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I. SYNTHESIS GAS

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MANUFACTURE OF SYNTHESIS GAS

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.

Procedure

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

Gas
Generators

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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.

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

Gas
Composition

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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	10,650
H ₂	50.7	63.9	55.3	629,000	301,000	735,000	17,730	8,430	21,370
CH ₄	0.4	0.3	0.4	5,000	1,400	5,500	150	40	150
N ₂	5.1	2.3	2.8	38,400	10,900	35,200	1,020	310	1,000
Total	100.0	100.0	100.0	1,240,000	471,000	1,355,000	33,000	13,270	35,650

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

The harmful impurities in the synthesis gas were:

Gas Purification

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

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
Removal

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

Hydrogen
Sulfide
Contact

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.

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).

Hydrogen
Sulfide
Content

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.).

Organic
Sulfur
Removal

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% carbon-oxy sulfide 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.

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.

Preheating
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.

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

Contact
Chambers

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

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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.

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 140,000 pounds (65 tons), or 5500 cubic feet (160 cubic meters), of

Gas
Rates

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.

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.

Life of
Contact

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

Sulfur
Content

	<u>Inlet</u>	<u>After 1st Tower</u>	<u>After 2nd Tower</u>	
H ₂ S - 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 ₂ S - 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.

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:

Contact
for Organic
Sulfur
Removal

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

Luxmasse

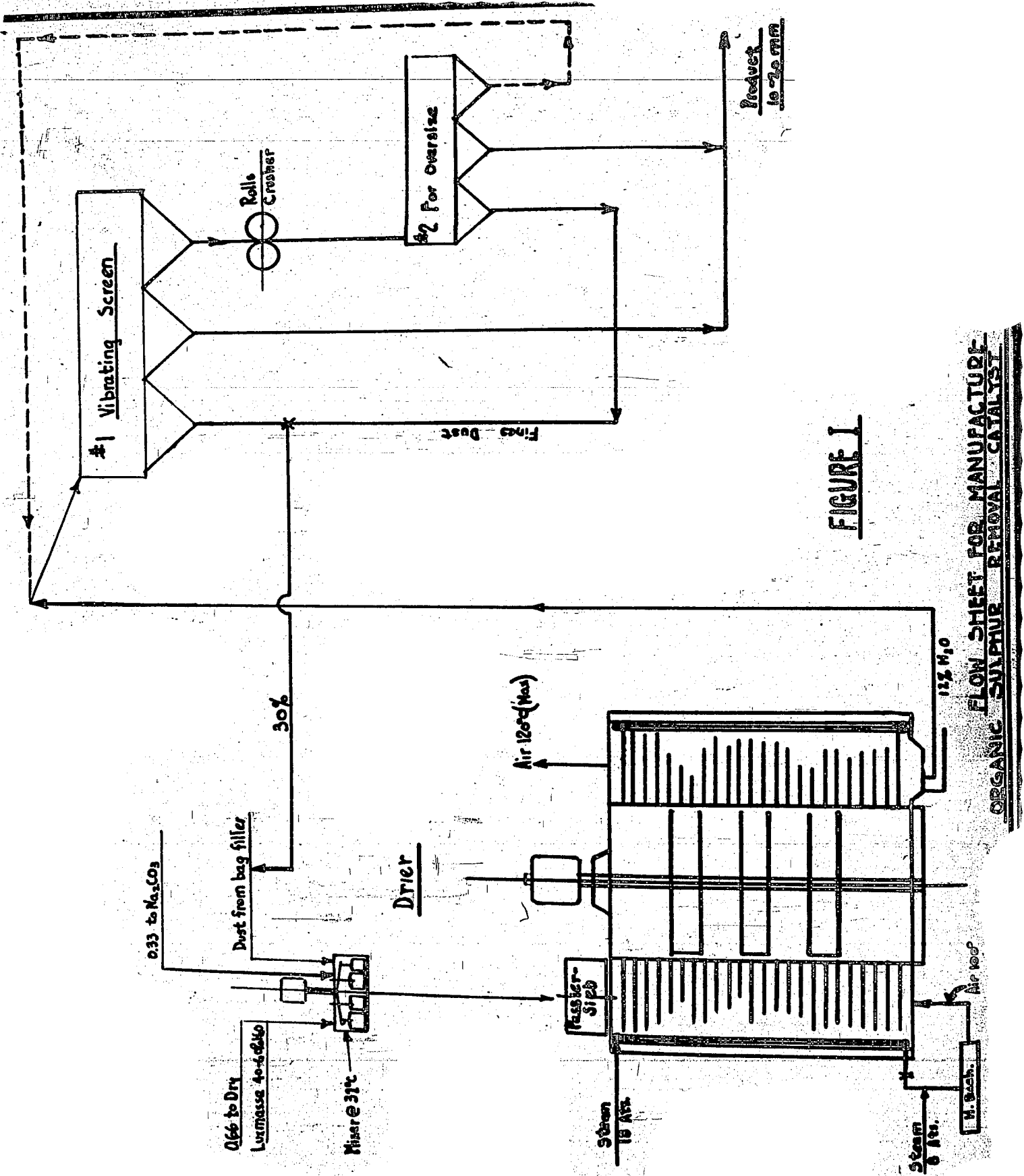


FIGURE I

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.

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.

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.

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

Soda

Flow Sheet
for
Manufacture
of Contact
for
Organic
Sulfur
Removal

Figure I

Mixing
Luxmasse
and Soda

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.

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

Extrusion
of the
Mixture

the perforations.

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

The Passiersiebs were of two sizes:

Extruders

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.

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.

Drying the
Extruded
Contact

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.

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.

Sizing

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.

Capacity
of Plant

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.