

BENCH-SCALE STUDIES OF THE FISCHER-TROPSCH SYNTHESIS OVER IRON, NICKEL, AND NICKEL-COBALT CATALYSTS (JAPAN)

BY SHIRO WATANABE
(REVISED AND EDITED BY R. C. GRASS)

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With Preface by R. C. Grass

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Note. - Compiled from Reports Nos. 3 and 4 of the Hokkaido Synthetic
Petroleum Co., Inc. (Japan), 1942.

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PREFACE

In the summer of 1945, when it was evident that invasion of the Japanese home islands was imminent, the U. S. Naval Technical Mission to Japan was established to evaluate the accomplishments of the Japanese in naval technology and related fields. Of primary importance to the mission was the acquisition of the maximum amount of information in the shortest possible time after the country was entered. Each day's delay would have allowed additional Japanese equipment and documents to be destroyed and would have made it easier for key Japanese personnel to disappear. With this in mind, the first entry into Japan by mission personnel occurred early in September, and the activities of the mission were highly concentrated over the next few months, terminating in December 1945.

One of the many phases of the Japanese technical war effort in which mission investigators were interested was the program directed toward obtaining liquid fuels from coal and other sources. The Japanese navy attached tremendous importance to research in this direction, and, in 1945, approximately 3,200 persons, including about 400 technically trained personnel, were employed at the First Naval Fuel Depot at Ofuna, where every known phase of fuel and lubricant technology was being investigated. Research and development work involving both direct and indirect coal-hydrogenation processes also was being carried out in such places as the Institute of Fuel Technology at the Imperial University of Kyoto, the Imperial Fuel Research Institute of the Department of Commerce and Industry, the Hokkaido Synthetic Petroleum Co., Inc., and the Tokyo Institute of Physical Chemical Research. The relation of the Imperial Fuel Research Institute to the Japanese economy corresponds rather closely to that of the Bureau of Mines in the United States. In coal-hydrogenation investigations conducted there, emphasis was placed on assays and fundamental studies rather than on production. It was said that over a hundred Japanese coals had been so studied.

As Japan is extremely deficient in petroleum resources, it is not surprising to discover that organized effort had been expended to obtain liquid fuels from sources that would otherwise appear fantastic. In attempts to supplement their supplies of motor fuel, so necessary to the prosecution of mechanized warfare, the Japanese investigated the potentialities of such source materials as orange peels, rubber, and pine needles, and studied the hydrogenation of coal more extensively than any other nation except Germany and Great Britain. Their rewards for these efforts, however, were meager. Although plants for producing synthetic liquid fuels were constructed and operated, their output fell disastrously short of the magnitude necessary to support the Japanese military machine. Maximum production was attained in 1944 when the total yearly synthetic-fuel output was reported as 1,055,000 barrels, divided among the various processes as follows: Hydrogenation (of tars and other oils), 5,780 barrels; Fischer-Tropsch process, 149,250 barrels; and low-temperature carbonization, 899,970 barrels.

To provide an insight into Japanese research methods and to determine the direction taken by synthetic-fuel research in Japan both before and during World War II, mission investigators obtained a number of papers and reports from the organizations listed above. These papers, of which the following is exemplary, have been translated and examined carefully. For many reasons, the English translations must be regarded with reservations. The conversion of Japanese text to its English equivalent is complicated by extreme language difficulties; in many cases, words do not exist in the one language for ideas expressed in the other. The task was complicated further by a lack of familiarity on the part of some of the translators with the field of synthetic liquid fuels. In addition, it must be emphasized that many of the discussions to be found in these papers were based upon theories which at that time were accepted as valid by most of the scientific world but which have since been discarded in the light of subsequent experimental evidence. Despite the foregoing qualifications, it is felt that these papers are instrumental in establishing an appreciation of Japanese research efforts in the field of synthetic liquid fuels.

FOREWORD

The synthesis of hydrocarbons from carbon monoxide and hydrogen in the presence of cobalt catalysts is well known. In time of international emergency, however, cobalt was quite difficult to obtain in Japan, and the substitution of some other material as a suitable catalyst was imperative. Readily available for this purpose was nickel, and the effect of substituting this metal for cobalt, either in whole or in part, is described in this paper.

Although iron was found to be a very effective catalyst for the synthesis of petroleum hydrocarbons, its substitution for cobalt had been discouraged previously by the belief that iron catalysts were associated with a short catalyst life. That this was not necessarily true was demonstrated by the Hokkaido Synthetic Petroleum Co. in conjunction with the Kita Laboratory of the Kyoto Imperial University in experiments described in this report. A 100-day operation was carried out successfully by using an iron catalyst and recirculating the gases under pressure. The liquid hydrocarbon product obtained in such an operation was a valuable raw material for supplementing the manufacture of top-grade lubricating oils, and the gasol from the synthesis was highly satisfactory as a hydrocarbon raw material for the production of iso-octane.

HYDROCARBON SYNTHESIS WITH NICKEL CATALYSTS

OBJECT

To determine the potentialities of nickel as a substitute for cobalt in catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen.

RESULTS

The maximum oil yields obtained in bench-scale equipment were as follows:

Using 100Ni:20Mn:100 kaolin:200 diatomaceous earth catalyst, a maximum yield of 133.8 cm.³/m.³ of pure CO+2H₂ was obtained from one pass of the feed gas. With a nickel:cobalt mixed catalyst (Ni:Co = 3:7) having the composition 100(Ni+Co):6MgO:5ThO₂:200 diatomaceous earth, a maximum of 172.2 cm.³/m.³ of pure CO+2H₂ was obtained.

EXPERIMENTAL PROCEDURE

Pure Nickel Catalysts

Experiments were performed with a nickel catalyst by using a report^{3/} from the Fischer Laboratories as a basis for preparation methods and for determining the catalyst composition. At first, to acquire experience in the preparation of this catalyst, experiments were performed along lines identical with those of Fischer. Oil yields of approximately 120.0 cm.³/m.³ were obtained. In subsequent catalyst preparations, the composition and experimental conditions were varied in an attempt to prepare a nickel catalyst producing the highest oil yield possible.

3/ Fischer, F., Roelen, O., and Feist, W. [Present Technical Position of the Benzine Synthesis] : Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 501-516.

Effect of Metals Content

Alumina-promoted Catalysts

Fischer's standard catalyst - 100Ni:20Mn:10Al₂O₃:100 Kieselguhr - was prepared first by using K₂CO₃-precipitation instead of Na₂CO₃-precipitation. Tests of this catalyst (experiments VII-B, VII-C, V-A, and V-B, table 1) produced a maximum yield of 121.4 cm.³/m.³ (V-D). This is comparable to the average yield of 122 cm.³/m.³ achieved in the Fischer laboratories by using Na₂CO₃-precipitation.^{4/}

In the next group of experiments, the concentration of nickel in the catalyst was adjusted to the metal concentration found in the industrial German cobalt catalyst. That is, twice as much kieselguhr, based on nickel content, was used in the catalyst; precipitation was carried out with Na₂CO₃, which was then used in all subsequent catalyst preparations. The results are given in experiments V-C, V-D, VIII-C, and VIII-D (table 1). Although the synthesis conditions were similar to those previously used, the maximum yield in these experiments was only 112.5 cm.³/m.³, indicating that an excessive kieselguhr content lowers the oil yield. In an attempt to find a superior catalyst using this amount of kieselguhr, the effect of substituting acid kaolin^{2/} for Al₂O₃ was studied. Upon analysis, the kaolin used was found to contain 18.7 percent of Al₂O₃, and an amount of kaolin equivalent to 100 percent of nickel was added, thereby maintaining the original Ni:Al₂O₃ ratio. The resulting maximum oil yield of 120.3 cm.³/m.³ shown in experiments VI-A, VI-B, VIII-B, and XIV-B (table 1), was comparable to the original Fischer-type catalyst containing 100 percent kieselguhr. Acting on a report by Tsutsumi,^{6/} which stated that the addition of manganese lowers the catalyst reduction temperature, samples of this kaolin-containing catalyst were reduced at 400° C. instead of 450° C. The results are shown in experiments XV-B', XII-D, and XV-D' (table 1). A maximum yield of 132.6 cm.³/m.³ was obtained. As 400° C. was approximately the same temperature at which it was customary to reduce cobalt catalysts, this experiment was significant in regard to the industrial preparation of nickel catalysts in which the greater reduction temperature had loomed as an obstacle in the substitution of nickel for cobalt.

Thoria-promoted Catalysts

Ni:Mn:ThO₂ catalysts (used by Tsuneoka and Fujimura) were then studied by using a composition of 100Ni:20Mn:3ThO₂:200 Kieselguhr. Experiments VII-B, VII-C, XI-B, IX-B, and IX-A (table 1) showed a maximum oil yield of 129 cm.³/m.³ and proved the effectiveness of thoria as a promoter. Because thoria is expensive, however, a mixture of 1 percent thoria and 100 percent kaolin was tried, but the results were unsatisfactory (table 1, experiments X-A and X-C). Increasing the amount of manganese to 20 percent produced the results shown in table 2, experiments XII-A and XII-C; a maximum oil yield of 129.4 cm.³/m.³ was obtained. The life of a catalyst containing this additional amount of manganese should not be greatly decreased by lowering the reduction temperature to 400° C., and, if a nickel catalyst is found to be industrially practicable, this composition may be worthy of consideration.

- ^{4/} Fischer, F., and Meyer, K., [Influence of Conditions of Preparation Upon the Efficiency of a Nickel-Manganese Aluminum Catalyst] : Ges. Abhandl. Kerntria Kotle, vol. 11, 1934, pp. 542-548.
- ^{5/} Tsuneoka, S., and Fujimura, Z. [Manufacture of Gasoline by Reduction of CO] : Japanese Patent No. 106,560, June 15, 1934, Appl. Apr. 5, 1933.
- ^{6/} Tsutsumi, S., [Catalysts for Synthesis of Gasoline] : Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 55-60.

TABLE 1. - Composition of pig-iron sinters, effect on sintering synthesis

(continued in pp. 41, 42, 43, 44, 45, 46, and 47 of this issue)

Lab. No.	Amount of sinter used, lb.	Sinter composition, %	Oxidation, %	Analysis of sinter					Percentage of liquid, percentage				Sintering rate, percentage						Two-week test, %	Average sintering rate, %	Ratio						
				SiO ₂	CaO	MgO	FeO	Fe ₂ O ₃	Fe	Ca	Mg	Fe	Ca	Mg	Fe	Ca	Mg	Fe				Ca	Mg	Fe			
101-122	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

1/ Analyzed using the Kysor method instead of the Kysor method.
 2/ Reheated at 1400° C. instead of 1500° C.
 3/ Miller's ratio: The theoretical composition in this composition listed at 1.0 percent is obviously in error, as judged by the text, and should be, instead, 1 percent.

Summary

The catalyets found to be the most effective are:

- (A) In the Ni-Mn- Al_2O_3 group, 100 Ni:20Mn:100 kaolin:200 kieselguhr.
Oil yield = 133.8 $cm.^3/m.^3$ of synthesis gas.
- (B) In the Ni-Mn- ThO_2 group, 100Ni:20Mn:1Th O_2 :100 kaolin:200 kieselguhr.
Oil yield = 129.4 $cm.^3/m.^3$ of synthesis gas.

The above catalyets are not only strong and active, but the metal constituents are cheap (thoria in (B) is expensive, but only 1 percent is added); moreover, the large amount of kaolin and diatomaceous earth contained in these catalyets results in a low density and allows a large reactor to be packed with an efficient catalyst containing only a small amount of metal. These two catalyets were adopted, therefore, as standard nickel catalyets.

Effect of Reduction Temperature

The effect of reduction temperature was studied by using the two best catalyets containing 20 percent manganese and 15 percent manganese, respectively - namely, 100Ni:20Mn:100 kaolin:200 kieselguhr and 100Ni:15Mn:3Th O_2 :200 kieselguhr. The results shown in experiments VI-A, VI-B, XI-D, and XV-D' (table 2) indicate that reduction at 400° C. is better with a manganese content of 20 percent. When the manganese content is decreased to 15 percent, as shown in experiments XI-B and XI-D, a reduction temperature of 450° C. is required; reduction at 400° C. produces no oil formation but large amounts of methane (77 percent of the tail gas).

The minimum amount of manganese that is effective in lowering the reduction temperature, therefore, is 20 percent, based on the nickel content.

Effect of Using Acid-washed Diatomaceous Earth

Theories vary as to the suitability of using nitric acid-washed diatomaceous earth in catalyets. To study its effect in nickel catalyets, tests were made with 100Ni:20Mn:100 Kaolin:200 kieselguhr catalyst prepared from both acid-washed and unwashed diatomaceous earth. The results in table 3 show that unwashed diatomaceous earth is definitely inferior to the washed. At reduction temperatures of 450° and 400° C., the yield is decreased to one-half or one-third by use of unwashed earth.

Nickel-Cobalt Mixed Catalyets

Consideration of the work of Tsutsumi^{7/} and Tsuneoka and Murata^{8/} and the results of previous experiments with nickel catalyets suggested that investigation of nickel-cobalt mixed catalyets may be profitable. Accordingly, the following studies were made.

7/ Tsutsumi, S., [Synthetic Gasoline from Carbon Monoxide and Hydrogen] : Jour. Fuel Soc., Japan, vol. 24, 1935, pp. 110-116.

8/ Tsuneoka, S., and Murata, Y., [Properties of Nickel and Cobalt and the Influence of the Addition of Copper to the Precipitated Nickel-Cobalt Catalyets] : Jour. Soc. Chem. Ind., Japan, vol. 41, Suppl. Binding, 1938, pp. 52-59.

TABLE 2. - Requirements of mixed catalyst, effect of temperature on hydrogenation of benzene at 100°C. and atmospheric pressure.

Exp. No.	Catalyst composition, % Pt Ni Co	Reaction temperature, °C. 100	Reaction time, hr. 30	Conversion, % 100	Reaction products			Hydrogen gas composition, percent by volume			Hydrogen gas composition, percent by volume			Molar ratio of CO ₂ to CO after reaction				
					Benzene			Hydrogen			Hydrogen							
					CC	HC	CO	CC	HC	CO	CC	HC	CO					
71-6	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-7	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-8	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-9	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-10	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-11	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-12	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-13	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-14	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0
71-15	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0	0

TABLE 3. - Requirements of mixed catalyst, effect of pressure on hydrogenation of benzene at 100°C. and atmospheric pressure.

Exp. No.	Catalyst composition, % Pt Ni Co	Reaction temperature, °C. 100	Reaction time, hr. 30	Conversion, % 100	Reaction products			Hydrogen gas composition, percent by volume			Hydrogen gas composition, percent by volume			Molar ratio of CO ₂ to CO after reaction			
					Benzene			Hydrogen			Hydrogen						
					CC	HC	CO	CC	HC	CO	CC	HC	CO				
71-16	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-17	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-18	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-19	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-20	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-21	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-22	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-23	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-24	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-25	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-26	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-27	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-28	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-29	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0
71-30	100	100	30	100	100	0	0	0	100	0	0	0	0	0	0	0	0

Effect of Metals Content

Nickel:Cobalt Ratio = 7:3

Catalysts containing manganese. - The first mixed catalyst investigated contained a nickel:cobalt ratio of 7:3 in a composition of 100(Ni+Co):15Mn:11ThO₂:100 kaolin:200 Kieselguhr; it was reduced at 420° C. and was operated at a reaction temperature of 195° C. This lower reduction temperature was possible because of the presence of cobalt. As shown in experiments XV-A, XV-B, XV-C, and XV-D of table 4, the results obtained with this composition were good; a yield of 172 cm.³/m.³ of synthesis gas was obtained in experiment XV-B. The next preparation, containing 3 percent thorium and no kaolin, gave good results (experiment XVII-C'), but, as the industrial-scale preparation of a uniform catalyst of this composition proved to be difficult, 25 parts of kaolin were added. As shown in experiments XIX-A and XIX-C (table 4), this catalyst not only gave excellent results but also retained a uniform efficiency.

In attempts to decrease the reduction temperature, the manganese content was increased from 15 percent to 20 percent, and the amounts of kaolin and thorium were varied. Reduction was carried out at 410° C., and the results given in table 4 may be summarized as follows for 70Ni:30Co:20Mn catalysts:

- (A) The optimum concentration of kaolin is about 25 parts of kaolin. Equal parts of (Ni+Co) and kaolin is worse than no kaolin at all.
- (B) The presence of thorium is essential, but an increase to 3 percent from a value of 1 percent showed only a slight advantage.
- (C) Best results were obtained with a catalyst of the following composition: 70Ni:30Co:20Mn:3ThO₂:25 kaolin:200 Kieselguhr. An oil yield of 151.5 cm.³/m.³ of synthesis gas was obtained (experiment XXI-B).

Catalysts containing magnesium. - A catalyst was next prepared similar to the German type, except that (70Ni:30Co) was substituted for pure cobalt. This catalyst, containing 70Ni:30Co:5MgO:5ThO₂:200 Kieselguhr (experiments XXIV-C and XXIV-D, table 4), yielded 160.5 cm.³ of oil per cubic meter of synthesis gas, the results being comparable to those obtained with catalysts containing manganese. The effect of kaolin concentration was studied by adding 50 and 100 parts of kaolin per 100 parts of (Ni+Co). With a 100(Ni+Co):50 kaolin mixture, results were obtained similar to those produced in the absence of kaolin (experiments XXV-A and XXV-C and D, table 4).

Nickel:Cobalt Ratio = 5:5

Catalysts containing manganese. - After reduction at 400° C., a representative composition - 50Ni:50Co:15Mn:3ThO₂:200 Kieselguhr - was operated, but the highest oil yield obtained was 147.3 cm.³/m.³ of synthesis gas. The addition of kaolin did not prove advantageous, but further study of this type of catalyst (experiments XXI-D' and XXI-D') may be desirable.

Catalysts containing magnesium. - Tests of a catalyst having the composition 50Ni:50Co:5MgO:5ThO₂:200 Kieselguhr gave excellent results, and, as can be seen from experiments XXV-C and XXV-D, unlike similar catalysts containing manganese the addition of 50 parts of kaolin per 100 of (Ni+Co) increased the oil yield to 162.0 cm.³/m.³ of feed gas.

DATA 4. - Vertical moment and displacement of feet in transmission compliance
(Rounded for 5 hrs. in 8 hr. flow of 17.5/hr.; operational at 15% C. and transformer pressure.)

Exp. No.	Date test run (M.D.)	Initial air temperature (F.)	Initial pressure (lb./sq. in. gage)	Initial load (pounds)	Initial deflection (in.)	Axial force (lb.)						Total span deflection (in.)				Per cent of total deflection noted in this									
						Left			Right			P	Q	R	S		T								
						W	X	Y	U	V	W														
XI-4	100	100	100	200	0.00	390.4	324.4	50.3	0.2	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0						
	100	100	100	400	0.05	372.0	311.0	61.0	0.3	0.1	0.6	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1					
	100	100	100	600	0.15	352.0	294.0	58.0	0.4	0.2	0.4	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2					
	100	100	100	800	0.30	330.0	275.0	55.0	0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3				
	100	100	100	1000	0.45	306.0	254.0	52.0	0.6	0.4	0.2	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4				
	100	100	100	1200	0.60	280.0	231.0	48.0	0.7	0.5	0.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
	100	100	100	1400	0.75	252.0	206.0	44.0	0.8	0.6	0.0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6			
	100	100	100	1600	0.90	222.0	179.0	40.0	0.9	0.7	0.0	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7			
	100	100	100	1800	1.05	190.0	150.0	36.0	1.0	0.8	0.0	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8		
	100	100	100	2000	1.20	156.0	119.0	32.0	1.1	0.9	0.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9		
XI-5	100	100	100	200	0.00	390.4	324.4	50.3	0.2	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
	100	100	100	400	0.05	372.0	311.0	61.0	0.3	0.1	0.6	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	100	100	100	600	0.15	352.0	294.0	58.0	0.4	0.2	0.4	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
	100	100	100	800	0.30	330.0	275.0	55.0	0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	100	100	100	1000	0.45	306.0	254.0	52.0	0.6	0.4	0.2	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	100	100	100	1200	0.60	280.0	231.0	48.0	0.7	0.5	0.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	100	100	100	1400	0.75	252.0	206.0	44.0	0.8	0.6	0.0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	100	100	100	1600	0.90	222.0	179.0	40.0	0.9	0.7	0.0	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
	100	100	100	1800	1.05	190.0	150.0	36.0	1.0	0.8	0.0	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
	100	100	100	2000	1.20	156.0	119.0	32.0	1.1	0.9	0.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

Nickel:Cobalt Ratio = 3:7

Catalysts containing magnesium. - Because of the unpromising results obtained with manganese-containing catalysts having a Ni:Co ratio of 5:5, only magnesium-containing catalysts were studied at a Ni:Co ratio of 3:7. The results from experiments XXIII-A', XXIII-C', XXIII-B', and XXIII-D' are shown in table 4. Good results were obtained both with and without kaolin. A composition of 30Ni:70Co:8MgO:5ThO₂:200 kieselguhr yielded a maximum of 172.2 cm.³ of oil per cubic meter of feed gas and proved to be the best. The addition of kaolin to this composition, however (30Ni:70Co:8MgO:5ThO₂:25 kaolin:200 kieselguhr), resulted in a maximum oil yield of 167.2 cm.³/m.³ and would be a more desirable composition industrially.

Summary

These tests suggest that the most promising catalysts are:

- (A) With a Ni:Co ratio = 7:3, a composition of 100(Ni+Co):15Mn:3ThO₂:25 kaolin:200 kieselguhr,
Oil yield = 164.4 cm.³/m.³ of feed gas.
- (B) With a Ni:Co ratio = 5:5, a composition of 100(Ni+Co):8MgO:5ThO₂:50 kaolin:200 kieselguhr,
Oil yield = 162.0 cm.³/m.³ of feed gas.
- (C) With a Ni:Co ratio = 3:7, a composition of 100(Ni+Co):8MgO:5ThO₂:25 kaolin:200 kieselguhr,
Oil yield = 167.2 cm.³/m.³ of feed gas.

Effect of Using Acid-washed Diatomaceous Earth

In determining the effect of acid-washed diatomaceous earth on catalyst activity, the efficiency of the washing method becomes important, and it is sometimes difficult to conclude whether a certain result was due to the effect of washing the diatomaceous earth or whether the washing procedure was inadequate.

Accordingly, the results listed in table 5 are not conclusive. They suggest, however, that if the washing method is efficient, the use of acid-washed diatomaceous earth may be desirable. The inferior results obtained in experiments XVII-B, XVII-C, XVI-B, and XVI-C were attributed to some fault in the washing method. It is probable, therefore, that, pending the development of a reliable washing technique, the use of unwashed kieselguhr will be more desirable, even at the sacrifice of a certain amount of yield.

Effect of Type of Diatomaceous Earth

In nickel-cobalt-manganese catalysts, the Shima diatomaceous earth of Sanuki seemed somewhat superior to the Miyagi-ken diatomaceous earth; in nickel-cobalt-magnesium catalysts, however, the Miyagi-ken product gave excellent results (table 6, experiments XIII-A' and XIII-C'). This suggests that the choice of diatomaceous earth depends on the composition of the catalyst.

TABLE 1. - *Drosophila melanogaster*, effect of 100% humidity on fertility of males: results of 21 days of mating. (Data from 50 males, 10 females per male, mated at 100% R. and 100% humidity pressure.)

Sex	Females				Males				Fertility				Fecundity				Fecundity				
	Age	Days	Days	Days	Age	Days	Days	Days	Age	Days	Days	Days	Age	Days	Days	Days	Age	Days	Days		
100% R.	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
100% H.	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

100% R. = 100% relative humidity; 100% H. = 100% humidity pressure.
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TABLE 2. - *Drosophila melanogaster*, effect of 100% humidity on fertility of males: results of 21 days of mating. (Data from 50 males, 10 females per male, mated at 100% R. and 100% humidity pressure.)

Sex	Females				Males				Fertility				Fecundity				Fecundity					
	Age	Days	Days	Days	Age	Days	Days	Days	Age	Days	Days	Days	Age	Days	Days	Days	Age	Days	Days	Age	Days	
100% R.	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
100% H.	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

100% R. = 100% relative humidity; 100% H. = 100% humidity pressure.
 100% R. = 100% relative humidity; 100% H. = 100% humidity pressure.
 100% R. = 100% relative humidity; 100% H. = 100% humidity pressure.

Effect of Kaolin on Nickel-Cobalt Mixed Catalysts

Catalysts Containing Manganese

The optimum kaolin:catalyst-metal ratio is indicated in table 7 to be 25:100. Thus, the oil yield of 154.5 cm.³/m.³ of feed gas in experiment XVIII-C' was increased to 164.4 cm.³/m.³ (experiment XIX-A) by the addition of 25 percent kaolin. Similarly, in experiment XVIII-D' the yield of 122.7 cm.³/m.³ was boosted to 143.7 cm.³/m.³ (experiment XVII-D') by the addition of 25 percent kaolin. Addition of 100 percent kaolin in this case (experiment XIX-D) reduced the yield to 112.0 cm.³/m.³, and consideration of the results from experiments XXIII-A, XXIII-B, XXIV-D', and XXV-B' showed that although a 25 to 50 percent addition of kaolin produced much better results than when no kaolin was present, a 100 percent addition produced results as inferior as those obtained when no kaolin was added.

Catalysts Containing Magnesium

In experiments XXIV-C, XXIV-D, XXV-A, and XXV-B only kaolin concentrations above 50 percent had an appreciable effect. Addition of 100 percent of kaolin brought about a 12 percent decrease in the activity as compared to the case where no kaolin was used. Thus, when MgO is present, the addition of kaolin has no effect on the catalyst activity, and its use is warranted only if it is desired to increase the bulk of the catalyst. These tests were conducted on catalysts of 7Ni:3Co ratio; similar tests of catalysts containing Ni:Co ratios of 5:5 and 3:7 gave comparable results (experiments XXII-A', XXII-D', XXV-C, XXV-D, XXIV-A', and XXIII-B', table 7).

Type of Kaolin

Within experimental limits, table 8 shows no noticeable influence exerted by different types of kaolin, but further tests may be advisable.

Effect of Method of Preparation

In the preparation of nickel-cobalt-manganese catalysts, the following method, a combination of the Fischer-Standard and the Kyoto-Imperial-University methods, was used. First, the nitrates of the metal catalyst constituents were dissolved in water, and the required amount of diatomaceous earth was added to the solution. As this was being stirred, a solution of 30 percent excess sodium carbonate was added, and the resulting precipitate was boiled and filtered. The filter cake was then placed in a beaker, boiled, and filtered, and this operation was repeated several times. The final product, containing a slight amount of alkali, was dried for several hours at 100° to 120° C. The finished product was then used in the form of powder or granules.

For nickel-cobalt-magnesium catalysts, the Milk method of preparation, described below, was used. The nitrate solution and the carbonate solution were heated to their respective boiling points, after which the nitrate solution was mixed with the latter. While the solution was being agitated, the diatomaceous earth was added. (When kaolin was used, it was added before the diatomaceous earth.) Boiling was maintained for 1 to 2 minutes, after which the mass was filtered immediately with a []². The filter cake was then removed and washed in a manner similar to that used in the first method.

2/ Editor's note: This word was not translatable.

To conclude which method of preparation is superior is difficult at this time. Within the limits of the control experiments shown in table 9, the second method appears to give a better yield. Thus, experiment XXVII-B, prepared by the Fischer-Kyoto method, gave an oil yield of 120 cm.³/m.³, whereas experiment XXVII-C, prepared by the Miike method, gave an oil yield of 127.9 cm.³/m.³, but the difference is not outstanding.

HYDROCARBON SYNTHESIS WITH IRON CATALYSTS

OBJECT

To determine the durability of iron catalysts when used for the synthesis of petroleum hydrocarbons; to study the yield and quality of the products thus obtained; and to evaluate iron catalysts as a potential substitute for cobalt catalysts in the hydrocarbon synthesis.

RESULTS

The results of continuous tests carried out in semi-industrial scale apparatus are summarized below.

1. Single-pass operation over a period of 20 days resulted in virtually no decrease in catalytic activity.
2. Operation with recirculation of the exit gases, conducted continuously for 61 days at a constant synthesis temperature of 230° C., produced no significant decrease in catalyst activity.
3. The total yield of petroleum hydrocarbons obtained by exit-gas recirculation exceeded that from single-pass operation by approximately 10 percent.

EXPERIMENTAL PROCEDURE

General

Since May 1941, experiments have been conducted on a semi-industrial scale at the Rumo Laboratory No. 1 on the synthesis of hydrocarbons under pressure using cobalt catalysts. The recent scarcity of cobalt, however, indicated the desirability of expanding the Kita recirculation process for synthesizing hydrocarbons over iron catalysts under pressure from a bench-scale to semi-industrial scale process. This work was carried out by the Kyoto Imperial University and the Hokkaido Synthetic Petroleum Co. at the Rumo Laboratory.

A flow diagram of the experimental apparatus is shown in figure 1. Special attention was given to converter design (figs. 2, 3, and 4), and it was decided to circulate hot water as a cooling medium between concentric tubes in a manner similar to that used in the synthesis over cobalt catalysts under pressure (fig. 5). The converter was 4.55 meters long and contained 19 tubes; a feed gas throughput of 10 cubic meters per hour was used. A catalyst prepared at the Kyoto Imperial University and containing 100Fe:250Cu:2Mn:20H₂BO₃:7K₂CO₃:125 diatomaceous earth was employed.

Actual industrial-scale conditions were simulated in every possible way during the experiment. A fresh-gas space velocity of 120 to 130 volumes of gas per volume of catalyst per hour was used (a space velocity of 70 to 80 volumes was maintained during atmospheric-pressure operation of cobalt catalysts on an industrial scale; a space velocity of 90 to 100 was employed for pressurized operation, and 100 to 110

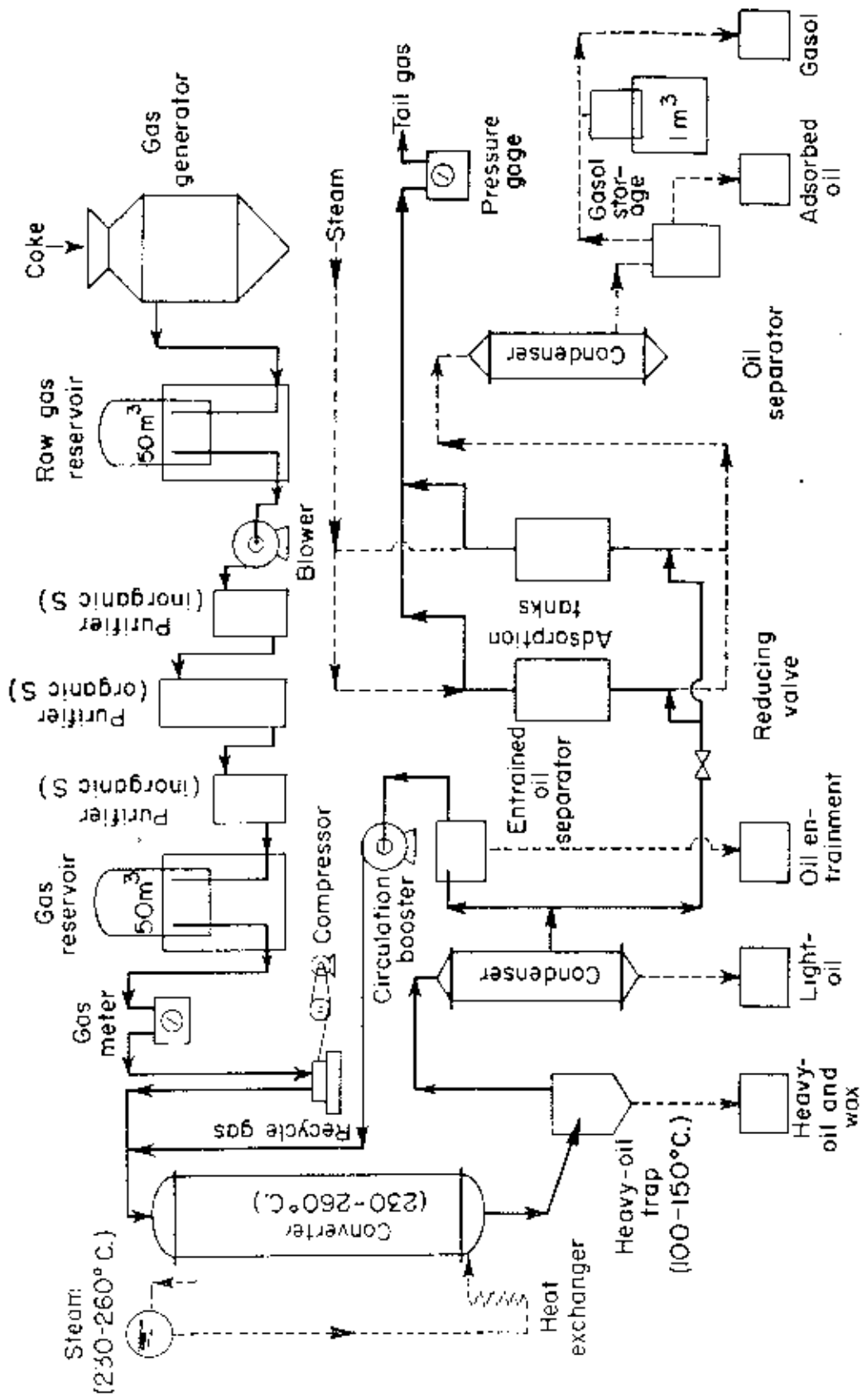


Figure 1.- Flow diagram for hydrocarbon synthesis using iron catalyst under pressure.

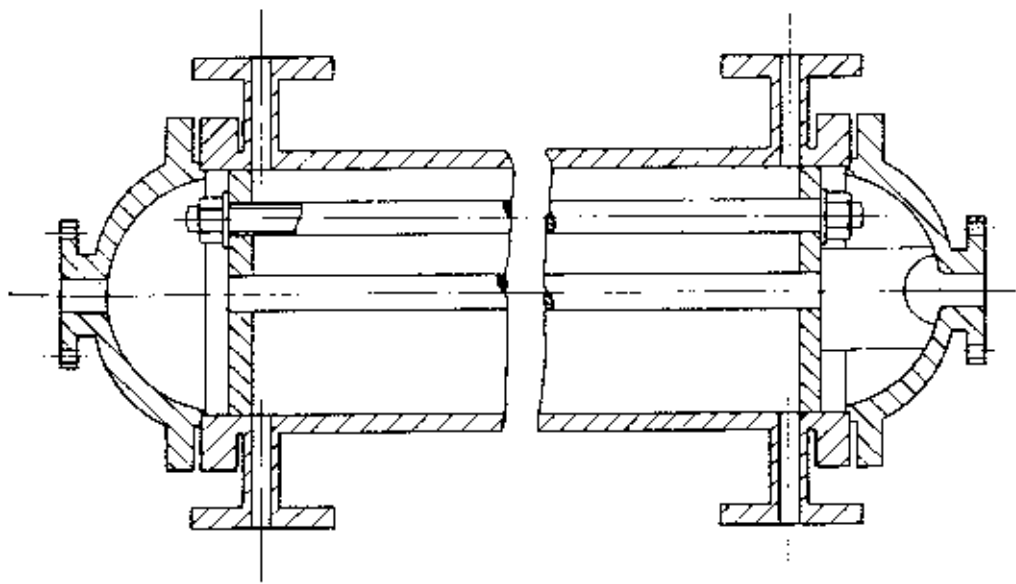


Figure 2.—Converter design

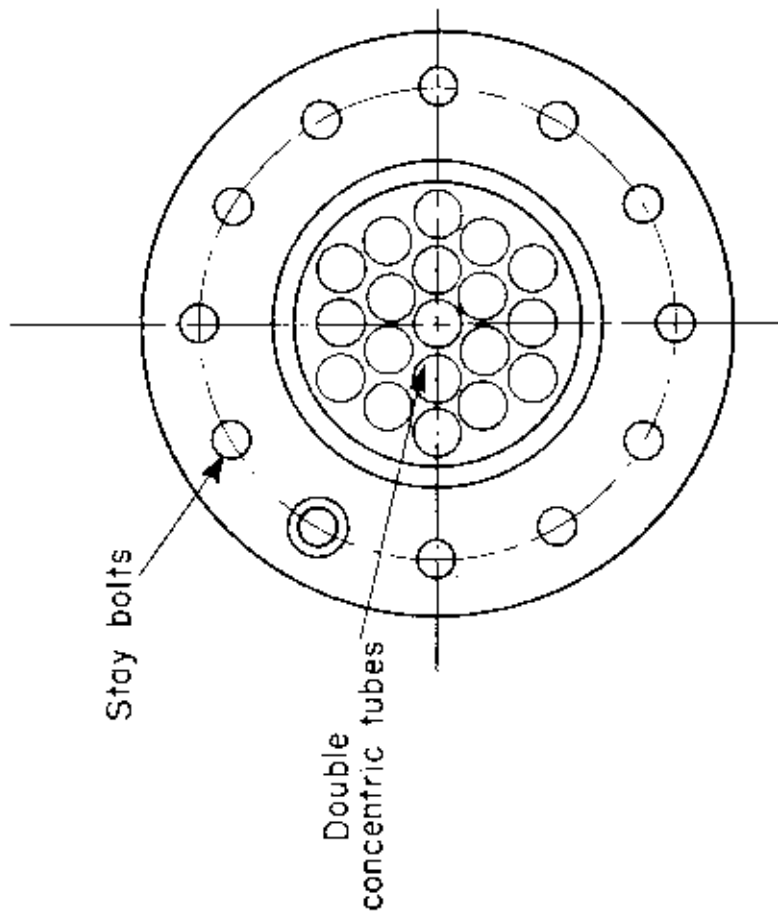


Figure 3.— Cross section of converter.

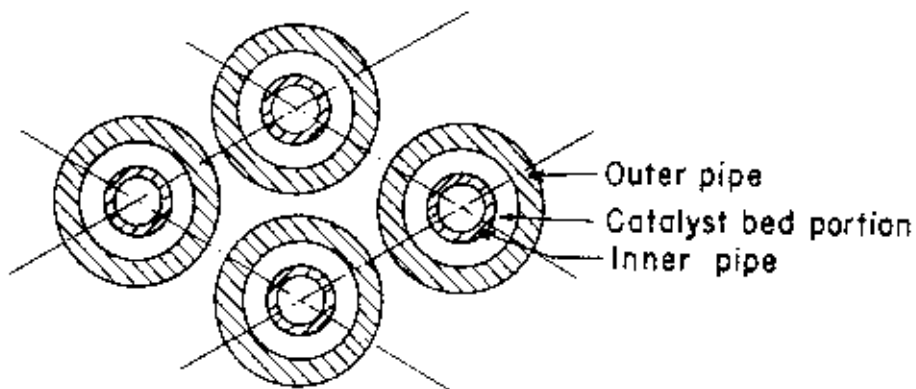
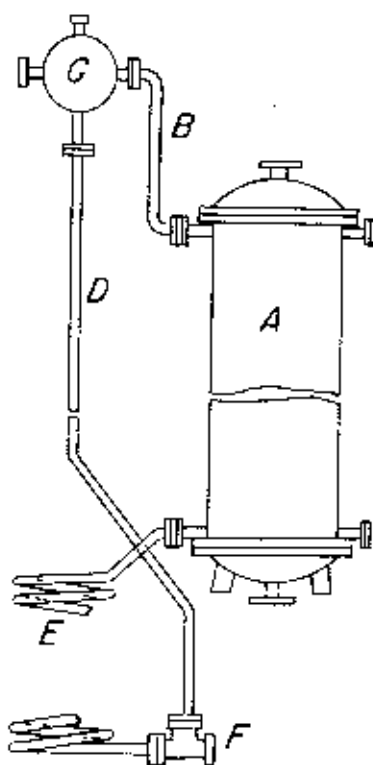


Figure 4.- Cross-section of concentric tubes.



A - Converter *B* - Hot-water riser *C* - Steam collector

D - Hot-water downcomer *E* - Seamless pipe, internal diameter, 25 mm; thickness, 4.5 mm; 17m. long; 10 turns.

F - Feed pipe

Figure 5.- Flow diagram of hot-water system for converter.

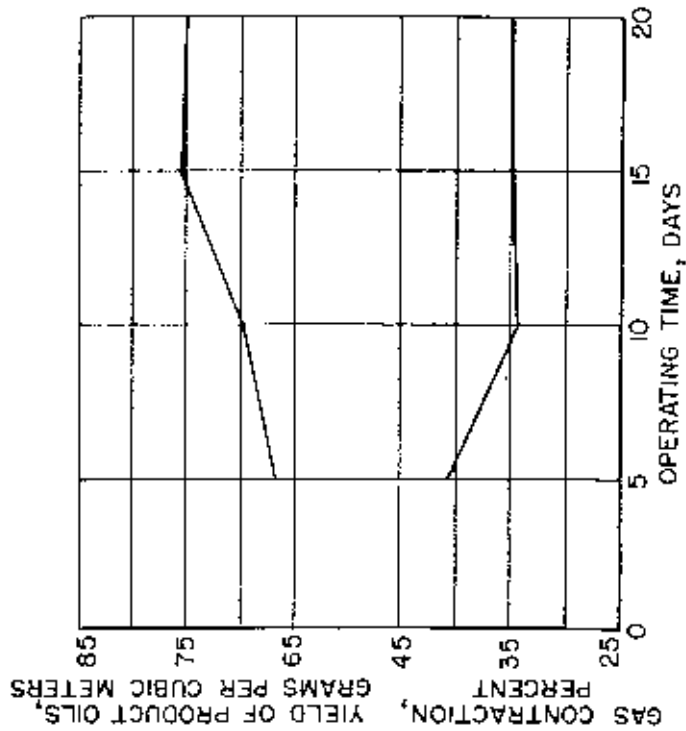


Figure 6.- Yield of product oils and gas contraction during single-pass operation.

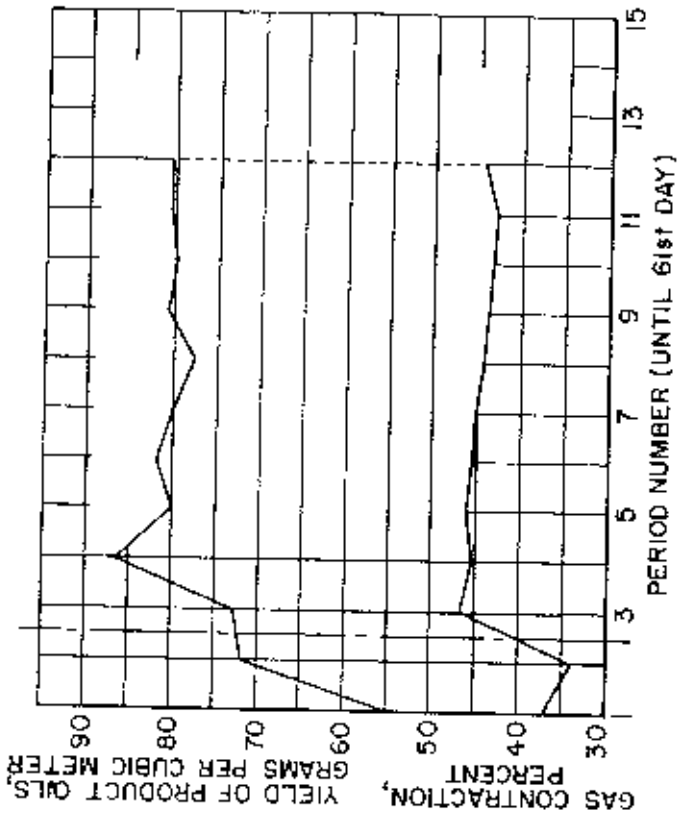


Figure 7.- Yield of product oils and gas contraction during gas-recycle operation.

was used for pressurized operation with recirculation of the exit gases). A pressure of 10 kg./cm.² and a synthesis temperature (maximum catalyst temperature) of 230° C. were established for the test. To study the durability of the catalyst, the synthesis was carried out for 20 days in the case of single-pass operation and for more than 2 months in the case of multiple-pass operation (recirculation of exit gases).

Hydrocarbon yields and gas contractions are shown in figure 6 for single-pass operation. No decrease in catalyst activity was observed during the 20-day operating period.

During multiple-pass operation, the average throughput of fresh feed gas was 8 cubic meters per hour (space velocity approximately 120), whereas the flow of recirculated exit gases averaged 13 cubic meters per hour, resulting in a recirculation coefficient of 1.65. Thus, the total quantity of synthesis gas flowing over the catalyst was 21 cubic meters per hour, which corresponded to a space velocity of 300. For comparing this test with the previous single-pass operation, the first 11 days (250 hours) of this test were devoted to single-pass operation. The remaining 55 days (1,250 hours) of the test were then used to study synthesis by the multiple-pass method. Figure 7 shows that the hydrocarbon yield in the multiple-pass operation was greater by about 10 percent than in single-pass operation, and that no significant decrease in activity occurred during the 61 days of synthesis at 230° C.

One of the features of iron catalysts is that the products, in general, contain a large percentage of unsaturated hydrocarbons that are applicable to a large market. The olefin content in the gasoline fraction amounts to approximately 70 percent, which suggests its use directly in automobiles. This fraction also serves as a high-quality starting material for the synthesis of lubricants and is suited to the manufacture of high-grade aviation lubricating oil. In addition, the amount of olefins in gasol is as high as 64 percent (36 percent butylene and 28 percent propylene), which makes this product a practicable starting material for the synthesis of iso-octane.

The multiple-pass process compares with the single-pass process in the following manner:

1. The hydrocarbon yield is about 10 percent greater.
2. The yield of light hydrocarbons is large; the amount of gasol produced is particularly large.
3. Considering all fractions, only a small difference in olefin content exists in the products of the two techniques (56.2 percent for multiple-pass operation; 58.2 percent for single-pass operation).
4. The acid number of the products is low.
5. The H₂:CO usage ratio is 1.20 for the multiple-pass and 0.94 for the single-pass processes, respectively.
6. The superior control of the catalyst temperature which is possible in the multiple-pass process results in an increased catalyst life.

Description of Apparatus and Catalysts

After leaving the converter, the exit gases are passed through the condenser and the oil separator, and a portion of the remaining gas is then sent through the booster compressor and recirculated with fresh feed gas through the converter. The equipment

employed in this process and in the single-pass process, which simply omits the recirculating section, is described below.

Gas Generator

A Hidaka model gas-generating furnace with a capacity of 1 ton per day was used. Coke was used as the feed stock, and water gas with an average CO content of 36 percent was obtained. This gas was used as the fresh feed gas.

Desulfurizing Equipment

Four inorganic, two organic, and one final desulfurizing chambers were provided to reduce the sulfur content of the feed gas from a concentration of 300 to 500 mg./m.³ to a concentration of 1 mg./m.³.

Converter

Figure 2 shows the construction of the converter, which consisted of 10 sets of 2 steel concentric tubes (51 mm. O.D. by 37 mm. I.D. and 29 mm. O.D. by 16 mm. I.D.) arranged in a container 600 mm. O.D., 5,233 mm. long, with a wall thickness of 29 mm. The catalyst (50 liters) was packed into the annular space between the concentric tubes; this annular volume was 7.5 mm. thick and 4,550 mm. long. Further construction details are shown in figures 3 and 4.

Temperature Control

The catalyst temperature was regulated by natural circulation of hot water. Water that had adsorbed the excess heat of reaction from the catalyst within the converter was collected as steam in the space above the reactor. The condensed water then descended into the coil heater below, where it was heated and passed into the lower part of the converter. The hot water circulation system is shown in figure 5.

Heating System

Heat was supplied to the converter from the following sources:

Electricity. - Chromium resistance wire placed around the walls of the converter provided a means of electrical heating. The wiring was divided into seven sections, and each section was supplied with 3 amperes, a total of 21 amperes (200 volts) or 4.2 kw.

Fuel Gas. - The coil heater used to preheat the water consisted of a 10-turn, 500-mm.-diameter coil of 1-inch steel pipe 17 meters long. This coil was heated by burning gas at a rate of 15 cubic meters per hour. Assuming a heat of combustion for the gas as 2,500 kcal./m.³ and the thermal efficiency of heat transfer as 20 percent, the heat provided by the gas firing was 7,500 kcal./hr. Coupled with the heat provided by the electric winding (3,600 kcal./hr.), the total heat supplied was then 11,100 kcal./hr.

Instruments

Thermometers were used to measure the temperature at two points in the catalyst bed, three points in the hot-water system, and four points through the exit-gas system (table 10). The pressure was measured at one point in the hot-water system and two points in the exit-gas system by means of Bourdon gages (table 11).

TABLE 10. - Points of temperature measurement

Point No.	Instrument	Location
1	Thermocouple	Catalyst bed - 500 mm. below upper portion of converter.
2	do.	Catalyst bed - 2,270 mm. below.
3	Thermometer	Hot water - 1,000 mm. below outlet for hot water.
4	do.	Hot water - 200 mm. above inlet.
5	do.	Hot water - center of steam collector.
6	do.	Exit gas - between converter and heavy-oil trap.
7	do.	Exit gas - center of heavy-oil trap.
8	do.	Exit gas - inlet to condenser.
9	do.	Activated carbon - center of adsorption chamber.

TABLE 11. - Points of pressure measurement

Point No.	Location
1	Hot water - steam.
2	Synthesis gas - inlet to converter.
3	Exit gas - after the condenser.

Catalyst

In both tests, catalyst prepared at the Kyoto Imperial University and containing 100Fe:25Cu:2Mn:20H₃BO₃:(K₂CO₃:125 diatomaceous earth was used; the particles were shaped like cylinders 2 mm. in diameter and 5 mm. long. The unreduced catalyst was comparatively easy to pulverize. Apparent bulk density was 0.47 before packing and 0.54 after shaking.

Single-pass Operation

Reduction of the 71.1-liter catalyst charge proceeded at a converter temperature of 245° C. and atmospheric pressure in a throughput of synthesis gas equal to 7 m.3/hr. (space velocity = 100) for 12 hours. The gas contraction during the reduction period averaged 38.3 percent. Changes in the gas composition during this period are shown in table 13. The data show that the consumption of carbon monoxide and hydrogen was 31.5 percent and 22.5 percent, respectively, and that 13.2 percent and 1.9 percent of carbon dioxide and methane, respectively, were formed (all values expressed in terms of volume of synthesis gas).

Operating conditions for the experiment were adjusted to maintain the following characteristics:

1. Reaction temperature. - A difference of several degrees was maintained between the temperature of the catalyst bed and that of the cooling water.
2. Fresh-feed gas throughput. - 9 m.3/hr.; space velocity, 130 volumes of gas per volume of catalyst per hour.
3. Pressure. - 10 kg./cm.².
4. Temperature of heavy-oil trap. - 100° to 140° C.
5. Duration of experiment. - 26 days (500 hours).

6. Process control. - Over-all gas analysis made every 5 hours; synthesis gas analyzed every 3 hours with improved Hempel and Orsat gas analysis equipment.

7. Product collection. - Heavy oil and wax removed every 6 hours; middle oil removed every 3 hours; light oil removed every 24 hours.

On November 18, 1941, the catalyst was placed in the converter, and, on the 19th, heating of the converter was begun. At 8 a.m. of the 20th, reduction of the catalyst was started, and, after 20 hours, the converter temperature was lowered to 225° C., after which it was raised to 230° C. at a pressure of 10 kg./cm.², and synthesis was started. Results of the experiment are summarized in table 12.

The gas contraction averaged more than 40 percent until the fourth day, after which it gradually decreased to 35 percent (average of 36.5 percent). Until the ninth day, a small yield of paraffin accompanied a yield of product oil of about 23 liters per day; after the tenth day, the production of oil increased to a steady 16 liters per day. Gasol production was 300 liters per day, or 1.7 l./m.³. The yield of the product oils, exclusive of gasol, reached a maximum of 78.9 gm./m.³ and maintained an average value of 71.5 gm./m.³ (53.6 cu.3/m.³). The yield of product oil and the gas contraction are shown as a function of operating time in figure 6. Variations in the compositions of the feed and exit gases are shown in table 13. This fluctuation in feed-gas composition was a result of the small capacity of the gas generator.

The consumption of carbon monoxide and hydrogen first obtained was 26.5 percent and 25 percent, respectively, which decreased to 24 percent and 23 percent, respectively. From these average gas-consumption values (25.0 percent and 23.5 percent), the average usage ratio was calculated as H₂:CO, 0.94. A CO conversion of 80 percent was first obtained, but a gradual decrease to 63 percent resulted in an average conversion of 68.8 percent. The production of carbon dioxide remained fairly constant (9 percent), but the production of methane (an average of 21.1 percent) showed a tendency to increase.

The specific gravities of the products proved to be 0.6905 for absorbed (light) oils and 0.7457 for condensed (heavy) oils. The results obtained by distillation of these fractions are shown in table 14. The light-oil and heavy-oil fractions were found to contain 73.5 percent and 61.1 percent of olefins and acid numbers of 0.12 and 1.94, respectively.

TABLE 12. - Yields obtained in single-pass operation at 10 kg./cm.² with iron catalyst

Operating time, days	Reaction temperature, °C.	Throughput		Con- traction, percent	Total oil, l./day	Gasol. l./day	Yield of product oil fractions, gm. per m. ³ synthesis gas			Water produced, gm./m. ³ syn. gas	
		Synthesis gas m. ³ /hr.	Exit gas, m. ³ /day				Heavy oil	Middle oil	Light oil		Total oil
1-5	230.1	8.9	219.1	42.4	13,670	191	14.7	34.8	16.8	66.3	63.8
6-10	229.8	8.7	201.4	34.3	13,414	299	25.4	30.6	13.6	69.6	60.0
11-15	230.0	8.9	213.0	35.2	16,088	276	28.3	30.8	16.4	75.5	54.5
16-20	230.2	9.0	211.0	35.0	15,829	319	27.6	31.4	15.7	74.7	58.8
Average	230.0	8.9	211.1	36.5	14,750	300	24.0 (28.2)	31.9 (42.8)	15.6 (22.6)	71.5 (93.6)	59.3 (cm ³ /m ³)

TABLE 13. - Changes in gas composition during single-pass operation at 10 kg./cm.² with iron catalyst

Oper. time, days	Synthesis gas, volume, percent			Exit gas, volume percent			Consumption, percent				Con- version, percent		Production, percent				
	CO ₂	CO	H ₂	CH ₄	H ₂	CO	CO ₂	C ₂ H ₆	CH ₄	N ₂	CO	H ₂ /CO	CO	CO ₂	CH ₄		
Re- duction																	
1-5	8.2	0.3	35.1	47.6	0.5	8.3	29.6	1.0	0.5	13.2	38.5	3.8	31.5	22.5	0.72	13.2	1.9
6-10	8.0	0.3	36.0	47.4	0.5	7.8	25.6	1.0	0.3	18.5	37.8	3.4	27.3	25.0	0.92	9.1	1.7
11-15	7.9	0.2	37.3	45.9	0.6	8.1	26.4	1.1	0.3	19.6	35.5	4.5	23.9	22.0	0.95	8.5	1.7
16-20	8.7	0.2	36.9	46.8	0.5	6.9	27.4	1.1	0.2	19.4	36.3	4.5	11.1	24.3	0.95	9.0	2.4
Average	8.2	0.3	36.3	46.9	0.5	7.8	27.3	1.0	0.3	17.7	37.0	4.1	12.6	25.0	0.94	9.0	2.1

TABLE 14. - Distillation of product oils from single-pass operation at 10 kg./cm.² with iron catalyst

	Middle (condensed) oils	Light (adsorbed) oils
Specific gravity, d_{4}^{15}	0.7457	0.6905
First distillation point, °C.	51	32
10 percent	88	48
20 percent	107	54
30 percent	124	61
40 percent	140	69
50 percent	159	77
60 percent	178	87
70 percent	200	99
80 percent	226	117
90 percent	271	150
Distillation complete	321	230
Total distilled, percent	98.0	96.6

Multiple-pass (Recycle) Operation

The equipment used in this experiment was the same as that used in the previous (single-pass) operation, except for the addition of gas-circulating and other auxiliary units. The catalyst charge (67.4 liters) was reduced at a temperature of 230° C. in a flow of 9 m.³/hr. of raw synthesis gas at atmospheric pressure for 20 hours. The average gas contraction during the reduction period was 15.7 percent; the variations in the composition of this and other gas streams are shown in table 15. Reduction of the catalyst was reflected in the data observed during this period. Gas contraction decreased from 38.3 percent to 15.7 percent; consumption of carbon monoxide and hydrogen decreased from 31.5 percent and 22.5 percent to 16.3 percent and 10.8 percent, respectively; and formation of carbon dioxide was decreased from 13.2 percent to 8.7 percent.

During the synthesis, the following conditions were maintained:

1. Reaction temperature. - The catalyst bed was adjusted to a maximum temperature of 230° C. The temperature of the central part of the catalyst bed was 3.5° less, and that of the cooling water was still less by 0.5° to 1° C.
2. Gas throughput. - The fresh feed gas throughput was 8 m.³/hr., and the throughput of recycled exit gas was 1.5 to 2 times that of the fresh feed gas, or 12 to 16 m.³/hr. Thus, the total gas flow through the catalyst bed was 20 to 24 m.³/hr., corresponding to a space velocity of 300 to 350 volumes of gas per volume of catalyst per hour.
3. Pressure. - 10 kg./cm.².
4. Temperature of heavy-oil trap. - 100° C.
5. Duration of experiment. - 66 days (1,500 hours).
6. All other conditions similar to those used in the single-pass operation.

TABLE 15. - Changes in gas composition during single-pass and gas-recycle operations with iron catalyst (I).

Run No.	Operating time, hrs.	Feed gas, vol.-%				Synthesis gas (fresh feed gas plus recycle gas), vol.-%				Exit gas, vol.-%				Conversion, percent		Production, gm./hr.				
		CO ₂	CO	H ₂	CH ₄	CO ₂	CO	H ₂	CH ₄	CO ₂	CO	H ₂	CH ₄	CO ₂	CO					
1	1-5	10.0	6.2	36.9	45.4	6.5	7.0	0.0	0.0	22.0	0.6	2.0	21.1	81.2	2.5	0.9	15.3	110.6	0.65	0.7
2	6-11	9.7	6.2	37.6	44.7	6.7	6.3	0.0	0.0	26.6	0.9	2.0	20.7	84.1	4.5	13.3	23.2	0.92	0.0	0.8
3	12-16	9.1	6.2	36.4	45.0	6.6	6.3	0.0	0.0	26.1	1.0	2.0	20.7	85.1	5.1	13.3	24.1	0.91	0.0	0.7
4	17-23	9.7	6.2	36.3	45.0	6.6	6.3	0.0	0.0	27.3	1.3	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
5	24-26	7.6	6.2	35.9	45.3	6.6	6.3	0.0	0.0	27.3	1.3	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
6	27-31	7.6	6.2	36.4	45.0	6.6	6.3	0.0	0.0	27.3	1.3	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
7	32-35	7.8	6.2	36.6	44.9	6.6	6.3	0.0	0.0	26.3	1.3	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
8	36-42	6.9	6.2	36.9	45.0	6.6	6.3	0.0	0.0	27.4	1.4	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
9	43-46	6.9	6.2	36.9	45.0	6.6	6.3	0.0	0.0	27.3	1.4	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
10	47-51	12.4	6.2	36.6	44.8	6.6	6.3	0.0	0.0	26.3	1.3	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
11	52-56	9.9	6.2	34.8	46.8	6.6	6.3	0.0	0.0	26.3	1.3	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
12	57-61	10.6	6.2	33.2	47.6	6.6	6.3	0.0	0.0	29.9	1.5	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7
3-12 average		8.6	6.2	35.4	46.1	6.6	6.3	0.0	0.0	28.1	1.4	2.2	19.5	87.4	0.7	15.3	22.4	1.23	5.1	0.7

TABLE 16. - Summary of operating conditions and yields during single-pass and gas-recycle operations with iron catalyst.

Run No.	Days	Temperature of catalyst bed, °C.		Pressure, kg./sq. cm.	Throughput, gm./hr.		Synthesis gas, m ³ /hr.		Total, gm./hr.	Feed of product, all fractions, gm. per m ³ synthesis gas			Molar produced synthetically, gm.	
		Top	Bottom		Feed, gm./hr.	Exit, gm./hr.	Feed, m ³ /hr.	Exit, m ³ /hr.		Heavy oil	Middle oil	Light oil		Total
1	1-5	230.3	225.1	10.0	10.0	306.2	117.9	6.6	8.9	265	11.2	0.8	21.1	34.0
2	6-11	230.0	225.5	10.0	10.0	204.7	136.8	8.9	8.9	273	11.2	0.8	21.1	34.0
3	12-16	228.7	225.6	10.0	10.0	300.3	100.5	8.2	8.2	258	11.2	0.8	21.1	34.0
4	17-23	229.0	225.9	9.9	9.9	161.4	99.2	7.5	7.5	227	11.2	0.8	21.1	34.0
5	24-26	229.0	226.0	10.0	10.0	167.0	100.0	8.0	8.0	229	11.2	0.8	21.1	34.0
6	27-31	230.0	225.7	9.9	9.9	197.2	102.0	7.6	7.6	224	11.2	0.8	21.1	34.0
7	32-35	229.7	225.6	10.0	10.0	188.4	105.0	8.0	8.0	224	11.2	0.8	21.1	34.0
8	36-42	229.9	226.5	9.9	9.9	183.4	96.6	7.8	7.8	168	11.2	0.8	21.1	34.0
9	43-46	229.0	226.3	9.9	9.9	190.3	105.0	7.9	7.9	206	11.2	0.8	21.1	34.0
10	47-51	230.0	226.7	10.0	10.0	181.1	105.0	7.4	7.4	206	11.2	0.8	21.1	34.0
11	52-56	230.1	227.1	10.0	10.0	188.7	107.3	7.9	7.9	199	11.2	0.8	21.1	34.0
12	57-61	230.0	227.0	9.9	9.9	195.0	103.1	7.0	7.0	216	11.2	0.8	21.1	34.0
3-12 average		229.9	226.7	9.9	9.9	186.7	101.6	7.9	7.9	205	11.2	0.8	21.1	34.0

1/ Calculated on basis of standard conditions of temperature and pressure.

2/ Calculated on basis of pure synthesis gas; that is, CO + H₂ in ported 1 and 2, and H₂ + 1.2H₂ in ported 3-12.

3/ Calculated from gas analysis.

4/ Specific gravity of all fractions.

Wt.-% (condensed) oil
0.755
0.756

Single-pass

Gas recycle 0.755 0.661

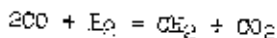
Testing of the converter was begun on February 23, 1942; reduction of the catalyst was begun at 7:00 p.m. on the 24th and completed at 3:00 p.m. on the 25th, at which point the pressure was gradually increased to 10 kg./cm.², and synthesis was begun. For comparison with the previous single-pass operation, for the first 11 days (about 250 hours) exit gases were not recirculated. Except for the 9th and 39th days, when the experiment was stopped temporarily because of a steam leak, the experiment proceeded smoothly. At a constant reaction temperature of 230° C. over a period of 56 days (1,500 hours), no significant change in catalytic activity was observed. Experimental results are summarized in table 16, which lists average values for 5-day operating periods. Periods 1 and 2 include the single-pass operation and periods 3 to 12, the multiple-pass operation.

At an average recycle-gas:fresh-feed-gas ratio of 1.65 the gas contraction increased at the start of the multiple-pass operation to an average of 44.9 percent, where it remained for 50 days. Figure 7 shows the gas contraction and the yield of product oils as a function of time. Of the hydrocarbon products, no great difference in yield of heavy oil was observed between single-pass and multiple-pass operation, but recirculation of the exit gases resulted in a large increase in yield of middle (condensed) oil (40.5 gm./m.³) and a decrease in yield of light (absorbed) oil (15.7 gm./m.³). The yield of gasol increased to 351 liters/day on converting to multiple-pass operation. The total hydrocarbon yield, exclusive of gasol, attained a maximum of 27.8 gm./m.³. During multiple-pass operation, 83.4 cm.³ of water was produced per cubic meter of synthesis gas, compared with 59.3 cm.³/m.³ produced during the single-pass operation.

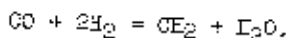
The changes occurring in the compositions of the various gas streams are summarized in table 15. The flow of recycle gas is a major factor that influences both the composition of the synthesis gas and the reaction conditions. Similarly, with a constant flow of recycle gas, a change in the composition of the fresh feed gas changes the composition of the exit gas and affects the synthesis operation similarly. The relationships existing between the fresh feed, exit, and synthesis gases and the H₂:CO usage ratio are shown in table 17 and figure 9. With an increase in the H₂:CO ratio, the H₂:CO usage ratio also increased, but all the additional hydrogen thus introduced was not consumed in the synthesis. Accordingly, the hydrogen content of the exit gas increased, and as a portion of the exit gas was recycled, the H₂:CO ratio of the synthesis gas increased. In this manner, only a small increase in the H₂:CO ratio of the fresh feed gas caused a large increase in the H₂:CO ratio of the synthesis gas passing through the converter and influenced the product distribution considerably.

It is evident that the conditions under which carbon monoxide and hydrogen are consumed in the multiple-pass process differ considerably from those of the single-pass process, in that, with only a slight increase in the consumption of carbon monoxide in the recycle process, the hydrogen consumption increased sharply, and the usage ratio, which in the case of the single-pass method is 0.94, was increased to 1.20. This is shown in figure 8.

Virtually no change occurred in the 0.8 percent-production of C₂H₄ by changing to recycle operation. The formation of carbon dioxide was reduced from an average of 9.0 percent in single-pass operation to 6.2 percent in the recycle process. This is believed to be a result of a suppression of the reaction



in favor of the reaction



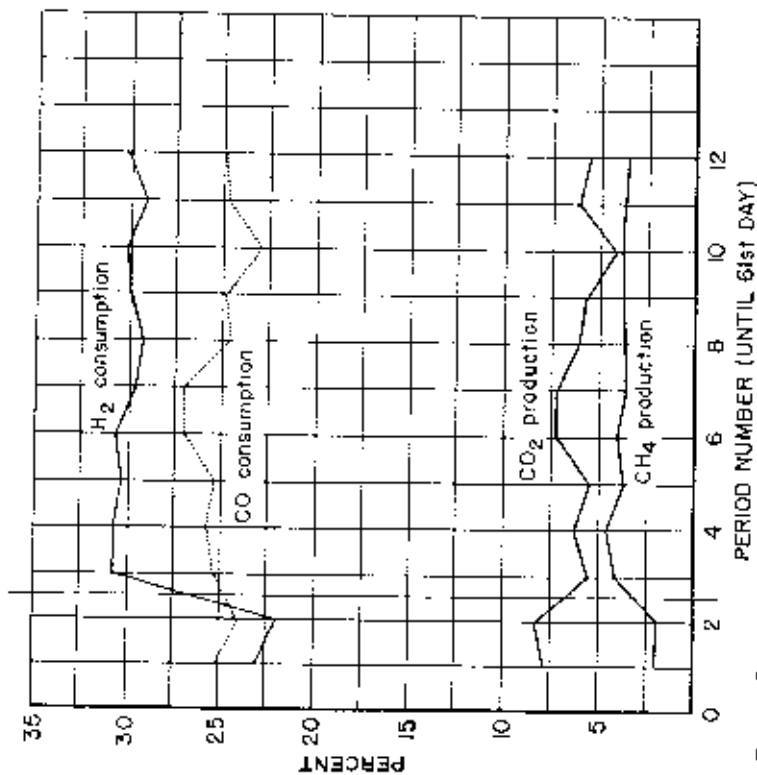


Figure 8.- Changes in gas composition during gas-recycle operation. (I)

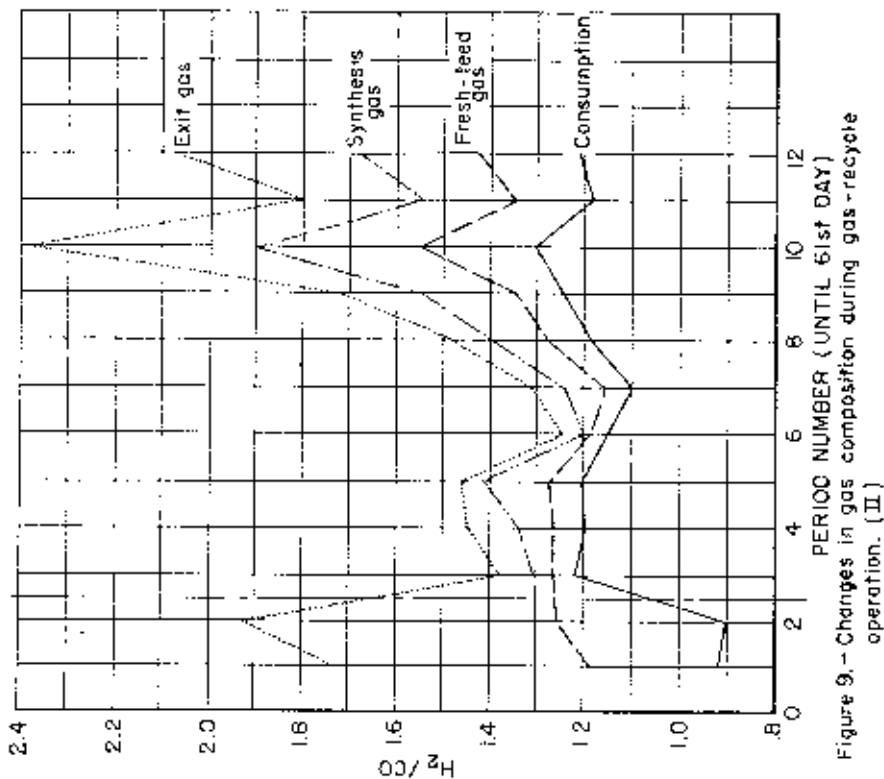


Figure 9.- Changes in gas composition during gas-recycle operation. (II)

TABLE 17. - Changes in gas composition during single-pass and gas-recycle operation with iron catalyst (II)

Period No.	Operating time, days	Fresh feed gas, H_2/CO	Synthesis gas, H_2/CO	Exit gas, H_2/CO	Consumption, H_2/CO
1	1-5	1.19	-	1.73	0.92
2	6-11	1.26	-	1.93	0.91
3	12-16	1.27	1.30	1.39	1.22
4	17-21	1.27	1.34	1.46	1.20
5	22-26	1.28	1.42	1.47	1.20
6	27-31	1.19	1.20	1.24	1.15
7	32-36	1.16	1.24	1.31	1.10
8	37-41	1.29	1.40	1.18	1.19
9	42-46	1.35	1.55	1.73	1.25
10	47-51	1.37	1.91	2.36	1.31
11	52-56	1.35	1.54	1.79	1.18
12	57-61	1.13	1.68	2.08	1.21
3-12 average	12-61	1.32	1.46	1.65	1.20

The use of cobalt catalysts in the recycle process results in a decrease in the formation of methane, whereas in the presence of iron catalysts the production of methane is increased from 2.2 percent (single-pass operation) to 4.1 percent (multiple-pass operation). This is believed to be a result of the large increase in the hydrogen content of the synthesis gas in the latter case.

As carbon dioxide is not removed from the recycle gas, the carbon dioxide content of the synthesis gas reached an average of 21.3 percent, but no deleterious effects were observed. The unsaturated content of the product oils from the recycle process was only slightly less than that of the single-pass method, attaining an average value of 56.2 percent (heavy oil, 50 percent, and light oil, 65.5 percent). The acid number decreased from an average of 1.35, obtained during the initial single-pass operation, to 1.05 (heavy oil, 1.49; light oil, 0.06). The average specific gravity for the heavy-oil products was 0.755, and for the light oils, 0.661; the freezing points were found to be $-16^{\circ}C$. for the heavy-oil fraction and $-45^{\circ}C$. for the light-oil fraction. A distillation of the product oils is shown in table 18.

TABLE 18. - Distillation of product oils from gas-recycle operation with iron catalyst

	Product oils ^{a/}	Condensed oils	Absorbed oils
Initial distillation point, $^{\circ}C$	23	54	23.0
10 percent	71	105	31.0
20 percent	74	124	35.5
30 percent	98	143	41.5
40 percent	120	165	47.5
50 percent	145	165	54.5
60 percent	173	224	63.5
70 percent	210	246	74.5
80 percent	254	290	92.0
90 percent	315	359	125.0
Distillation complete, $^{\circ}C$	375	385	168.0
Total distilled, percent	97.5	97.5	95.0

^{a/} "Product oils" consisted of a mixture of condensed and absorbed oils.

The yield of gasol was increased considerably by recycle operation (3.6 l./m.3), and as this product, as shown in table 19, contains large amounts of C_4H_{10} , it is highly suitable as a starting material for the synthesis of iso-octane. The ratio between the n- C_4H_{10} and iso- C_4H_{10} in the gasol is approximately 10:1.

TABLE 19. - Analysis of gasol obtained in gas-recycle operation

Constituents ^{a/}	Percent
C_4H_{10}	36
C_4H_8	9
C_3H_8	28
C_3H_6	22
C_2H_6	3
C_2H_4	1
C_2H_2	1

a/ CO_2 and residual gases were neglected.

A final comparison between the recycle and single-pass methods of synthesizing hydrocarbons from carbon monoxide and hydrogen over iron catalysts brings out the following observations pertinent to the recycle process:

1. The yield of heavy (paraffin) hydrocarbons does not vary significantly, but the yields of middle (condensed) oil, light (absorbed) oil, and gasol increase, resulting in an over-all increase in yield of 15 percent. Especially evident is the increase in the yield of light hydrocarbons.
2. Comparison of the products obtained by the two processes is shown in tables 20, 21, and 22 and in figures 10, 11, and 12. The specific gravity of the product oils is lower. The olefin content of the product oils decreases slightly, but results show these oils to be superior as a raw material for preparing lubricating oils. The acid value of the products decreases considerably.
3. The gasol fraction had a high content of n- C_4H_{10} and iso- C_4H_{10} and is of high utility as a raw material in the synthesis of iso-octane.
4. By varying the composition of the fresh feed gas and the gas-recycle rate, the conditions of the reaction can be varied over a wide range permitting operation at selective conditions to yield a predetermined type of product.
5. As a result of a smaller effective concentration of reactive constituents in the synthesis gas passing through the catalyst bed, and because the gas flow is greater, excessive local overheating of the catalyst is prevented, and temperature distribution in the catalyst bed is equalized; hence, the durability of the catalyst is increased.
6. Recirculation of the exit gas containing a large concentration of hydrogen increases the $H_2:CO$ ratio of the synthesis gas and promotes the reaction $CO + 2H_2 = CH_4 + H_2O$, with the result that the $H_2:CO$ usage ratio increases and the formation of CO_2 increases. The increased concentration of hydrogen in the synthesis gas is believed to be the cause for the slightly increased methane production observed in recycle operation.

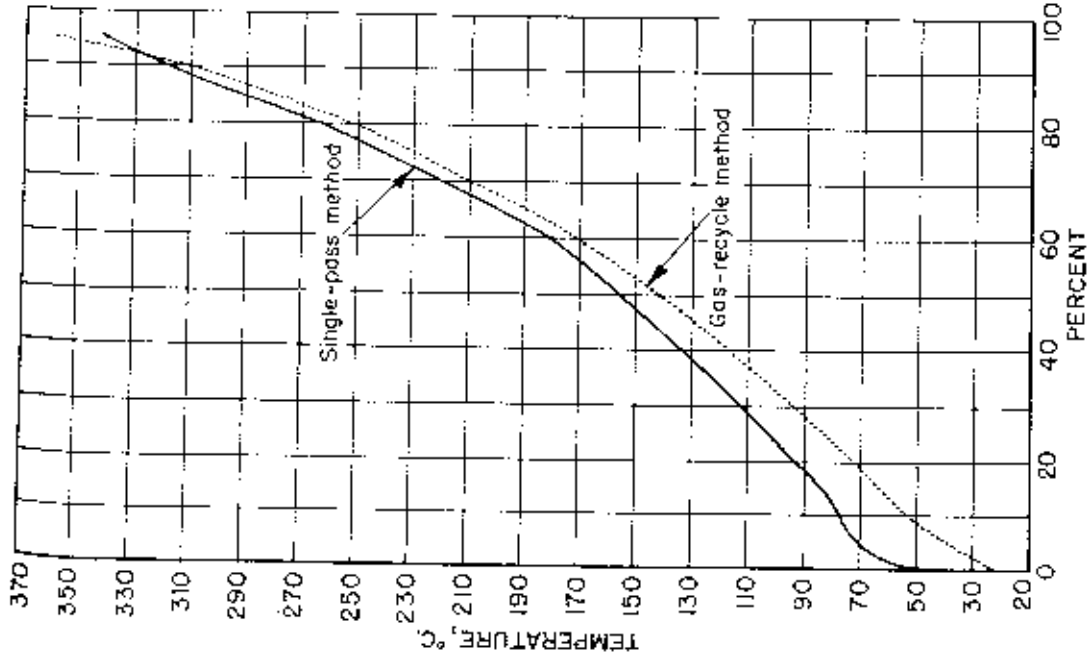


Figure 10. - Distillation of product oils from both single-pass and gas-recycle operations.

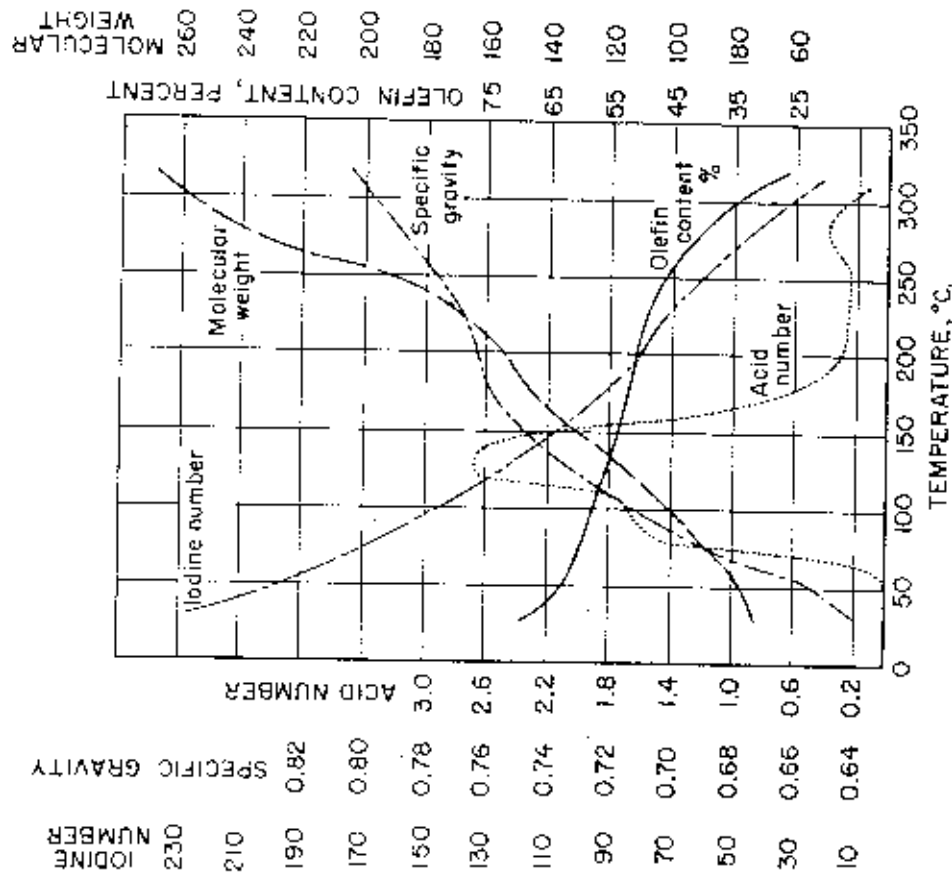


Figure 11. - Properties of product oils from gas-recycle operation.

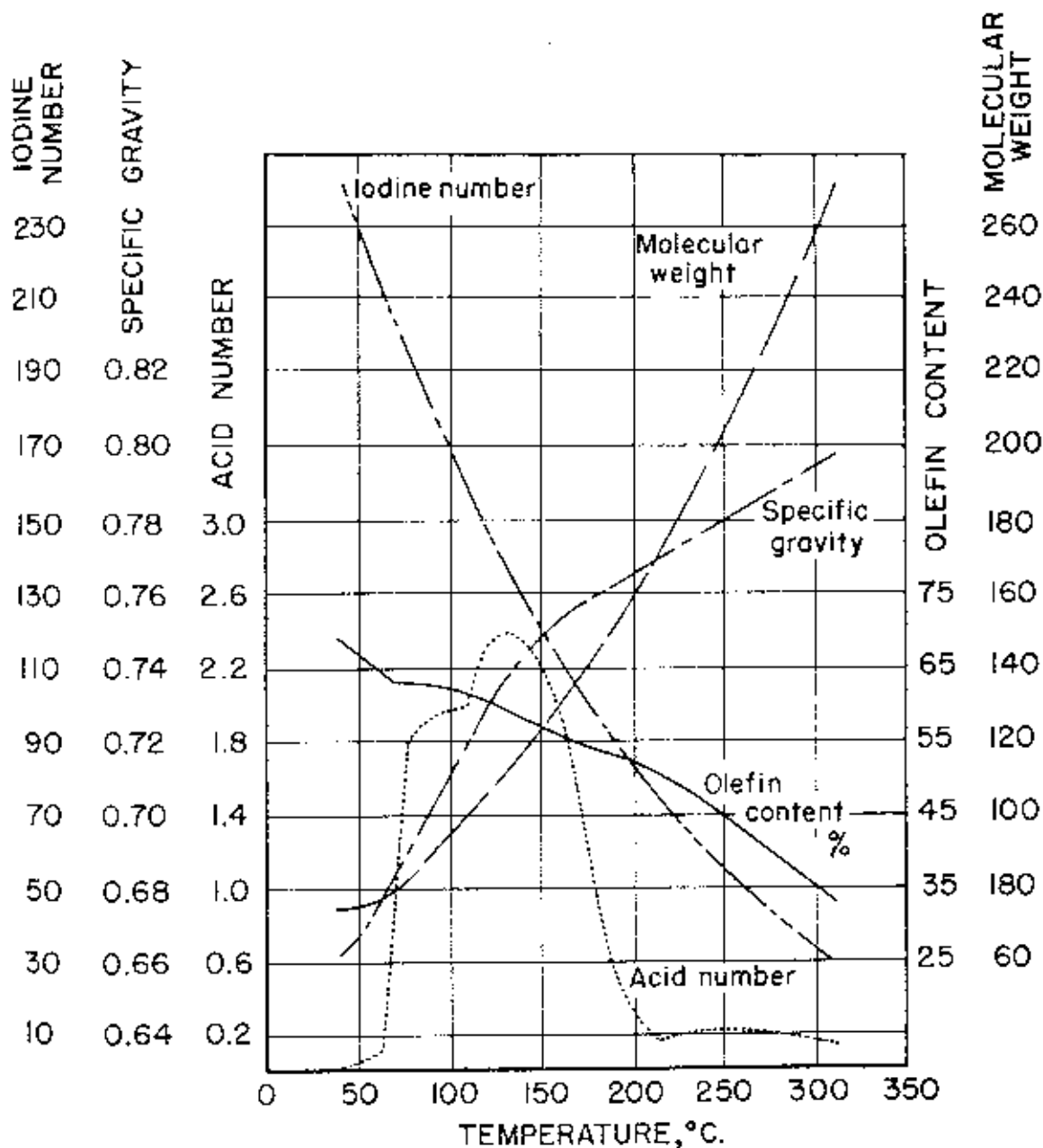


Figure 12.-Properties of product oils from single-pass operation.

TABLE 20. - Comparative distillations of the product oils from single-pass and gas-recycle operations with iron catalyst

	Single-pass	Gas-recycle
Specific gravity, d_{4}^{15}	0.7442	0.7309
Fractional distillation:		
Initial distillation, $^{\circ}\text{C}$	49.0	23.0
Percent, distillation temperature, $^{\circ}\text{C}$.:		
10	79.5	54.0
20	94.5	74.0
30	115.0	98.0
40	133.0	120.0
50	156.5	145.0
60	183.0	173.0
70	219.0	210.0
80	260.0	254.0
90	326.0	315.0
Maximum temperature during distillation, $^{\circ}\text{C}$	345.0	374.0
Total distilled, percent	97.0	97.5
Residue, percent	1.8	1.6

TABLE 21. - Properties of product oil fractions obtained from gas-recycle operation with iron catalyst

Fraction No.	Boiling range, $^{\circ}\text{C}$.	Specific gravity, d_{4}^{15}	Acid number	Iodine number	Molecular weight	Olefin content, percent ^{a/}
1	-40	0.6397	0.00	228.0	75.2	68.3
2	10-60	0.6550	0.00	192.0	76.5	59.6
3	60-80	0.5807	0.42	172.5	88.0	60.3
4	80-100	0.7024	1.62	153.0	96.5	58.1
5	100-120	0.7170	1.80	138.0	107.0	58.2
6	120-140	0.7364	2.66	114.0	118.0	53.0
7	140-160	0.7470	2.14	105.0	128.0	53.3
8	160-180	0.7551	0.87	94.0	146.8	54.3
9	180-200	0.7614	0.38	85.0	152.0	50.8
10	200-220	0.7636	0.28	81.0	158.0	50.4
11	220-240	0.7677	0.27	74.5	169.0	49.6
12	240-260	0.7777	0.23	59.5	192.0	45.0
13	260-280	0.7864	0.54	44.9	235.0	41.7
14	280-300	0.7935	0.35	40.0	247.5	39.0
15	300-320	0.8033	0.13	25.3	267.5	26.7
16	320-	0.8651	0.30	21.3		
17		0.7309	1.03	118.0	121.0	56.2
18		94.5 d_{4}^{15}	0.15			

a/ Value for olefin content based on calculations.

TABLE 22. - Properties of product oil fractions obtained from single-pass operation with iron catalyst

Fraction No.	Boiling range, °C.	Specific gravity, d ₁₅ ⁴	Acid number	Iodine number	Molecular weight	Olefin content, percent ^{a/}
1	-50	0.6614	0.00	241.0	73.5	69.8
2	50-60	0.6699	0.00	216.0	75.5	64.2
3	60-80	0.6841	0.03	205.0	76.5	63.3
4	80-100	0.7002	1.93	180.8	90.0	53.7
5	100-120	0.7210	2.00	154.0	104.5	63.4
6	120-140	0.7337	2.41	135.0	110.5	52.8
7	140-160	0.7432	2.16	112.0	129.0	56.5
8	160-180	0.7538	1.45	104.5	133.0	54.8
9	180-200	0.7591	0.51	88.5	151.0	52.6
10	200-220	0.7681	0.19	75.6	167.0	49.3
11	220-240	0.7726	0.23	66.0	189.0	49.1
12	240-260	0.7796	0.21	54.0	203.0	43.2
13	260-280	0.7856	0.18	46.5	224.5	41.2
14	280-300	0.7905	0.17	39.8	242.5	38.0
15	300-320	0.7996	0.15	29.8	275.5	32.3
16	320-	0.8455	0.35	23.1		
17		0.7442	1.36	152.0	132.0	52.2
18		10 ³ c.	0.32			

^{a/} Values for olefin content based on calculations.

Author's note: Operation using the recycle technique was continued without interruption until June 30, when the experiment was completed. During this period, virtually no deterioration of catalyst activity was observed.