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 object of 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 allowed additional Japanese equipment and documents to be destroyed and made it easier for key Japanese personnel to disappear. With this in mind, the first entry into Japan by mission personnel was made early in September, and the activities of the mission were highly concentrated over the next few months, terminating finally in December.

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 upon assays and fundamental studies rather than 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 made 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. 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, for which the total yearly synthetic-fuel output was reported as 955,000 barrels, divided among the various processes in the following manner: 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 carefully examined. 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 with the field of synthetic liquid fuels on the part of some of the translators. In addition, it must be emphasized that many of the discussions to be found in these papers were based on 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 accompanying qualifications, it is felt that these papers are instrumental in establishing an appreciation of Japanese research efforts in the field of synthetic liquid fuels.

ABSTRACT

Starting on a small scale, the equipment for processing synthesis gas to form liquid hydrocarbons was expanded to handle 100 $m.^3/hr.$ This reactor was successfully designed and constructed, and a basis for future design methods was established. Because, however, this work was carried out on an empirical basis, it is felt that a more thorough theoretical study should be made in an effort to increase the efficiency of the process, particularly in the development of a simpler converter.

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INTRODUCTION

It is well known that the development of a new reaction on a laboratory scale does not by any means guarantee its successful application in an industrial-scale operation. As a matter of fact, the history of industrial chemistry contains numerous examples of where much more time and effort were consumed in developing a certain reaction to a commercial scale than were consumed in its discovery. The difficulties encountered in accomplishing this transition usually fall into two general classes, namely, (1) the selection of a suitable construction material to withstand the corrosive effects of the substances to be used in the process, and (2) the design and fabrication of suitable equipment to carry out the particular reaction on a commercial scale. These problems generally can be solved by constructing an experimental pilot plant where such chemical and mechanical difficulties can be anticipated and where important design data can be obtained.

Fortunately, in the synthesis of hydrocarbons no great problem exists in the choice of materials, but the design of the equipment presents many difficulties. The design of equipment for the chemical process industry constitutes one of the most important departments in the science of chemical engineering. This branch of science, however, has not developed as yet to a level where such design may be achieved successfully solely by the use of pencil and paper. One reason for this may be the inadequacy of the actual theories on which the science of chemical engineering is currently based. However, it seems probable that incomplete knowledge of the actual values for constants, such as the heat conductivity and elasticity of construction materials, has been a greater obstacle.

In conducting the pilot-plant experiments on the hydrocarbon synthesis at Kyoto Imperial University, a 5-year program was planned to culminate in operations on a scale representative of that of an actual industrial plant. This size was thought to be a pilot plant one-tenth the size of that to be used industrially, or one that would handle 100 $m.^3/hr.$ of gas. The objectives of the experimental program were proposed as follows:

1. To use as many theoretical calculations as possible in the design of the pilot plant.

2. To derive the most accurate figures possible by laboratory methods for all experimental data, even if they appear to be of dubious value.

3. To enlarge gradually the scale of the equipment employed to approach commercial-scale operation.

In the opinion of the author, the above criteria should be applied to all pilot-plant experiments. Much time, labor, and money have been wasted in Japan on pilot-plant experiments because such a program was not followed. Of course, depending on the time and money available and, perhaps, on the knowledge of the scientists involved, rigid adherence to such a pattern may not be possible. It is believed, however, that the success of the program at Kyoto, which was completed in 3-1/2 years instead of the anticipated 5, was strongly dependent on this program. In the final expansion of the equipment to a throughput of 100 $m.^3$/hr., it was not even necessary to make a preliminary test of the equipment. Actual operations were conducted immediately after construction was completed; continuous operations were carried out for 2 weeks with no significant difficulty at any time.

Since 1927, extensive studies have been conducted on catalysts for the synthesis of petroleum hydrocarbons from carbon monoxide and hydrogen (Fischer-Tropsch process) in the laboratories of Professor Kita of Kyoto Imperial University. Among the successful catalysts discovered was one containing iron as the main constituent. Bench-scale studies of the Fischer-Tropsch synthesis made with cobalt catalysts were begun in 1939 in a water-cooled reactor at a throughput of 6 cubic meters of synthesis gas per hour. The successful completion of these studies in the fall of 1939 led to a contract for the design and construction of a pilot plant to accomodate a synthesis-gas throughput of 100 cubic meters per hour, the work to be completed by July 1940. On July 17, 1940, experimental operations were begun in this pilot plant. A continuous operation, experiment No. 17, was started on August 3 and continued for 18 days; a detailed description of the experiment is given in this report. On the basis of these results, the Hokkaido Synthetic Fuel Co., Ltd., proposed the design and construction of a commercial-scale plant to accomodate a throughput of 1,000 cubic meters of synthesis gas per hour. Because of the acute shortage of cobalt, however, these plans, which called for the use of cobalt catalysts, were temporarily abandoned, and intensive research on iron catalysts was begun in the 100 $m.^3$/hr. converter.

Extensive studies of iron catalysts at the Kita laboratory showed that 151 cc. of liquid products could be obtained from 1 cubic meter of a 1-to-1 mixture of CO and H_2, a yield that compared favorably with cobalt catalysts. Although a short life was anticipated for iron catalysts, laboratory tests demonstrated that it was possible to extend the effective life considerably in several ways, among them by lowering the reaction temperature and by using a hydrogen-rich synthesis gas. Enough iron catalyst was prepared, therefore, to allow operation on a pilot-plant scale. The experiment covering this work (No. 18) extended from October 17 to November 6, 1940, and the actual life of the catalyst was found to be even greater than that predicted by laboratory tests.

IMPORTANT ASPECTS OF PLANT DESIGN

The equipment comprising the pilot plant for the synthesis of hydrocarbons consists of many units, such as the desulfurizer, the converter, the condenser, the activated charcoal absorber, and others, but the most important, and the most difficult in its design, is the converter in which the catalytic reactions take place. The greater part of the following discussion is devoted, therefore, to the converter.

The difficulty in designing a suitable converter lies in the fact that the reactions occurring in the synthesis of hydrocarbons are chiefly heat-producing and that the temperature of the catalyst bed as a whole must be maintained at a constant value with little or no fluctuation. According to calculations made in this laboratory, the heat produced by the hydrocarbon synthesis using 1 cubic meter of gas containing pure carbon monoxide and hydrogen[3] reaches 450 kcal. If the reaction is conducted adiabatically, the catalyst bed may reach temperatures over 1,000° C. This obviously cannot be tolerated, as the catalysts found to be effective in the synthesis of hydrocarbons have proved to be extremely sensitive to temperature; a variation of more than 2° C. in the catalyst temperature produced undesirable results. Thus, for each catalyst used in the hydrocarbon synthesis, there exists an optimum temperature. A slight decrease in this temperature will cause an immediate decrease in the reaction velocity with the formation of smaller amounts of hydrocarbons; similarly, a slight increase in this optimum temperature will tend to produce a large amount of methane and other gaseous hydrocarbons, with the result that less liquid products are formed. Therefore, in the design of a converter, it is of utmost importance to arrange to remove the heat of reaction and to maintain the catalyst bed within the required temperature limits. Eventually this problem can be reduced to one of heat transfer.

The basic relationship for the transfer of heat is well known. If the cooling surface area is represented by "A" and the heat transfer coefficient is "K" when the average temperature difference is "Δt," then the amount of heat that will flow in a unit of time will be:

$$q = K A \Delta t.$$

Where a simple wall separates the cooling medium from the heat source, the heat-transfer coefficient, K, may be defined as:

$$\frac{1}{K} = \frac{1}{h_a} + \frac{\delta}{\lambda} + \frac{1}{h_b}$$

Where h_a is the film coefficient on the side of the wall containing the heat source (in this case, a gas), and where h_b is the film coefficient on the side of the wall containing the cooling (liquid) medium; δ represents the thickness of the separating wall, and λ is its thermal conductivity.

Studies by such investigators as A. P. Colburn[4] on the film coefficient existing when gas is passed through a tube filled with catalyst are very incomplete. This lack of fundamental information discourages any successful design of a converter by theoretical considerations alone. Either water or oil can be used as coolants, but because no method is known for computing the film coefficients for these substances when they are used in an apparatus of complicated shape, it was necessary to determine experimentally the area of cooling surface required per unit volume of catalyst. At first, synthesis was carried out in an apparatus into which 100 l. of gas was introduced per hour.

3/ To be published.

4/ Colburn, A. P., Ind. Eng. Chem., vol. 23, 1931, P. 910.

From consideration of previous results, the experimental scale was gradually enlarged, and the type of coolant and the distribution of the cooling pipes were varied to obtain the data necessary for subsequent expension. A detailed description of the converters studied follows; table 1 lists the types of converters investigated.

TABLE 1. - Types of converters investigated in pilot-plant synthesis of hydrocarbons by Fischer-Tropsch process

Hourly gas flow rate	Type of heat removal employed	Date testing completed
100 l.	Hot oil outside of catalyst tubes.	July 12, 1937
10 m.^{3}	do.	May 13, 1938
3 m.^{3}	Hot oil inside tubes, catalyst outside.	July 13, 1938
10 m.^{3}	do.	November 13, 1938
6 m.^{3}	Hot water inside tubes, catalyst outside.	September 14, 1939
100 m.^{3}	do.	July 15, 1940

INNER-CATALYST CONVERTER (100 l./HR.) USING OIL AS COOLANT

Description of Equipment

Three converters, each differing in catalyst-volume:cooling-area ratio, were constructed. Three tubes, possessing inside diameters of 25 mm., 35.7 mm., and 55 mm., were each filled with 1005/ cm.^{3} of catalyst. A gas flow of 100 l./hr. was then passed through each tube while hot oil was circulated around the tubes as a cooling medium.6/ The formation of product oil was then correlated with the temperature difference between the cooling medium and the catalyst.

The flow diagram of the process as it was carried out in this test is shown in figure 1. The synthesis gas used was first passed through a flow meter (1), where its volume was measured, following which it was passed through a dehydrater (2), where its water content was removed. The dried gas was then heated to approximately reaction temperature in a preheater (3), from which it was sent into the converter (4). The products and the unreacted gases were led to a cooler (5), where the oil fraction of comparatively high boiling point (Diesel oil) and the water were condensed and collected (6). The volatile oil product and the gaseous fractions such as propane and butane, which did not condense in the cooler, were then adsorbed in activated charcoal traps (7). The remaining gas was passed through the wet test meter (8) before it was released. A constant temperature was maintained in the converter in the following manner: The coolant oil stored in

5/ Editor's Note: This figure is given as 1,000 cm.^{3} in later paragraphs.
6/ Editor's note: Same as German "inner-catalyst converter." Refer to Bureau of Mines Inf. Circ. 7567, The Evaluation of Converters for Exothermic and Endothermic Catalytic Reactions Occurring within Narrow Temperature Limits, by Gustav Wirth, translated and revised by R. C. Grass and H. J. Kandiner.

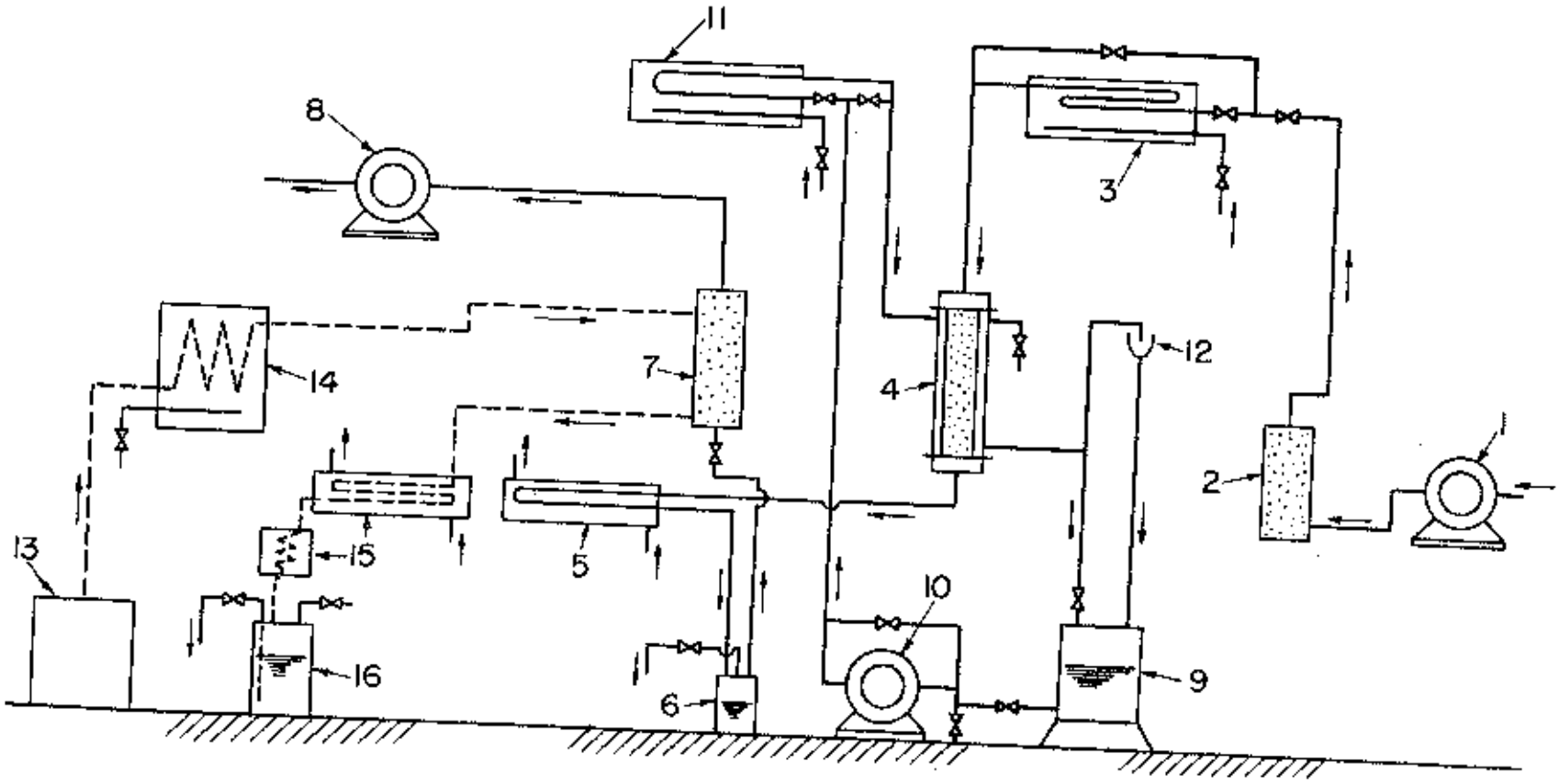

Figure 1. - Flow diagram (100 l./hr, inner-catalyst converter).

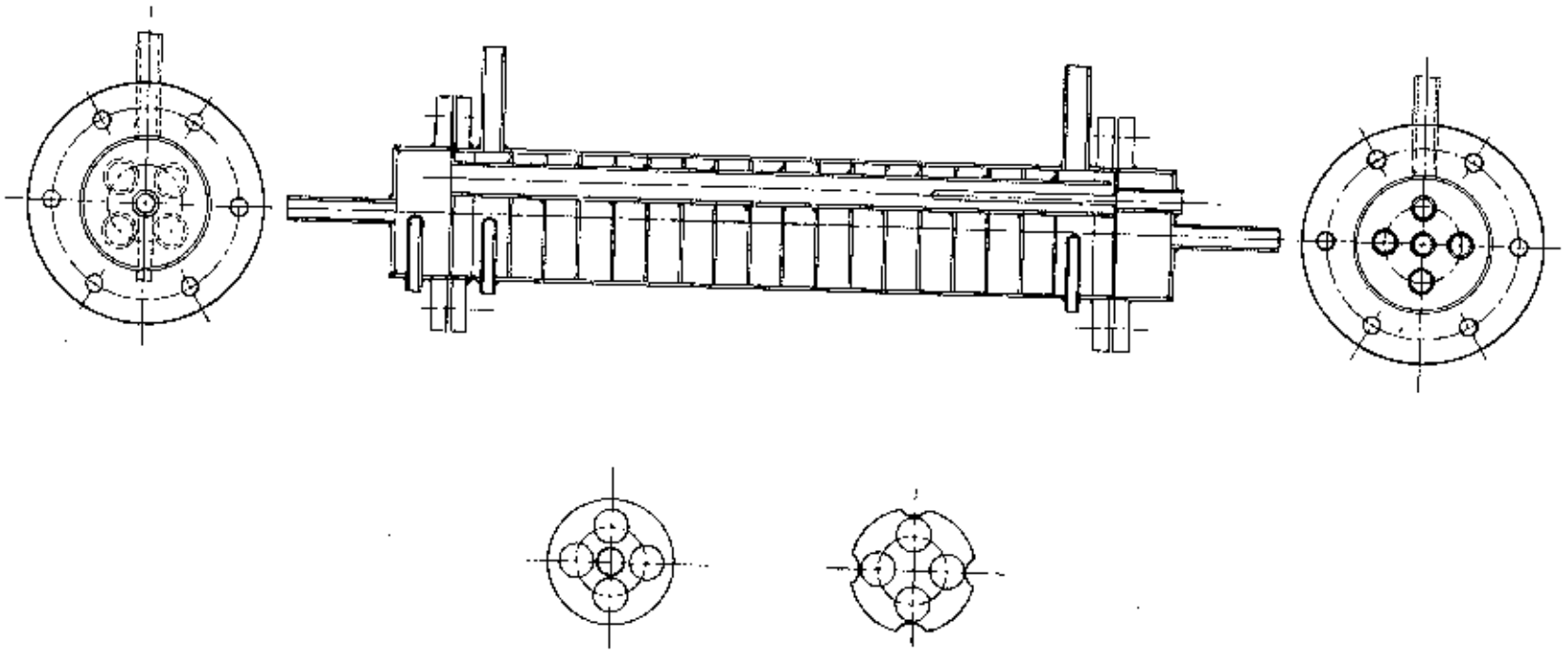

Figure 2. - 25-mm. I.D. inner-catalyst converter.

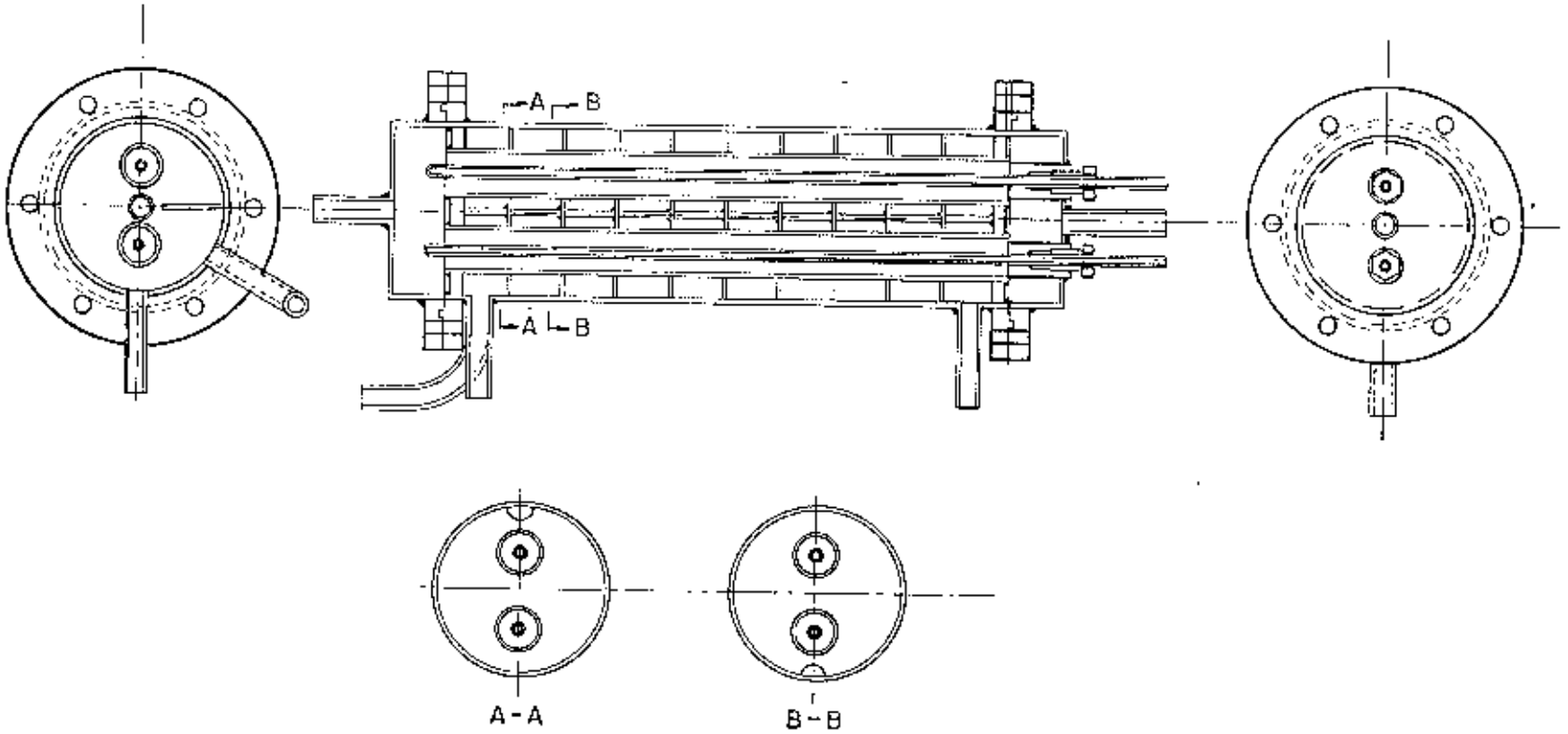

Figure 3. - 35.7-mm. I.D. inner-catalyst converter.

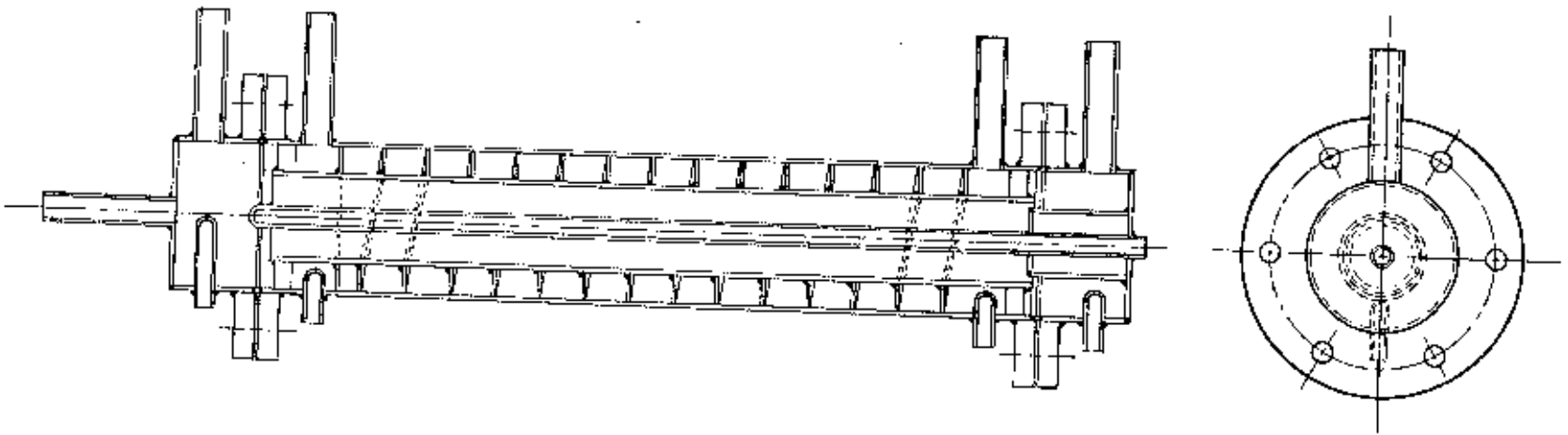

Figure 4. - 55-mm. I.D. inner-catalyst converter.

tank (9) was sent into a preheating apparatus (11) by pump (10). The oil, heated to the desired temperature, was then passed through the converter (4), after which it was collected in tank (12) and returned to the storage tank (9).

The volatile oil fraction adsorbed on the activated carbon was stripped off with superheated steam. Auxiliary equipment included the steam boiler (13), the steam superheater (14), the cooling equipment for the discharged volatile oil and steam (15), and the collecting tank (16).

Cross sections of the converters used in this test are illustrated in figures 2, 3, and 4, which show respectively, that four 25-mm I.D. catalyst tubes, two 35.7-mm. I.D. catalyst tubes, and one 55-mm I.D. catalyst tube were contained in the converters. In all three cases, approximately 1,000 cm.3 of catalyst was used. Special attention was devoted to obtaining the maximum possible velocity of the cooling oil and to eliminating dead spaces in the flow of cooling medium. Baffle plates were distributed throughout the convertor to promote thorough mixing of the cooling medium and thus maintain a maximum thermal conductivity to the cooling oil.

Catalyst

The catalyst employed had the following composition: 100 Co: 12.5 Cu:2.5 Th:1.25 U:125 diatomaceous earth. In laboratory experiments using this catalyst,1/ an oil yield of 100 to 110 cm.3/m.3 of synthesis gas was obtained. The cooling oil was held as near to 205° C. as possible. Synthesis gas composed of one part CO to two parts H_2 was used. The results of these tests are summarized in table 2.

TABLE 2. - Summary of results obtained with inner-catalyst converter using hot oil as a cooling medium

(Flow rate of $2H_2$:1CO gas = 1.00 l./hr.)

Inside diameter of catalyst tube, mm.	Maximum temperature difference between cooling medium and catalyst, °C.		Oil yield, cm.3/m.3	Catalyst efficiency, cm.3/m.3
	At start	At standard conditions		
25	3	3	98	110
35.7	46	10	78	101
55	138	23	40	101

Synthesis Operation

After reduction of the catalyst in the 55-mm. I.D. catalyst tube, the temperature of the cooling oil was raised to nearly the proposed synthesis temperature of 205° C. On initiating a flow of synthesis gas, however, the

1/ Kyoto Imperial University, Chemical Research Institute Lecture Series No. 8, 1938, p. 11.

temperature of the catalyst bed suddenly increased until, at 342.5° C., it was evident that maintenance of a constant temperature in the catalyst bed was impossible with this type of operation. Nevertheless, the synthesis was continued by lowering the temperature to which the cooling oil was preheated, thereby controlling the increase in temperature of the catalyst bed. Control was also facilitated as the catalyst became deactivated and evolved less and less heat of reaction, but, even after 30 hours of operation, a temperature difference of 23° C. was observed. The oil yield was only about 40 percent of that obtained in the laboratory, and it was concluded that, in a converter of these dimensions, the cooling surface was not sufficient to remove effectively the heat produced by the synthesis reactions.

Similar unfavorable results were obtained in the 35.7-mm. I.D. catalyst tubes. Although, by carefully controlling the preheating temperature of the cooling oil, it was possible to continue the operation, the product oil yield was inferior.

On the other hand, the results obtained with the 25-mm. I.D. catalyst tubes were very good. Throughout the operation, approximately 36 hours, the catalyst-coolant temperature difference remained within 3° C., and no difficulty was encountered in controlling the temperature of the catalyst bed. Furthermore, the product oil yield from a continuous 12-day period was superior to that obtained in the laboratory.8/ These results indicate that for effective removal of the heat of reaction in the hydrocarbon synthesis, a minimum cooling surface equivalent to that of a 25-mm. I.D. catalyst tube is necessary.

INNER-CATALYST CONVERTER (10 $m.^3$/hr.) USING OIL AS COOLANT

The equipment used in this set-up was 100 times the capacity of that used in the previous experiments. It was constructed and operated for the following reasons:

(a) Up to this time, synthesis gas composed only of pure hydrogen and pure carbon monoxide, prepared from formic acid, was used. Progression to larger quantities of feed gas required the use of water gas made from coke. It therefore became necessary to construct an apparatus to remove undesirable feed-gas contaminants such as hydrogen sulfide and organic sulfides.

(b) Although, from the previous orienting experiment, a cooling surface equivalent to the 25-mm. I.D. catalyst tube was indicated to be sufficient, the short length of the catalyst tube (500 mm.) precluded any definite decisions. It was observed that, compared to the amount of heat carried off by the cooling oil through the walls of the catalyst tube, a great amount of heat also was carried away through the upper and lower parts of the catalyst tube, and this assisted considerably in cooling the catalyst bed. It was necessary, therefore, to determine whether a cooling surface equivalent to a 25-mm. I.D. tube would continue to be sufficient when the catalyst bed length was increased beyond 500 mm.

8/ See footnote 4.

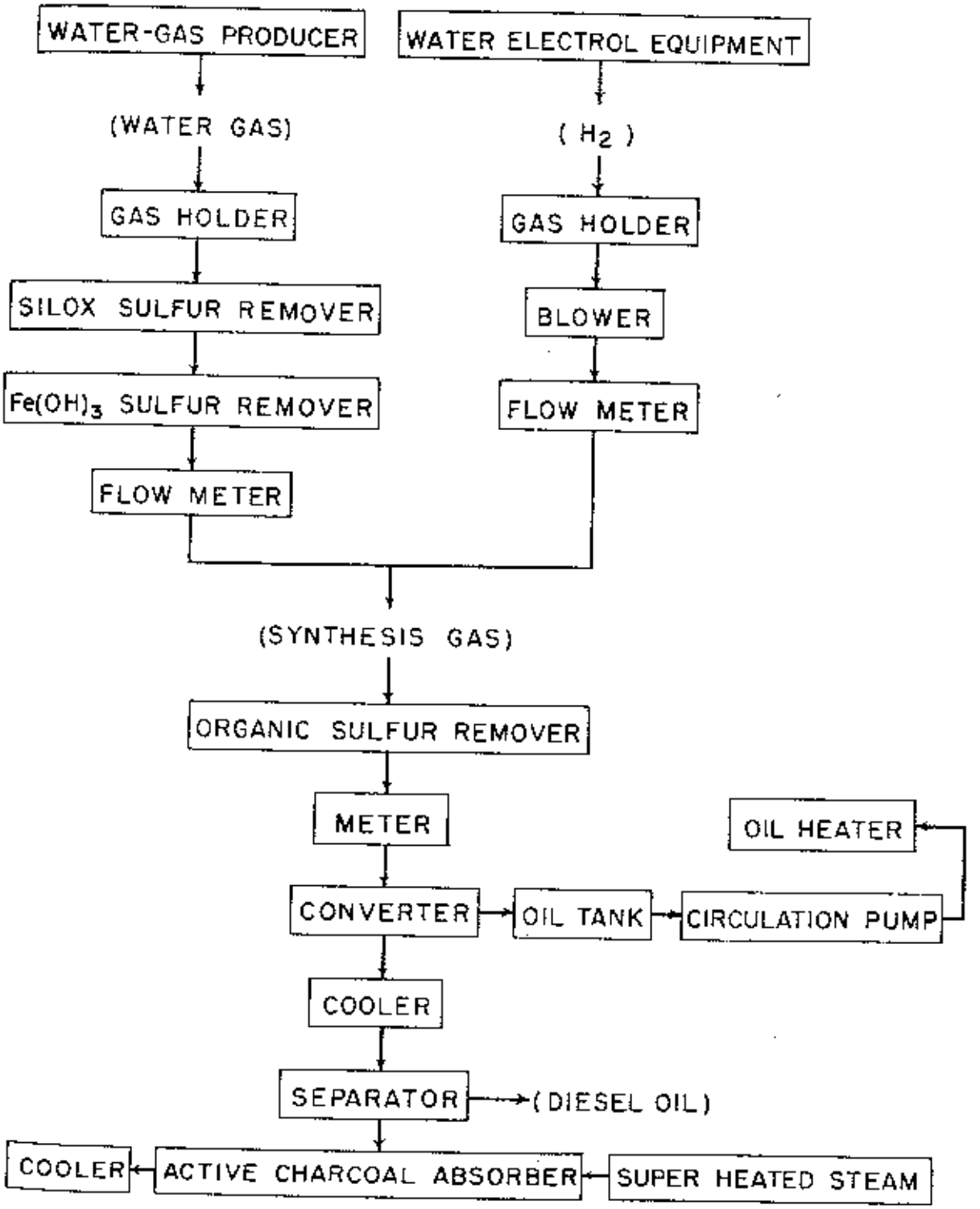

Figure 5. - Flow diagram (10 $m.^3$/hr. inner-catalyst converter).

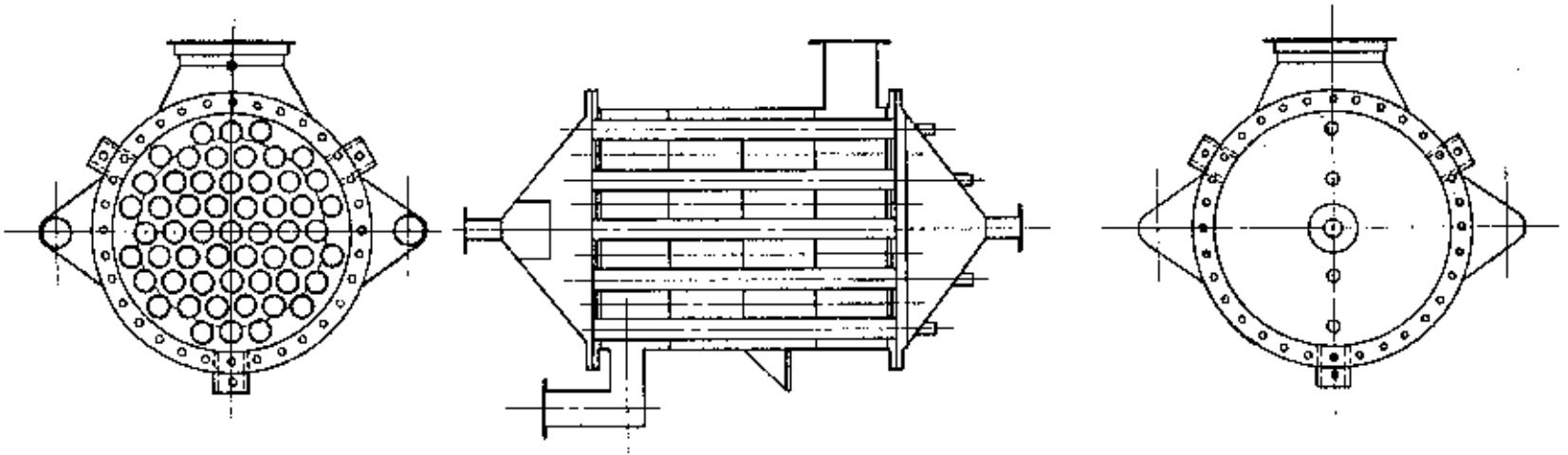

Figure 6. - Organic sulfur remover (10 $m.^3$/hr. inner-catalyst converter).

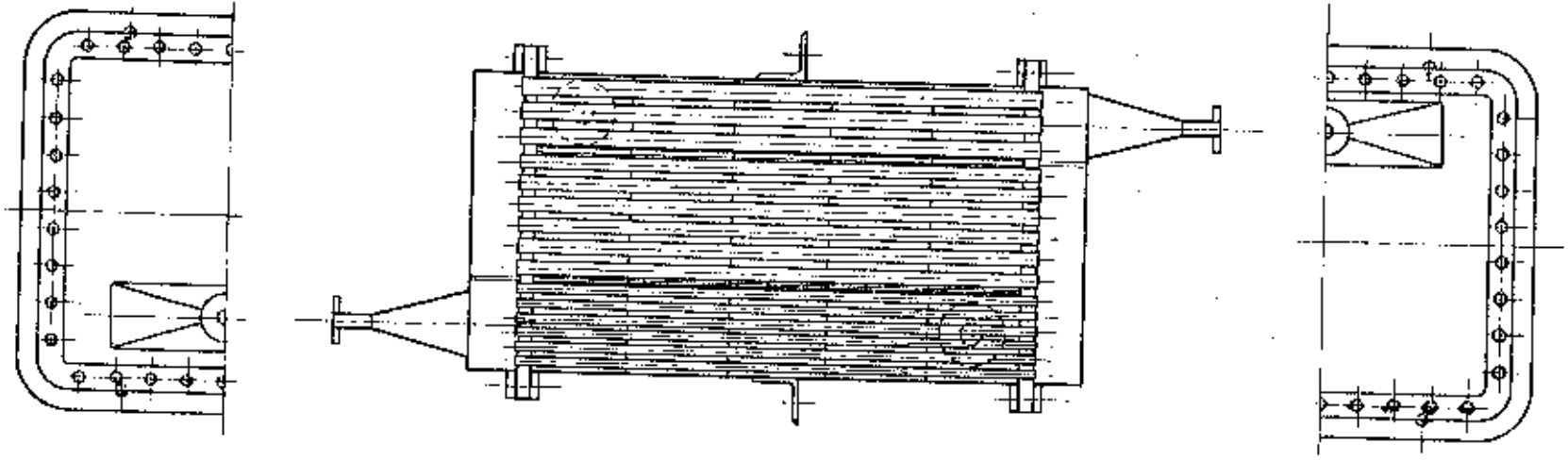

Figure 7. - 10 m.^{3}/hr. inner-catalyst converter.

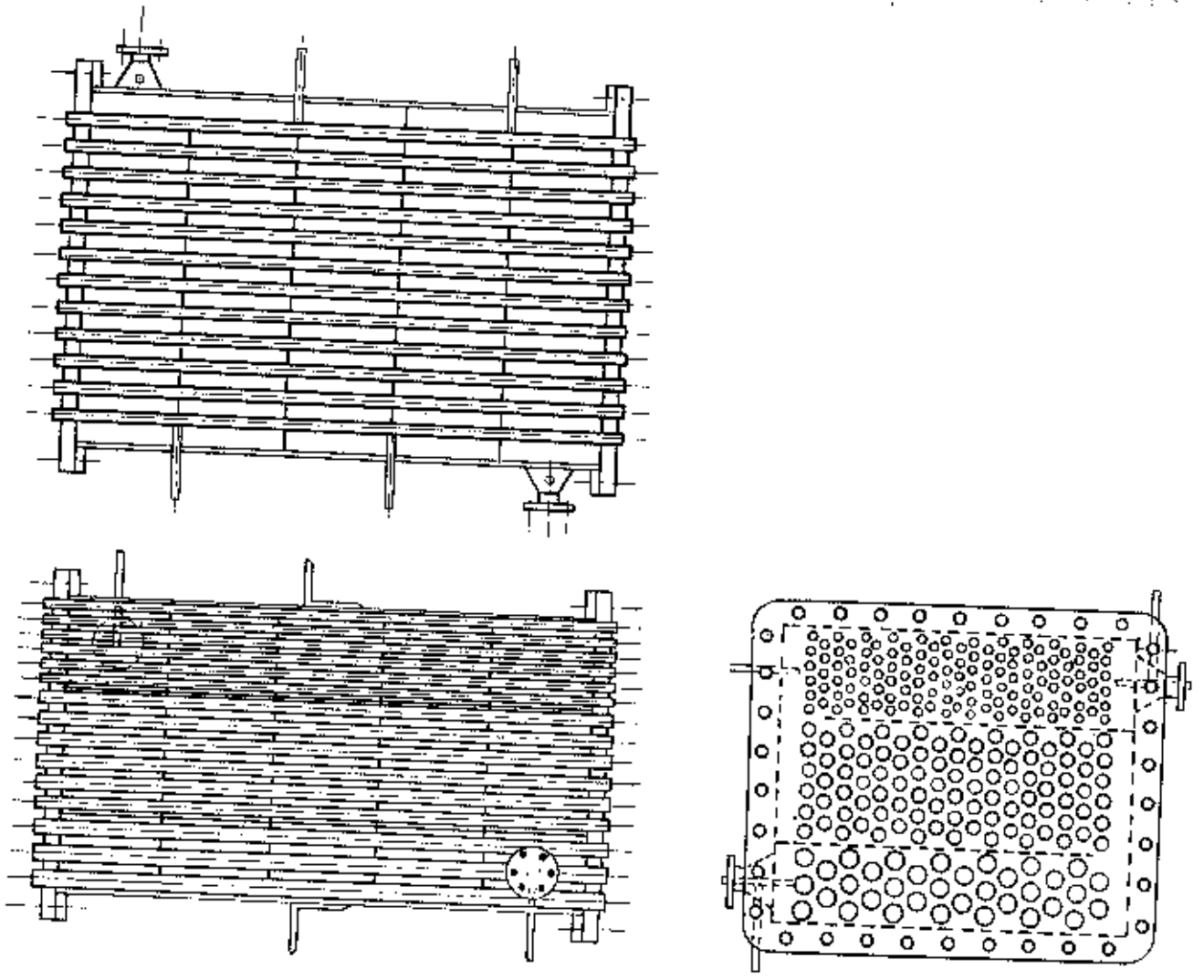

Figure 8. - Detailed construction of figure 7.

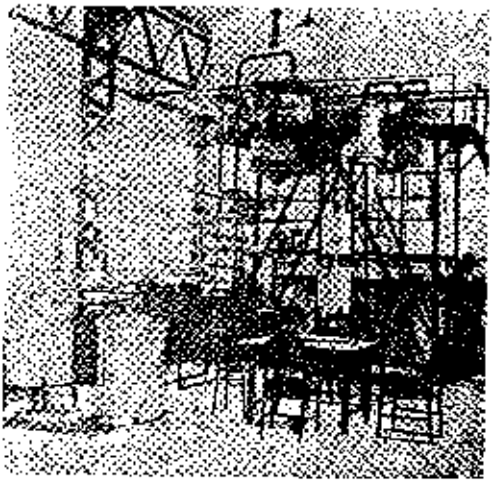

Figure 9. - Equipment located on downstream side of 10 cubic meter per hour inner-catalyst converter.

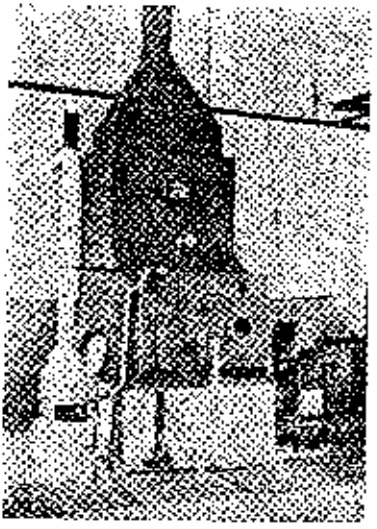

Figure 10. - Lamont boiler.

(c) Finally, in preparing for the eventual design and construction of commercial-scale equipment, it was necessary to design and build on a small scale (at least once) such units as the cooler and active charcoal absorber. The flow diagram for the synthesis of hydrocarbons in this unit is shown in figure 5.

Description of Equipment

The construction of the organic sulfur remover is shown in figure 6. In this particular experiment the gas was passed through a pipe filled with luxmasse and containing 10 percent each of NaOH and $Cu(OH)_2$ and heated externally to 200°-260° C. by gas firing. In industry, organic sulfur is usually removed by preheating the gas to 200°-250°C. and passing it over the purifying agent. External heating of the purifying agent, itself, is not common. Where low mass flows (such as 10 m.3/hr.) are involved, however, the heat capacity of the system is so small that preheating cannot be relied upon to maintain the desired temperature. However, initial attempts to heat the raw gas by simply passing through an externally heated cylindrical container filled with the purifying agent were unsuccessful, because the heat conductivity of the granular purifying agent was very low, and uniform heating of the mass by external firing was extremely difficult. When heating was increased to raise the temperature of the inner portion of the granular materials, the outer sections of the granular mass became overheated, and a reaction was initiated that ultimately produced methane from CO and H_2. Moreover, this reaction, being exothermic, rapidly increased the temperature of the solid granules, once started, and created the problem of controlling this temperature rise and of cooling the agent to the desired temperature. For these reasons, the unit shown in figure 6 was designed to control the temperature of the purifying agent and maintain it uniform.

As shown in figures 7 and 8, the construction of the inner-catalyst converter with a throughput capacity of 10 m.3/hr. is identical in principle to that of the unit of 100 l./hr. capacity; i.e., the catalyst is contained inside the tubes, whereas the outside of the tubes is cooled with oil. This converter was constructed with three banks of tubes, consisting of 127 tubes of 5/8-inch I.D. (approximately 15 mm.); 94 tubes of 1-inch I.D. (25 mm.); and 35 tubes of 1-1/4-inch I.D. (31 mm.), respectively. The synthesis gas was passed through the unit in the direction of increasing tube diameter for the following reasons: (1) As the converter becomes larger, the cooling surface ratio provided by a 25-mm. I.D. tube arrangement might be insufficient; (2) the current synthesis theory2/ indicates a highly exothermic reaction near the entrance of the catalyst chamber, so that a large cooling surface at this point is desirable; and (3) by filling each bank independently, the effect of cooling surface could be studied. Baffle plates were used to increase the path traveled and the velocity of the cooling oil and to minimize dead space. Figure 9 is a photograph of the equipment on the downstream side of the converter.

2/ To be published.