

**RESTRICTED**

**ENCLOSURE (A)**

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

by

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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 COALA. 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/cm<sup>2</sup>, the hydrogenation of coal was not only incomplete, but a part of the hydrogenated product was converted to

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coke and gas. For continuous operation, a 200 kg/cm<sup>2</sup> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> solution gave good results. Since then, a number of experiments with the ZnCl<sub>2</sub> catalyst were made. Enclosures (B)10, and (B)18.

A ZnCl<sub>2</sub> 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<sup>2</sup> 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<sub>4</sub>Cl.

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<sub>3</sub> or WS<sub>3</sub>, 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<sub>3</sub> or a mixture of MoO<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub>, and acid clay.

D. Material Balance

Typical yields for hydrogenation of Oyama coal, using Fe<sub>2</sub>O<sub>3</sub> 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<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub> and acid clay catalyst, are given in Table II(A). (See Article 2 of this series, Enclosure (B)16.)

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## 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 preceding experiments showed that commercial development was possible only with government assistance. Then the Chosen Nitrogen Fertilizer Company (AGOSHI, 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, UBS 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 <sup>2</sup> )	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	53.7	54.0	55.5
Solid Residue	8.2	10.8	8.5	8.1
Gas and Loss	5.0	4.7	6.1	7.0

\* Charge stock for secondary hydrogenation of coal.  
\*\* Reycle oil for preparation of parts.

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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 <sup>2</sup> )	200	200	200
Space Velocity	0.5	0.5	0.5
Yield of Products (wt.% of o.s.)			
Total Oil	95.2	92.2	99.0
Aviation Gasoline	23.4	50.1	18.6
H <sub>2</sub> 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	0.748
Vapor Press. (kg/cm <sup>2</sup> )	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.