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REPORT ON RESEARCH ON THE FISCHER TROPSCH PROCESS AT THE KYOTO IMPERIAL UNIVERSITY

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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 1936-1945, 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.

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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, apperently 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 HIWASAKA, 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

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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% kieselgühr + 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

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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:

$$Fe + 25\%\ Cu + 5\%\ Mg + 125\%\ \text{kieselguhr} + 6\%\ K_2CO_3$$

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:

$$\text{Ochre} + 0.5\%\ Cu + 0.5\%\ Mn + 6\%\ K_2CO_3$$

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 masskneaded. 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,

$$Fe + 25\%\ Cu + 125\%\ \text{kieselguhr} + 3\%\ K_2CO_3$$

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.

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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^3) Kerosene	Gasoline	Total	Life of Catalysts	Name of Investigator
Co-15%Mn-150% Kieselguhr	1:2	4	200	72.5	72	144.5	more than one month	Fischer & Koch
Co-18%ThO_2-180% Kieselguhr			190	100	53	153	about two months	
Co-5%Cu-12%U_3O_8-4%Mn-100%KSO		6	195			158.2	-	TSUTSUMI
Co-7%Cu-6%ThO_2-1.5%U_3O_8-125%KSO		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	45	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-3% K_2CO_3				40	33	73	30th day 39 cc/m^3	
Ochre-3%Cu-4% K_2CO_3				44	35	79	-	
Ochre-1%Cu-1% H_3BO_3-4% K_2CO_3				52	34	86	30th day 62 cc/m^3	
Ochre-1%Cu-3% H_3BO_3-8% K_2CO_3				51	35	86	30th day 57 cc/m^3	

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Table II(D)
COMPARISON OF CATALYSTS FOR MIDDLE PRESSURE SYNTHESIS LABORATORY TESTS AT KYOTO IMPERIAL UNIVERSITY

	Composition of Catalysts	Gas Comp. $CO:H_2$	Gas Flow over 40 cc cat. L/hr	Press Kg/cm²	Temp. °C	Yield inc. wax. g/m^3	Life of Catalysts (mean yield for each week) 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Cobalt	Co-[illegible]MgO-[illegible]ThO₂-200 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-[illegible]Cu-[illegible]Kies.-[illegible]K_2CO_3	1:1			190	41																		
					200	67																		
					210	85	85	84	79	76	74	78												
					220	101							92	87	85	79	78	79	-	70	65	70		
					230	105																		
					240	115																		
					250	106																		
	Fe-[illegible]Cu-[illegible]Kies-[illegible]K_2CO_3			15	210	120																		
	Fe-[illegible]-[illegible]Mg-[illegible]Kies-[illegible]K_2CO_3			10	210	111																		
				15	190	70																		
Natural	[illegible]-[illegible]Cu-[illegible]-[illegible]K_2CO_3			10	210	74																		
					230	99																		
					250	112																		

(1) Catalyst from CHUTA.

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Table III(D)
SUMMARY OF LARGE SCALE PILOT PLANT CATALYST TESTS

	Pressure	Composition of Catalyst	Gas Comp. $CO:H_2$	Gas Flow m^3/hr	Reaction Temperature °C	Avg. Yield Inc. Max g/m^3	Max. Life of Catalyst month	Distillation: Gasoline Initial b.pt.	Gasoline 10%	Gasoline 50%	Gasoline 90%	Kerosene Initial b.pt.	Kerosene 10%	Kerosene 50%	Kerosene 90%	Olefine Content % gasoline	Olefine Content % kerosene	Iodine No. gasoline	Iodine No. kerosene
Co[1]	norm.	Co·18%ThO·200% Kies. or Co·5%Mg·7%ThO·200% Kies.	1:2	1000	180-200	125g.	4	25	59	79	157	148	183	227	315	40	18		
Co[1]	mid.		1:2	1000	180-200	145g.	6									17	6		
Co[2]	norm.	Co·10%Cu·5%ThO_2·2% U_3O_8·125% Kies.	1:2	100	200-210	102cc	1	29	41	79	155	96	138	180	232			59	17
Fe[2]	norm.	[illegible] Kies.·20%K_2SiO_3·4% K_2CO_3	1:2	100	235	86cc	1	40	58	93	172	102	154	205	288			167	60
Fe[3]	mid.	Fe·25%Cu·15%Mn·125% Kies.·20%K_2SiO_3·7% K_2CO_3	1:1	10	230	106cc	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.

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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/cm^2	Gas Contraction %	Gas Consumption $CO:H_2$	Composition of Reaction Gas						Yield of Reaction Products g/m^3				
				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	13.6	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	33.8	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	23.8	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	28.5	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	6.7	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	2.2	12.3	7.5	3.1	0.5	3.5	7.1
	6	29.1	1.20	8.5	0.3	34.6	41.1	2.3	13.4	12.7	3.8	2.5	13.9	20.2
	10	32.3	1.15	8.1	0.3	36.7	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

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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 Berylium 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

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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 Synthetizsd 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

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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 K. FUKASAKA	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 R. 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.	H. 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
144603	1938, 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
144981	1939, Oct., 26	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 temperature.	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., 16	1943, Mar., 16	Activation of oil synthetic catalyst.	Activation of catalyst by preliminary heat treatment.	G. KITA S. KODAMA Y. MURATA
156987	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