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SYNTHESIS GAS

Introduction

The ideal composition of the synthesis gas varies with the type of catalyst over which the synthesis reaction is to be carried out.

The light, porous, very active, precipitated catalysts for the synthesis reaction operate at low temperatures and pressures, directing the synthesis reaction according to the equation:

$$CO + 2H_2 \longrightarrow (CH_2) + H_2O$$

The ideal synthesis gas for such a reaction will consist, therefore, of two parts of hydrogen and one part of carbon monoxide.

The dense, rugged catalysts prepared by reduction of a solid mass of fused oxides are not very active and consequently must be operated at high temperatures and relatively high pressures, under which conditions the synthesis reaction proceeds to about an equal extent by each of the reactions:

$$\begin{array}{l} CO + 2H_2 \longrightarrow (CH_2) + H_2O \\ \underline{2CO + H_2 \longrightarrow (CH_2) + CO_2} \\ 3CO + 3H_2 \longrightarrow 2(CH_2) + H_2O + CO_2 \end{array}$$

giving an overall reaction according to the latter equation. The ideal synthesis gas under these conditions will, therefore, consist of equal parts of hydrogen and carbon monoxide.

The usual raw materials for the manufacture of synthesis gas are: coke, anthracite, lignite, or hydrocarbon gases; although there is no reason why heavy oils and tars should not be used. The three solid fuels are lacking in hydrogen but the deficiency may be partially overcome by reaction of the solid with water according to the equation:

$$C + H_2O \longrightarrow CO + H_2$$

The synthesis gas directly from the three solid fuels, therefore, contains the hydrogen and carbon monoxide in the proper ratio for use with the high temperature synthesis catalysts. For use with the low temperature synthesis catalysts, a part of the carbon monoxide may be converted into carbon dioxide by the use of more water according to the equation:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The extent of the latter reaction was so regulated that the overall product contained hydrogen and carbon monoxide in the proper ratio of two-to-one:

$$3C + 4H_2O \longrightarrow 2CO + 4H_2 + CO_2$$

The removal of the carbon dioxide was advantageous.

The conversion of hydrocarbon gases into synthesis gas may be accomplished in a number of ways, depending upon the desired ratio of hydrogen to carbon monoxide. The one-to-one ratio of hydrogen to carbon monoxide, suitable for use with the high temperature synthesis catalysts, may be obtained by use of carbon dioxide:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

the source of carbon dioxide being the tail gases from the synthesis plant. The two-to-one ratio of hydrogen to carbon monoxide, suitable for use with the low temperature synthesis catalysts, may be obtained by use of oxygen:

$$CH_4 + 1/2\ O_2 \longrightarrow CO + 2H_2$$

or by the combined use of water and carbon dioxide:

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2$$

The subsequent material in this section represents the experience of the various companies in manufacturing synthesis gas from the several fuel sources. Also, where available, the gas purification procedures have been given.

MANUFACTURE OF SYNTHESIS GAS BY RUHRCHEMIE

Ruhrchemie Procedure

The synthesis gas used at Holten was obtained by treating coke with steam to make water gas and subsequently converting enough of the carbon monoxide, by treating with more steam over a catalyst, to maintain the hydrogen to carbon monoxide ratio at two-to-one. When the synthesis plant was operated at atmospheric pressure, the carbon dioxide was not removed from the gas but was passed through the synthesis chamber as an inert gas. When the synthesis plant was operating at seven atmospheres, it was planned to remove a large part of the carbon dioxide by scrubbing the gas with water.

Gas Generators

The gas generating plant consisted of eleven Demag generators, system Humphries, which were operated automatically. Coke was charged to the generators in batches of 440 pounds (200 kilograms) at three minute intervals. The cycle of three minutes was divided about equally between blowing with air, blowing with steam from top and blowing with steam from bottom. The reversing valves, which were operated with steam at a pressure of about 40 pounds per square inch, required two-to-three seconds for reversal. The temperature above the firebed in the generators varied between 1300 and 1500°F. (700 and 800°C.), and the gage pressure in the generators from 1.5 to 2 pounds per square inch. Each generator was equipped with one high pressure (265 pounds per square inch (18 atmospheres)) steam boiler for waste heat and with a furnace jacket which produced low pressure steam (45 pounds per square inch (2.5 atmospheres)) for blowing the furnaces.

Each of the generators had a capacity of about 282,000 cubic feet (8000 cubic meters) of water gas per hour, equivalent to 310,000 cubic feet (8800 cubic meters) of synthesis gas per hour. Each generator was down for repairs once each year for four-to-five weeks, so that in continuous full scale operation ten of the eleven generators would always be in use. The maintenance on the generators amounted to about 5% per year.

Gas Composition

Only four generators were in use at the time the plant was visited and these were producing 1,240,000 cubic feet (35,000 cubic meters) per hour of water gas, 340,000 cubic feet (9650 cubic meters) per hour of which were taken from the main gas stream, passed through the carbon monoxide converters, and then reunited with the

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TABLE I

HOLTEN GAS QUALITIES AND QUANTITIES

Constituent	Volume %			Volume in Cubic Feet			Volume in Cubic Meters		
	Init. Water Gas	After CO Conv.	Total Stream	Init. Water Gas	After CO Conv.	Total Stream	Init. Water Gas	After CO Conv.	Total Stream
CO_2	5.3	30.5	14.0	65,600	143,700	191,000	1,850	4,040	5,420
CO	40.5	3.0	27.5	502,000	14,100	375,300	14,170	400	10,630
H_2	50.7	63.9	55.3	629,000	301,000	755,000	17,750	8,480	21,370
CH_4	0.4	0.3	0.4	5,000	1,400	5,500	150	40	150
N_2	3.1	2.3	2.8	38,400	10,800	38,200	1,080	310	1,080
Total	100.0	100.0	100.0	1,240,000	471,000	1,365,000	35,000	13,270	38,650

main stream. Table I shows the gas composition and quantities for the gas plant. The carbon monoxide conversion was accomplished by passage of the water gas together with steam over a nickel catalyst at about 900°F. (490°C.). Other catalysts could be used in place of the nickel, for example: chromium oxide, iron oxide, etc.; but with no particular advantage.

Table I

Gas Purification

The harmful impurities in the synthesis gas were:

1. Hydrogen sulfide
2. Organic sulfur compounds
3. Resin-forming materials

The hydrogen sulfide can be removed by use of any of the several processes used in the gas industry, for example, by means of bog iron ore or extraction by scrubbing. The organic sulfur compounds can be removed by reduction (with the hydrogen of the synthesis gas) to hydrogen sulfide by passage over a catalyst at temperatures in the neighborhood of those used for the synthesis reaction, followed by removal of the hydrogen sulfide. The resin-forming materials may be largely eliminated by the choice of the conditions used in the synthesis gas manufacture. They may also be removed from the synthesis gas by adsorption on activated charcoal.

The sulfur purification of the gas at Holten consisted of two steps:

1. Hydrogen sulfide removal
2. Organic sulfur removal

Hydrogen Sulfide Removal

The hydrogen sulfide removal was quite similar to that used by city gas manufacturers in that the gas was contacted at low temperatures--75°F. (25°C.) entering, and 90-100°F. (35-40°C.) leaving--with porous, hydrated iron oxides with which the hydrogen sulfide reacted to form iron sulfides. A small amount of oxygen was added to the gas before entering the hydrogen sulfide removal stage, the function of the oxygen being to oxidize the sulfides to sulfates, at least partially, and thereby increase the length of time that the iron oxides would effectively remove hydrogen sulfide.

Hydrogen Sulfide Contact

The contact used was Luxmasse containing not more than 50% water. Without any pretreatment, the already porous Luxmasse was placed in 16-20 inch (400-500 mm.) layers in towers accommodating 16 layers each. The gas entered the tower from the side and the piping was such that the gas stream could be directed over only one contact layer or over any number of layers in series, the actual procedure being dependent upon the age of the contact, the amount of hydrogen sulfide in the gas, the gas velocity, etc. The usual gas velocity through the towers was about 0.2 feet (6 centimeters) per second. Normally, 700,000 cubic feet (20,000 cubic meters) of gas per hour was passed through four towers, each containing 140,000 pounds (65 tons) contact, but through only three towers when a tower was being recharged. In recharging a tower, only the top 80% of old contact mass was removed from each tray and replaced by fresh material mixed with the remaining 20% of the old contact mass.

Hydrogen Sulfide Content

Ordinarily water gas made from coke was said to contain from 230 to 280 grams of hydrogen sulfide per thousand cubic feet (8-10 grams hydrogen sulfide per cubic meter), but the gas made at Holten contained, on the average, only 85 grams per thousand cubic feet (3 grams hydrogen sulfide per cubic meter).

Organic Sulfur Removal

The organic sulfur removal was accomplished by passage of the gases, after the hydrogen sulfide removal, over a mixture of Luxmasse and sodium carbonate at higher temperatures, 400-570°F. (200-300°C.).

The organic sulfur compounds were present to the extent of three-to-four grams of sulfur per thousand cubic feet (12-15 grams sulfur per 100 cubic meters). The organic sulfur compounds consisted of about 40% carbonoxysulfide and 60% carbon disulfide, with only traces of mercaptans, sulfides, etc. All these compounds were reduced to hydrogen sulfide by contact with the catalyst in the presence of the reducing atmosphere of the synthesis gas. The hydrogen sulfide then reacted with either the soda or iron oxide to form, respectively, sodium sulfide or iron sulfide. The small amount of oxygen in the gas--0.2%--served to oxidize the sulfides to sulfates and thus prolong the useful life of the contact.

Preheating Gas

The gas preheater for the organic sulfur removal step was designed to heat the gas to a maximum temperature of 660°F. (350°C.) although the actual gas temperature averaged about 530°F. (275°C.). The fuel gas requirements for the preheater were about 11,200 B.T.U. per 1000 cubic feet (100 kilogram calories per cubic meter) of synthesis gas.

Ordinarily, the tail gas from the synthesis plant was used as fuel for the preheater.

The gas preheater consisted essentially of a combustion chamber lined with refractory brick work, fitted with a gas burner, an air blower, and a flue-gas circulating blower. The latter blower was so regulated that the temperature in the combustion chamber was maintained at 1470-1650°F. (800-900°C.). The gas heater proper was a tubular heater, of heat resistant tubes. Special attention had to be paid to the expansion of the tubes.

Contact Chambers

The towers for the organic sulfur removal were of two types:

1. Screen towers
2. Tray towers.

The former consisted of a series of removable screen trays which held the catalyst. The screen trays were removed from the tower jacket by means of a crane for filling or discharging. There was no particular advantage to either type of tower except that a lighter crane could be used for changing the contact in the screen type tower.

The crude gas entered at the bottom of the tower and was distributed in the inner cylinder over the four screen trays. The distribution was accomplished through four vertical gas channels at the periphery of the inner cylinder. The purified gas flowed through slots into an outer annular space and thence to the gas outlet.

The cover of the tower was fitted with a ring cup which sealed the crude gas compartment from the clean gas compartment. The cover was corrugated to allow for thermal expansion.

The second type of tower was fitted with two perforated sheet cylinders of different diameters, instead of the screen trays described above. The purifying mass was contained in the annular space between the perforated cylinders. The inner perforated cylinder was divided into several sections which could be removed from above. This construction made it possible to discharge the tower downward. The raw gas flowed into the outer annular space of the tower then through the outer perforated cylinder, through the contact mass and through the inner perforated cylinder and then out of the tower.

Gas Rates

The organic sulfur removal was accomplished by passage of the synthesis gas through two towers in series at the rate of 700,000 cubic feet (20,000 cubic meters) per hour at a temperature of 400-570°F. (200-300°C.). Each tower contained 140,00 pounds (65 tons), or 5500 cubic feet (160 cubic meters), of contact mass. These rates were thought to be safe for a gas containing five-to-six grams of organic sulfur per thousand cubic feet (20 grams per 100 cubic meters) and were ~~used at Holten~~ although, as previously stated, the gas actually contained only three-to-four grams of organic sulfur per thousand cubic feet (12-15 grams sulfur per 100 cubic meters). The reason for maintaining the lower gas rate with the purer gas was to allow a margin of safety for chance increases in the sulfur content.

Life of Contact

The catalyst was removed from the tower which contacted the fresh synthesis gas when the contact mass contained 7-10% sulfur. Thus the life of the contact was dependent upon the amount of sulfur in the synthesis gas. The tower that had been last in the series was then moved into the first position and a newly filled tower placed last in the series. On the average at Holten, a tower was kept in the last stage 44 days and then a like time in the first stage. It was necessary to cool the tower before emptying, since otherwise the spent catalyst had a tendency to catch fire on exposure to air.

Sulfur Content

The following tabulation shows the sulfur content of the gases at various stages:

	Inlet	After 1st Tower	After 2nd Tower	
H_2S - g/1000 cu.ft.	0.1	0.03	0.03)	0.06
Organic Sulfur - g/1000 cu.ft.	4.0	0.3-0.6	0.06)	
H_2S - g/100 cu.m.	0.4	0.1	0.1)	0.2
Organic Sulfur - g/100 cu.m.	14.6	1-2	0.2)	

The total sulfur was analytically determined by passing the gas over quartz pieces at 1800°F. (1000°C.) and precipitating the resultant hydrogen sulfide as cadmium sulfide.

Contact for Organic Sulfur Removal

The contact for removal of organic sulfur compounds consisted of 33 parts sodium carbonate and 67 parts of Luxmasse on the dry basis. The Luxmasse contained 7-10% soda as received so that it was only necessary to add soda to bring up the soda content to the desired 33 parts. The soda and Luxmasse were thoroughly mixed, formed, dried and screened, the details of which will be given below since there was a definite technique involved:

Luxmasse

Luxmasse is the residue from the extraction of alumina from bauxite. It was stored outside and exposed to

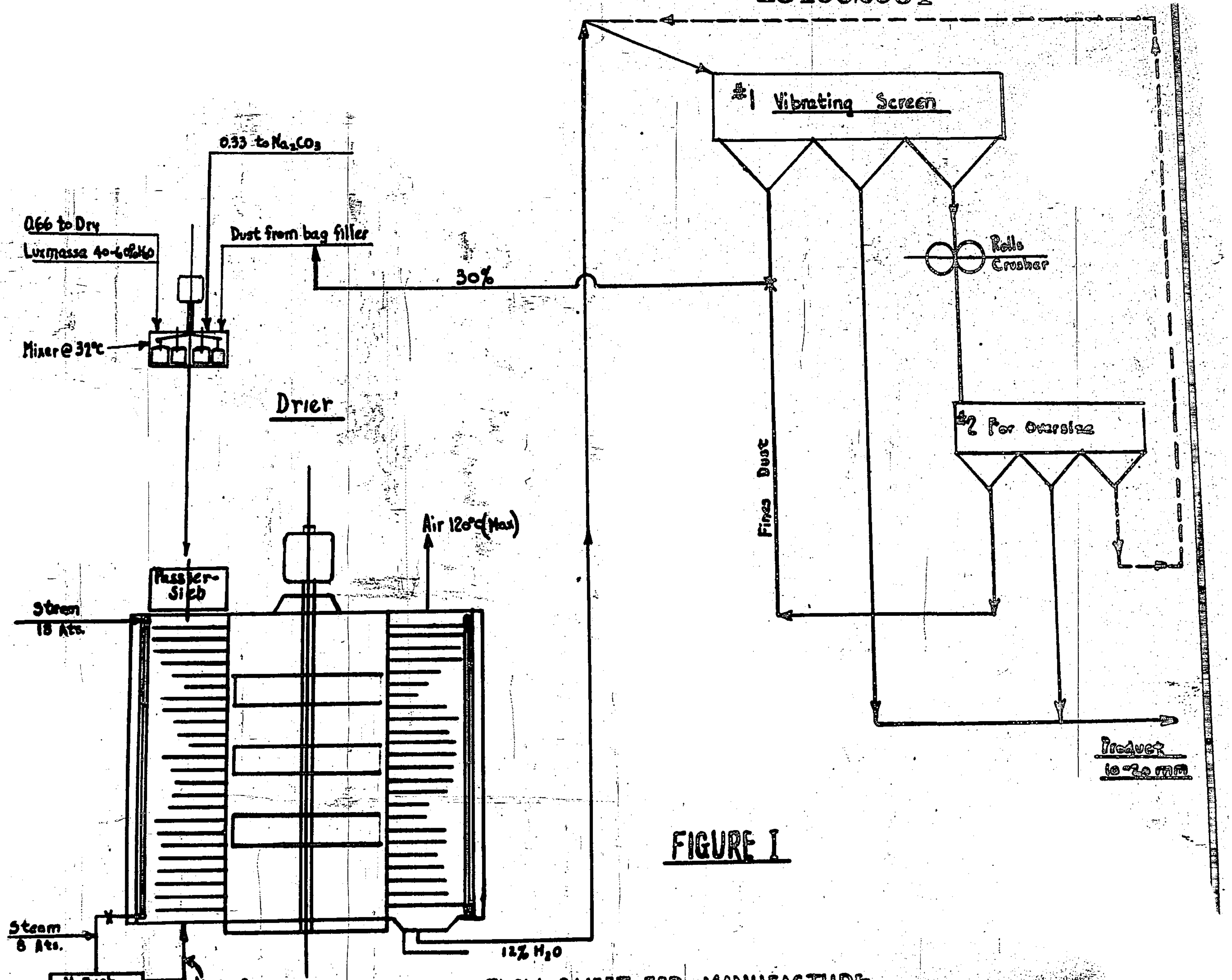

FIGURE I

FLOW SHEET FOR MANUFACTURE
ORGANIC SULPHUR REMOVAL CATALYST

the weather and consequently its water content varied with the humidity of the air and with the rainfall. The water content ranged from 40-60% over a period of one year, the average being about 50%. It was unnecessary to adjust the water content, but at least daily determination of the water content had to be made in order to adjust the soda to Luxmasse ratio. It was stated that any highly porous iron oxides or hydroxides could be substituted for the Luxmasse, but that burned masses should be avoided since the burning usually destroyed the porosity. The apparent density of the Luxmasse was 0.76-0.78.

Soda

Ordinary technical grade soda was used, which was about half sodium carbonate and half sodium hydroxide, the sodium carbonate containing a variable water of crystallization. The figures given for the ratios of soda and Luxmasse, however, were calculated on the basis of pure sodium carbonate.

Flow Sheet for Manufacture of Contact for Organic Sulfur Removal

Figure I

Figure I opposite is a schematic flow sheet of the plant for the manufacture of the contact for removal of the organic sulfur. The various operations represented on the figure will be discussed separately in the following paragraphs.

Mixing Luxmasse and Soda

The Luxmasse and soda were mixed batchwise, although a continuous plant for this mixing was under construction.

The batches then prepared, were of course, dependent upon the equipment sizes and amounted to:

1320 pounds Luxmasse (50% water)	(600 kilograms)
220 pounds soda (dry)	(100 kilograms)
480-500 pounds of fines from screening	(220-230 kilograms)

The luxmasse and soda were added together as solids to the mixer and stirred for fifteen minutes, during which time the temperature spontaneously rose to 100°F. (35°C.) or higher and the mixture became fluid. Then one-half of the fines was added and the mixing continued for ten minutes. The remainder of the fines was then added and the mixing continued for five minutes longer, at which time the mixture was ready for extrusion.

Extrusion of the Mixture

The material from the mixer, which was not provided with heating coils, had to be extruded within a certain definite time or the material would solidify and could be removed only with great difficulty from the mixer. The solidified material had to be discarded. The solidification took place rapidly at temperatures below 90°F. (32°C.) and less rapidly at somewhat higher temperatures. The semi-fluid mixture was fed to a Passiersieb, which was a small chamber with a perforated steel plate as a bottom and provided with rollers and blades to force the mixture through the perforations.

The perforations in the bottom plate were preferably about one centimeter in diameter for the desired particle size--from 5-15 mm.

Extruders

The Passiersiebs were of two sizes.

1. Perforated plate, 52 inches (1310 mm.) in diameter with 49-inch (1250 mm.) arms
2. Perforated plate, 37 inches (940 mm.) in diameter with 35 inch (880 mm.) arms

The smaller Passiersieb worked much better than the larger one, due probably to the better feed distribution in the smaller apparatus. At Holten the prepared mixture was fed to the Passiersiebs by hand shovel and as a consequence the extrusion was not very efficient from the standpoint of labor. Five-to-seven charges were prepared per eight-hour shift per Passiersieb.

Drying the Extruded Contact

The material from the Passiersiebs fell directly onto the top tray of a Büttner drier, which will be described in more detail under the section dealing with equipment. The drier was heated to slightly above 212°F. (100°C.) in order to maintain the catalyst at about 212°F. (100°C.). Steam at a pressure of 265 pounds per square inch (18 atmospheres) was used to heat the periphery of the drier and the exhaust steam from this to preheat the air circulated in the drier from bottom towards the top. The catalyst leaving the drier should contain about 12% water in order to maintain the porosity.

Sizing

The dried catalyst was screened into three sizes: fines less than five millimeters, useful from 5 to 15 millimeters; and larges more than 15 millimeters. The fines were returned and remixed with fresh Luxmasse and soda and the larges were crushed and rescreened.

Capacity of Plant

The plant for preparation of the sulfur removal contact at Holten consisted of four mixers, two Passiersiebs, and two driers, with screening and other facilities in proportion. The capacity of the plant was about 57,000 pounds (26 tons) of dried catalyst per day.

Resin Forming Materials

Cyclic organic sulfur compounds were not removed by the organic sulfur removal treatment. It had been determined that somewhat less than 0.1% of "tar-forming" substances were present in the purified synthesis gas at Ruhland. A sample of the tar-forming substances was extracted from a large quantity of synthesis gas and a distillation made. The various fractions were practically free from sulfur with the exception of the fraction boiling at 248-266°F. (120-130°C.). The various fractions were returned individually to synthesis gas and the gas passed over synthesis catalysts. Only the fraction boiling 248-266°F. (120-130°C.) had any detrimental effect upon the synthesis catalyst. Repeated passage of synthesis gas containing this fraction over the organic sulfur removal contact failed to lower the amount of sulfur. It was thought that the most effective way in which these undesirable materials could be eliminated from the synthesis gas was by the passage of the gas through a tube heated to about 2000°F. (1100°C.). These resinifying materials were thought to be chiefly responsible for the deactivation of the synthesis catalyst with use, since they were deposited on the catalyst and transformed into resins which ultimately blanketed the catalyst.

MANUFACTURE OF SYNTHESIS GAS BY I.G. FARBENINDUSTRIE

Synthesis Gas from Hydrocarbon Gases

A synthesis gas with a two-to-one ratio of hydrogen to carbon monoxide was prepared by the partial oxidation of methane with oxygen:

$$CH_4 + 1/2\ O_2 \longrightarrow CO + 2H_2$$

Methane and Oxygen

This reaction appeared simple on paper, but practically, was very difficult to accomplish. In order to obtain substantially complete conversion of the methane an excess of oxygen had to be used, and this led to the production of water. The presence of the water established the water-gas equilibrium and at low temperatures appreciable carbon was lost as carbon dioxide.

At 2400°F. (1300°C.), in the presence of an excess of oxygen, the residual methane in the product gas varied from 5 to 8%. By passage of the product gas over a catalyst at 1500°F. (800°C.), the residual methane could be decreased to 1-2%, but due to the unfavorable water-gas equilibrium at the lower temperature, the ratio of hydrogen to carbon monoxide was greater than two-to-one.

A special type of burner was finally developed which made it possible to produce at 2400°F. (1300°C.) a synthesis gas which contained only 1-2% methane. The process was readily operable and its chief draw-back was the cost of oxygen. From 1,000 cubic feet of methane and 620 cubic feet of oxygen, 2,400 cubic feet of ideal synthesis gas was obtained. The analysis of the product gas showed 4% carbon dioxide, 33% carbon monoxide, 58% hydrogen, 1% methane and 4% nitrogen.

Methane, Water and Carbon Dioxide

The production of synthesis gas, with a hydrogen to carbon monoxide ratio of two-to-one, was accomplished according to the equation:

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2$$

It was desirable to use a minimum of water in order to lessen the extent of the side reaction of water with the carbon monoxide to form carbon dioxide, but it was found that at least 50% excess of water had to be used in order to avoid deposition of carbon. Due to the cost of the carbon dioxide extraction from the flue gas, it was also desirable to use a minimum amount of this gas. The flue gas contained 7-10% carbon dioxide, which was extracted by the Alkacid process.*

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* The Alkacid process for carbon dioxide recovery was very expensive and other recovery processes were being examined, but the investigation had not been completed.

The catalyst employed for the conversion was nickel upon a support; the catalyst composition, the procedure and the technique being identical with those in use by the Standard Oil Company of Louisiana at Baton Rouge. To one cubic foot of catalyst in tubular reactors heated indirectly to 1400°F. (750°C.), the following reactants were introduced and products withdrawn hourly:

260 cubic feet methane	670 cubic feet hydrogen
140 cubic feet carbon dioxide	330 cubic feet carbon monoxide
236 cubic feet water (steam)	70 cubic feet carbon dioxide

The above rates for the indirectly heated reactor corresponded to a conversion of about 240 cubic feet of methane per hour per cubic foot of catalyst or to a production of 1,000 cubic feet of ideal synthesis gas per hour per cubic foot of catalyst. The regenerative process could be used in place of the continuous method employing indirect heating, but the catalyst requirements were much greater. The rate at which methane was converted was about 5 cubic feet per hour per cubic foot of catalyst and the production of ideal synthesis gas was about 20 cubic feet per hour per cubic foot of catalyst.

Other Hydrocarbons

It was found that hydrocarbons other than methane could be used; those up to and including butane presenting no difficulties. A few preliminary experiments on a

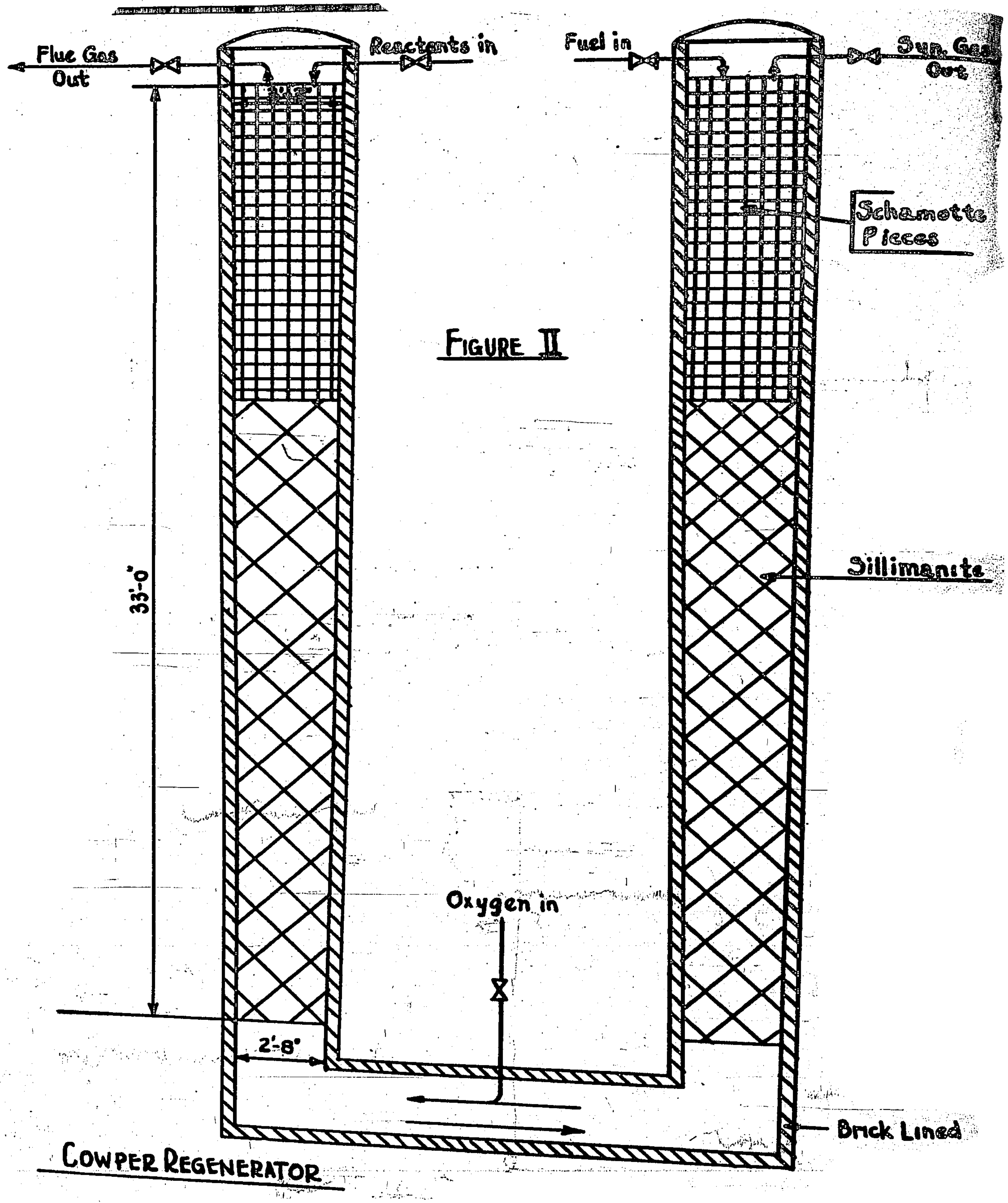

FIGURE II

COWPER REGENERATOR

laboratory scale indicated that heavy tars could be used, but the extent of the experimentation did not warrant a positive statement that such tars could be successfully used commercially.

Cowper
Regenerator

II

The Cowper regenerative process has been used to produce synthesis gas from the tail gas of a hydrogenation plant. A diagrammatic sketch of the regenerator is shown opposite on Figure II. Each of the vertical parts had a cross-sectional area of nine square feet (0.8 square meters) at the top and five square feet (0.5 square meters) at the bottom. The two vertical parts were connected together at the bottom by a masonry-lined chamber. The connecting chamber was open but the vertical parts were filled with refractory; the lower, hotter part with sillimanite, and the upper, cooler part with schamotte. Oxygen or air could be introduced into the open connecting chamber.

The gases to be converted were passed downward through the highly heated side of the furnace, through the connecting chamber where some oxygen was added, and upward through the other vertical part where a part of the sensible heat was given up to the packing. The above flow was maintained for about 30 minutes, the system purged with steam for about

10 seconds, and the fuel gas introduced, preheated in its downward passage, mixed with air in the connecting chamber and burned in its upward passage through the second vertical part. After about 30 minutes on the heating cycle, the system was again purged for about 10 seconds with steam, the valves reversed and the converting cycle repeated, except that the flow of gases was reversed.

The tail gases from the hydrogenation units had an average composition corresponding to $C_{2.2}H_{6.6}$ (about 40% hydrocarbons CH_4-C_5H_{12} and 40% hydrogen). The direct conversion of such a gas with water gave a synthesis gas containing 11-12% carbon monoxide and 77-78% hydrogen, the very high ratio of hydrogen to carbon monoxide being due to the formation of carbon in the process.

Since the tail gases from the hydrogenation units had too low a carbon content to furnish a synthesis gas with a two-to-one ratio of hydrogen to carbon monoxide, tests were made on the regenerative furnace charging both water and carbon dioxide with the tail gas. By this method, a synthesis gas was readily produced which contained about 29% carbon monoxide, 56% hydrogen and only about 0.8% residual methane. In general, the carbon formation was somewhat higher when carbon dioxide was present in the reactants fed to the furnace, amounting to 1-3 grams of carbon per normal cubic meter of synthesis gas.

The carbon formation did not interfere with the operation of the furnace, but the carbon entrained in the synthesis gas had to be removed and the removal was a difficult problem. The carbon formation could be decreased by:

1. Maintaining a higher temperature--2550-2650°F. (1400-1450°C.)
2. By the addition of more oxygen to the gas stream as it passed through the connecting chamber
3. By the use of metal oxides (iron oxide) as packing in the vertical parts of the furnace

The loss of carbon was negligible but the removal of the entrained carbon from the synthesis gas was troublesome. It was thought the carbon formation would be entirely eliminated in a larger furnace, where a more suitable connecting chamber could be used.

The capacity of the Cowper regenerator was 30,000 to 45,000 cubic feet of synthesis gas per hour. This corresponded to 70 to 100 cubic feet of synthesis gas per hour per cubic foot of packed furnace volume or to 20 to 30 cubic feet of tail gas ($C_{2.2}H_{6.6}$) converted per hour per cubic foot of packed furnace volume.

MANUFACTURE OF SYNTHESIS GAS BY THE KELLOGG COMPANY

Scope of Work

Laboratory experiments upon the manufacture of synthesis gas have been carried out which covered the following:

1. Conversion of methane with
   - (a) oxygen
   - (b) carbon dioxide
2. Conversion of city gas with
   - (a) oxygen
   - (b) carbon dioxide
3. The investigation of nickel, nickel-thoria and nickel-ceria catalysts for the above reactions.

The experiments were made in one-inch quartz reactors and in three-inch alloy steel tubes having catalyst volumes of from two to twenty liters.

In addition to the laboratory work, a paper study has been made of the problem of commercial manufacture of synthesis gas.

Laboratory Results

The results from the conversion of methane with oxygen showed that:

1. At temperatures from 1560 to 1650°F. (850-900°C.) synthesis gas could be produced at the rate

Methane and Oxygen

of 500-900 volumes of gas per hour per volume of catalyst, with the conversion of more than 97% of the methane.

2. At a temperature of 1470°F. (800°C.) synthesis gas could be produced at the rate of 500-1400 volumes of gas per hour per volume of catalyst with a conversion of about 94% of the methane.

3. The hydrogen to carbon monoxide ratio in the synthesis gas produced under the above conditions varied from 2.0 to 2.1.

City Gas and Oxygen

The experiments upon the conversion of city gas (53% hydrogen, 30% methane, 6% carbon monoxide) with oxygen showed that practically all the hydrogen present in the original gas was burned to water before substantially complete conversion of the methane was obtained. The water produced caused the conversion of an appreciable amount of the carbon monoxide to carbon dioxide by the water gas reaction.

Methane and Carbon Dioxide

The results from the conversion of equimolar quantities of methane and carbon dioxide showed that:

1. At temperatures from 1425 to 1550°F. (775-850°C.) synthesis gas could be produced at the rate

of 1000 volumes of gas per hour per volume of catalyst while converting the methane to the extent of 84 to 95%.

2. At temperatures from 1550 to 1750°F. (850-950°C.) synthesis gas could be produced at the rate of 400 to 1000 volumes of gas per hour per volume of catalyst while converting the methane to the extent of 95-99%.

3. The ratio of hydrogen to carbon monoxide in the synthesis gas was one-to-one.

City Gas
and
Carbon
Dioxide

The experiments upon the conversion of city gas with carbon dioxide showed that:

1. At a temperature of 1750°F. (950°C.) synthesis gas could be produced at the rate of 600 volumes of gas (containing 4.5% residual methane) per hour per volume of catalyst.

2. At a temperature of 1820°F. (995°C.) synthesis gas could be produced at the rate of 700 volumes of gas (containing 1.5% of residual methane) per hour per volume of catalyst.

3. The ratio of hydrogen to carbon monoxide in the synthesis gas produced under the above conditions was two-to-one.

4. The ratio of hydrogen to carbon monoxide in the synthesis gas could be varied by altering the ratio of city gas to carbon dioxide in the reactants.

Catalysts

Of the catalysts and supports tested, the nickel-thoria or nickel-ceria catalyst on Alfrax (electrically fused alumina) appeared to be the most satisfactory. The superiority of the promoted catalysts over nickel alone lay in the production of less carbon.

Commercial Estimates

The commercial estimates upon synthesis gas production covered:

1. The use of methane and oxygen
2. The use of methane, carbon dioxide, and water in:
    - (a) indirectly heated tubular reactors
    - (b) regenerative furnaces

The preliminary estimates of the cost of synthesis gas production indicated that the use of methane and oxygen or methane, carbon dioxide and water, in tubular furnaces was much more expensive than the last method mentioned above.

Later information has made it desirable to re-estimate the cost of synthesis gas production by the first two methods but the work has not been completed.

The reaction of methane with carbon dioxide and water in a regenerative process seemed the most economical method for synthesis gas manufacture. Furnaces of the regenerative type have been designed to operate at 1800-2200°F. (980-1200°C.) using a space velocity of 500 over a catalyst consisting of fire brick impregnated with nickel. The time of a complete cycle on the regenerators has been set at seven minutes. The furnaces were designed to operate at a gage pressure of 8 pounds per square inch.

MANUFACTURE OF HYDROGEN BY THE SHELL COMPANY

This material upon the production of hydrogen was presented in order to make available long-time commercial experience with large regenerative furnaces of the type which have been proposed for the production of synthesis gas.

Three regenerators were in operation, two of which had been in continuous use for about eight years. In that period of time, no operational troubles had been encountered, the oldest furnaces still containing the original brickwork.

Conversions and Gas Rates

The furnaces were used to decompose natural gas, although it was stated that heavy oils could be used with equal facility. The natural gas contained about 75% methane and 23% ethane and the cracked exit gas contained about 72% hydrogen and 24% methane and ethane, about 64% of the inlet carbon being recovered as elementary carbon. The above results corresponded to almost complete conversion of the ethane and about 50% conversion of the methane. The inlet and the exit gas rates corresponded to approximately four and seven cubic feet of gas, respectively, per hour per cubic foot of furnace volume.

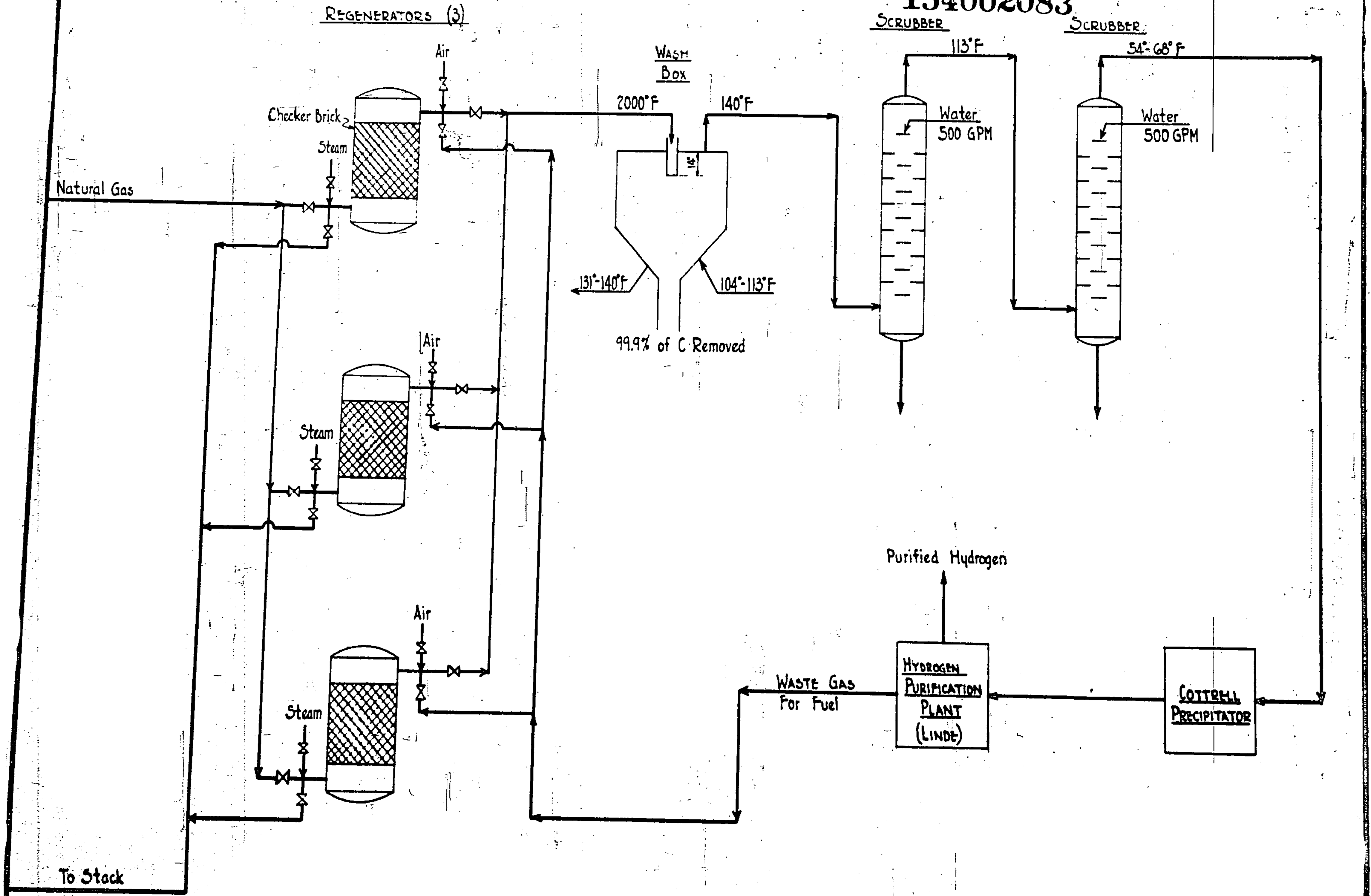

FIGURE III

HYDROGEN FROM METHANE PYROLYSIS (SHELL)

Regenerators

The furnaces had an internal diameter of 20 feet and a height of 55 feet. Each furnace would accommodate a throughput of about 1,750,000 cubic feet of natural gas per day, which corresponded to a cracked gas output of 2,800,000 cubic feet per day. The pressure in the regenerators was 40 to 50 inches of water, and the inlet gas entered the furnace at a pressure of 13-15 pounds per square inch.

The regenerators were manually controlled and were operated on cycles of 20 minutes. The labor requirements were three men per shift per three furnaces. Each furnace cost about $92,000.00 and required an additional blower expenditure of about $10,000.00.

Flow Sheet

Figure III

The diagram opposite (Figure III) shows the flow through the hydrogen production plant. Natural gas was introduced at the bottom of a hot regenerator, was cracked in its upward passage through the hot brick work, and was discharged from the top of the furnace. The hot, cracked gases were passed into a water wash box through a pipe whose outlet was about 14 inches below the surface of the water. About 99.9% of the elementary carbon was separated from the gas in the wash box, the gas being simultaneously

TABLE II

HYDROGEN MANUFACTURE FROM NATURAL GAS
THREE REGENERATIVE FURNACES
NOVEMBER, 1937

Inlet natural gas	157,569,000 cu.ft.	4,223,000 cu.m.
Exit cracked gas	250,283,000 " "	6,710,000 " "
Fuel gas	18,156,000 " "	487,000 " "

Heat consumption	68 B.T.U./cu.ft. gas produced (600 Cal./cu.m.)
Steam "	0.015 lbs./cu.ft. gas produced (0.24 kg./cu.m.)
Water "	15,400 lbs./hr. (7 cu.m./hr.)
Power "	94,000 KWH/month

Temperature - top	2000°F. (1093°C.)
Temperature - center	2060°F. (1127°C.)

20 minute cycle (total)

Operation	Time - mins.
Heat	5.5
Purge	2.0
Make	11.5
Purge	0.5
Blast	0.5
	20.0

Utilities per minute

Wastegas	530 cu.ft.	(15 cu.m.)
Air	13,400 cu.ft.	(380 cu.m.)
Steam	110+ lbs.	(50 kg.)
NaturalGas	2,400 cu.ft.	(68 cu.m.)
Steam	110+ lbs.	(50 kg.)
Air	13,400 cu.ft.	(3800 cu.m.)

Gas Analyses: % by Volume

Constituent	Natural Gas	Cracked Gas	Waste Gas
CO_2	---	---	---
CnHm	---	1.3	4.9
O_2	---	0.1	0.1
CO	---	1.7	3.2
H_2	---	71.3	2.2
CH_4	76.0	23.2	83.1
C_2H_6	22.7	0.8	2.0
N_2	1.3	1.6	4.5
Calorific Values:			
HHV	10,900+	4,750+	9,130+
LHV	9,840	4,170	8,250

cooled from about 2000°F. to 140°F. (1100 to 60°C.). The gas leaving the wash box flowed through two direct water-contact coolers, where the temperature was lowered to 54-68°F. The gas then passed to a Cottrell precipitator in order to remove the last traces of carbon. Hydrogen was separated from the clean gas in a Linde-type plant, the hydrogen going to the ammonia synthesis plant and the residual gas was burned in the furnaces.

Operating Data

The statistics in the tabulation opposite, (Table II), were given as representing typical operating data, being taken from operating results for the month of November, 1937. The figures refer to the overall operation of the plant, that is, three regenerators operating for thirty days.

Table II