
RPC REVOLUTIONS CONTROLLER
RRC REVOLUTIONS RECORDING CONTROLLER
HR H₂ PURITY RECORDER
HIGH PRESSURE BLOCK
HIGH PRESSURE BLOCK
MEASURING INSTRUMENT INSTALLATION BLOCK
HIGH PRESSURE VALVE
ADJUSTING VALVE
HIGH PRESSURE STOP AND CHECK VALVE
ORIFICE
HIGH PRESSURE TEE
HIGH PRESSURE CROSS
LOW PRESSURE VALVE
LOW PRESSURE CROSS
LOW PRESSURE TEE
SAFETY VALVE
SAFETY VALVE
ADJUSTING VALVE
CHECK VALVE



S NAVAL TECHNICAL MISSION TO JAPAN		RESTRICTED
FLOW. SHEET OF OIL HYDROGENATION PLANT		
TEIKOKU NENRYO UBE WORKS		
OV3,1945	PLATE IV J	X-38(N)-7