under these conditions reaction rates in the generator are low, and a state of equilibrium is not attained. It follows that the reactivity of the fuel is an important factor governing the degree of completeness of reactions and the composition of the gas made. A study of the basic gas reactions enumerated above with reference to these variables is helpful in understanding the reasons for certain operations employed in making gas by processes described in this publication.

Figure 1[3] shows the logarithm of the equilibrium constants for the reactions shown by equations (1) to (10). Although the rates of reaction are not indicated by the curves in this figure, the effect of changes in temperature upon the equilibria are clearly shown. In making ordinary water gas by reactions typified by equations (1) and (2), experience has shown that, at the average prevailing high temperatures the net result is substantially 90 to 92 percent of (1) and 10 to 8 percent of (2). Perhaps a more accurate statement of fact would be that the CO_2 formed by reaction (2) at high temperatures reacts with carbon of the fuel bed according to equation (6). The computed approximate composition of water gas made from carbon at equilibrium is shown in figure 2, over an appreciable range of temperature. The formation of CH_4 by reactions shown in equations (7) to (10) occurs to a limited extent only at high temperatures, whereas at low temperatures and at atmospheric pressure the latter reactions do not proceed at a rate usually considered sufficiently rapid for commercial application. Actually, in the low-temperature range of figure 2 some CH_4 is formed, but in actual commercial operations the amount formed at atmospheric pressure is less than indicated by the CH_4 curve, because the rate of reaction is normally slow and equilibrium is not approached.

Effect of Pressure upon the Composition of Gas

In the instance under particular consideration here, namely the production of gas in a Lurgi generator, the temperature of the fuel bed is rather low, for reasons which will become evident; hence, one must consider not only the nature of the gas that would be formed when a state of equilibrium is reached at the given temperature and pressure, but also the probability of approaching such a state when gas is generated at reasonably high velocity. The change in composition due to the use of O_2 with the steam must also be considered. Figure 3 shows the computed composition and calorific value of gas made when steam alone is reacted with carbon at 1,000° C. (1,832° F.) at different pressures; the values plotted are not absolute but are believed to be accurate enough to indicate the effects of change in pressure at the given temperature. It is obvious from the latter figure that as the pressure is increased reactions such as those shown, particularly in equations (7) and (10), occur increasingly; pressure favors these reactions. The total amount of CH_4 present, even at 20 atmospheres pressure and at the given temperature, is not large. Figure 4 is a plot showing variations in composition and calorific

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[3] Wagman, Donald D.; Kilpatrick, John E., Taylor, William J., Pitzer, Kenneth S., and Rossini, Frederick D., Heats, Free Energies, and Equilibrium Constants of Some Reactions Involving O_2, H_2, H_2O, C, CO, CO_2, and CH_4: Research Paper RP-1634, Journal of Research, National Bureau of Standards, vol. 34, February 1945, pp. 143-161.

value of raw gas with change in pressure at 1,340° F., employing O_2 and steam as gas-making fluids; the plot is based upon theoretical values established by the German engineer Otto Hubmann.[4] The temperature chosen for making this plot was lower than that used in figure 3, and, therefore, the conditions are more favorable for the formation of CH_4 when chemical equilibria are reached. In actual operation, one would expect the amount of methane formed to be lower than that shown in figure 4, and such was found to be the case. The hot zone or region of the fuel bed in which the combustion reactions of O_2 with the fuel are initiated and consummated is thinner in the Lurgi process than in ordinary practice making water gas. Furthermore, employing coals of low ash-softening temperatures and maintaining a maximum temperature in the fuel bed lower than the ash-softening point, there is a large volume of relatively low-temperature fuel through which the gas passes in the generator. Under these conditions one would expect to produce a gas containing less CO, more CO_2, and somewhat more H_2 than shown in the gas compositions in figure 4. Results obtained in practice are in accordance with expectations.

Referring again to equations (7) to (10), it will be noted that they are not only favored by increase in pressure but they are exothermic; hence, as the pressure is increased and these reactions occur increasingly, more heat is liberated in the fuel bed by them, and accordingly less O_2 is required in making gas. In considering equations (1) and (7) collectively, one might express the result by equation (11) as follows:

$$(11)\quad 2C + 2H_2O = CH_4 + CO_2 \quad - 44{,}820 \text{ B.t.u.}$$

In this reaction, 2 mols of gas are formed with the absorption of only 44,820 B.t.u., whereas in equation (1) 75,535 B.t.u. are required in producing the same volume of gas. However, twice as much carbon and steam are required to satisfy equation (11) as equation (1), but the gas made in (11) is 57 percent higher in heating value. In equation (11) excess steam, high pressure, and relatively low temperatures are favorable for CH_4 formation, whereas at high temperatures the reaction does not occur, but instead CH_4 and CO_2 combine to form CO and H_2.

Actual operating data[5] indicating how the composition and calorific value of the raw gas, made by gasifying reactive coal with O_2 and steam, varies with change in pressure are shown graphically in figure 5. The analyses used in plotting the latter figure were corrected for small amounts of N_2 initially associated with the O_2 used. The fuel used in making the gas was small (3/32- to 7/32-inch) and comprised broken pieces of briquetted, partly dried brown coal containing 20 to 25 percent moisture. The figure shows that the CH_4 content of the gas increases rapidly with increase in pressure up to about 10 atmospheres, but from 10 to 20 atmospheres the rate of increase diminishes with increasing pressure. In other words, as the CO_2 and CH_4 increase, conditions are not so favorable for the formation of more CH_4. The calorific value of the raw gas likewise increases with pressure.

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[4] Hubmann, O., Metallges: Periodic Rev., No. 8, 1934, pp. 9-15.
[5] Danulat, F., Mitt. Metallges, No. 13, 1938, pp. 14-22.

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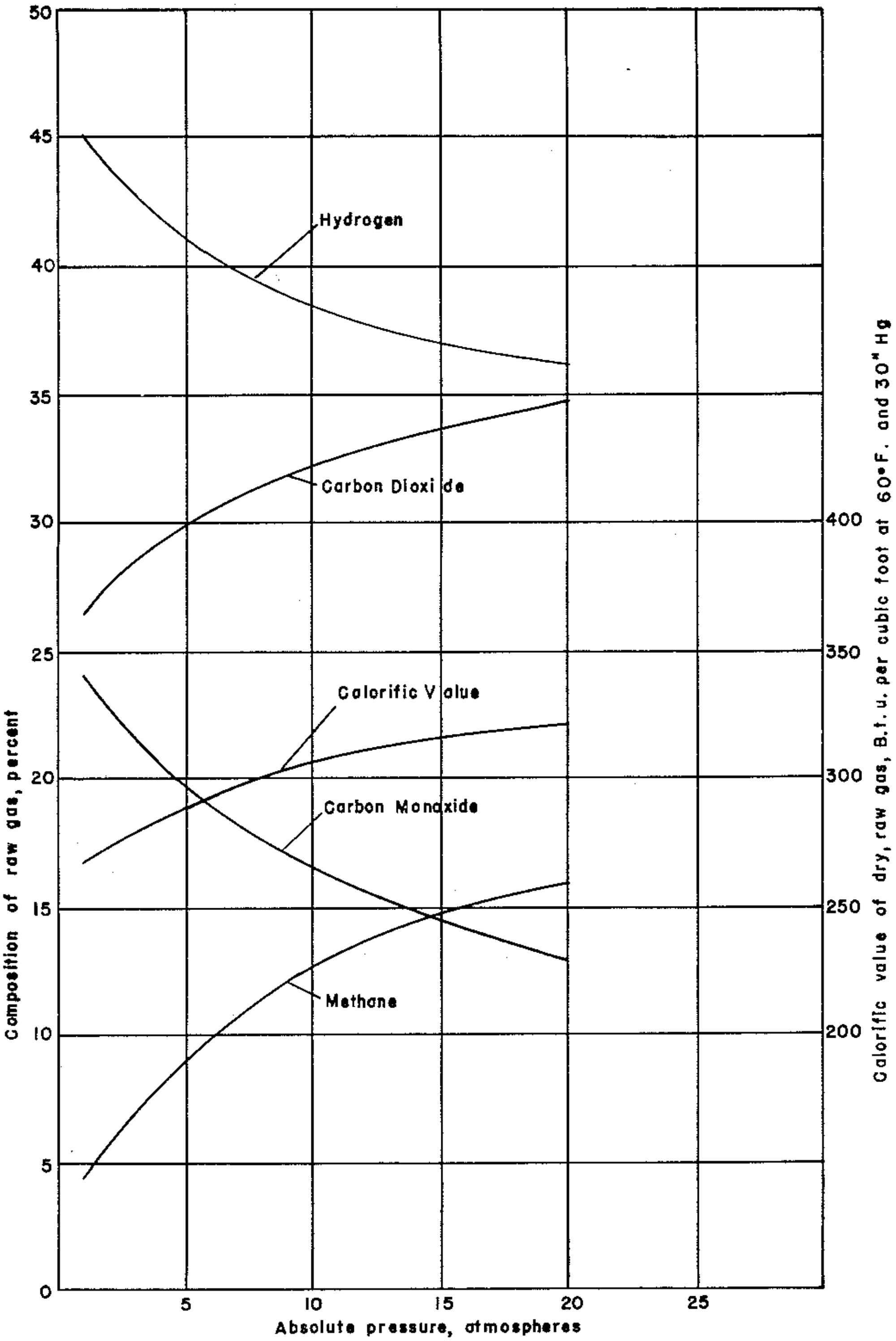

Figure 5.- Variation with pressure in composition and calorific value of raw gas as made in practice from brown coal, employing oxygen and steam as gas-making fluids.

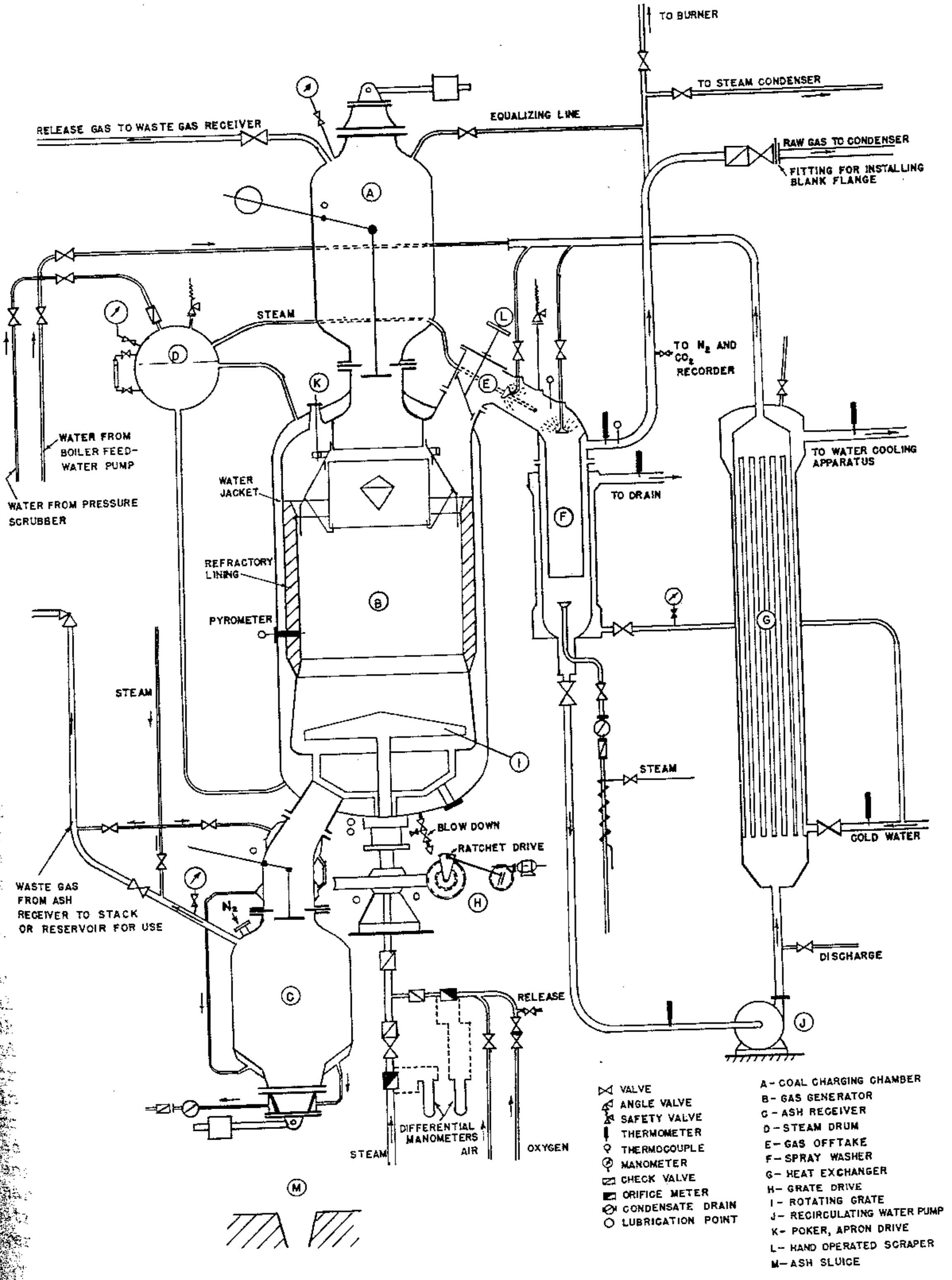

FIGURE 6.- DIAGRAM OF A LURGI HIGH-PRESSURE GENERATOR.

The Lurgi Gas-Generating Plant and Its Operation

In figure 6 is shown a sectional view, somewhat diagrammatic, of a Lurgi high-pressure gas generator and connections. The coal hopper, A, supplies coal to the generator, B, from which the ash is discharged beneath rotating grate I into ash reservoir C. Oxygen and steam are supplied through the conduits indicated to the hollow shaft, from which the mixture enters the generator from beneath the grate. The whole generator is water-jacketed, whereby some steam is generated and used as shown; the steam drum is designated D. The gas offtake, E, connects directly with a spray-cooler, wherein the gas discharged from the generator is immediately contacted by a water spray and cooled; the heavy tar condenses and is removed from the gas stream in this cooler, and the gas passes on to the regular scrubbing and purifying units. Only a portion of the generator is lined with refractory insulation, namely, that at and above the hottest portion of the fuel bed.

The generator is 16.40 feet high and has an external diameter of 9.84 feet and an internal diameter of 8.86 feet. The width of the annular space varies, as shown, from approximately 4.7 to 5.9 inches. The lining extends from substantially the top of the cylindrical portion of the generator down to within 3.25 feet of the grate. The fire bricks used for this purpose have been in service 4 years without replacement. Although the water jacket is connected with steam drum D of figure 6, the actual amount of steam generated is very small, being less than 132 pounds per hour in regular operation. This steam is conducted, as generated, directly to the gas offtake, so that the pressure inside the generator is the same as that within the water jacket.

The coal hopper, A, of figure 6 comprises a chamber approximately 9.8 feet high and 5.2 feet in diameter made of boiler steel. It has two valves, the upper one communicating with an overhead fuel bunker of 65 tons capacity and the lower one connecting the hopper with the generator; these valves are manually operated. The procedure for charging the hopper is as follows: The bottom hopper valve is closed, and the gas in the hopper is blown under its own pressure into a special holder provided for the purpose and is subsequently used as fuel for superheating the gas-making steam. The upper valve is now opened (lowered); this operation permits a cylinder supported by the valve to be lowered to an extent controlled by specially provided lugs, allowing the coal to flow through the cylinder from the bunker into the hopper. The upper valve is closed when the hopper is full. When the latter valve is raised, it makes contact with the movable cylinder, thus shutting off the supply of coal and leaving the valve clean. Gas is now let into the hopper from the generator, and subsequently the bottom hopper-valve is opened. It takes 5 to 6 minutes to charge a hopper, which is done about twice an hour. The total amount of gas blown to the holder from the hopper is 7 percent of the total gas made; it is not included in the reported volume of "make gas." Ventilating fans with conduits are provided to remove any gas escaping from the coal-charging valves. The coal bunkers are continuously purged with inert gas - nitrogen in this case - because the fuel used was highly reactive and was transported at a temperature of 80° C.

The top valve of the hopper, made of special alloy steel, seats against a rubber ring gasket which fits dovetailed into the top of the flange of the hopper. The normal life of this ring is about 3 months. The bottom valve of the hopper has a removable, conical, hard-steel insert, which contacts a chrome alloy-steel, sharp-edged seat, which is renewed yearly. The free opening of both valves is 10 inches.

A shield or skirt is provided in the generator beneath the coal inlet for the purpose of maintaining a free gas space above the fuel bed and supporting scrapers for removal of pitch and carbon from the upper wall of the generator. These scrapers are operated once every 1 to 2 hours for a period of 5 minutes. Inside of the skirt a conical ring is suspended, beneath which is a double cone for the double purpose of avoiding segregation of the fuel and equalizing the pressure across the fuel bed.

An essential step in operating the plant is to prepare the fuel, namely, crush, screen, and separate the dust and coarse particles from the desired sizes. Using the lignitic-type coal (Braunkohle) in Germany, the preferred sizes supplied to the generator are within the chosen limits, 0.12- to 0.39-inch. The coal as mined contains about 50 percent of water; a portion only of this water is eliminated by a drying operation before it is charged. It has been found desirable to leave 20 to 25 percent of moisture in the prepared fuel; it is fed to the fuel-supply hopper in this state.

Gasification is substantially continuous in the Lurgi generators. The time interval between charging the coal hoppers, which is, of course, dependent on their size, was approximately 20 minutes with the old generators at Böhlen, but with the new ones now in operation there the charging interval is approximately 40 minutes.

The grate is slightly domed and comprises three sections, in each of which is fitted a detachable portion that incorporates a plough arranged to direct the ash, which passes over the grate into a cylindrical space beneath the grate. A vertical vane, which is attached to the grate shaft, scrapes the ash into an offtake leading to the ash reservoir. The diameter of the grate is 5 feet 3 inches; the middle of the grate, on the top side, is 6 inches above the portion adjacent the generator wall. The grate sections are alloy steel (25 percent chromium) and are said to have a life of 3 years. The drive shaft of the grate is hollow to provide means for introducing a mixture of superheated steam and O_2 into the fuel bed. The grate is electrically driven by a 4.5-kw. motor connected with speed-control gearing and ratchet mechanism. The grate and driving mechanism are supported by the generator shell. The shaft is packed with metal-asbestos packing rings with provision for lubrication.

A bed of ashes is maintained in the generator to a considerable depth to protect the grate from rapid deterioration. Upon leaving the generator, the ash passes into the ash reservoir shown at C of figure 6, through a valve similar to the bottom valve of the coal hopper, except that its diameter is 1 foot instead of 10 inches. The ash reservoir is 9 feet 10 inches high and 4 feet 3 inches in diameter; its capacity is 124 cubic feet. The bottom of the reservoir is closed by a disk clamped by four swing bolts; a thin Klingerite packing ring set in the disk forms the actual joint and it is renewed after three discharges of ash. This reservoir is steam-jacketed, in part, to prevent condensation during cooling of the ash. The ash is discharged through a sieve into a water sluice approximately every 2 hours. When the pressure is released on the reservoir, prior to removing the ash, the oxygen and steam released pass into the atmosphere; whereas, after closing the reservoir the pressure is built up to working level by introducing live steam.

Apparently there have been no difficulties with clinker formation except during periods of irregular or abnormal operations; the ash as discharged is usually in fine granular condition. Clearly it is necessary that the temperature throughout the hot zone be lower than the ash-softening temperature at all times in order to avoid clinker troubles; this means that the temperatures must be carefully watched and controlled by proper adjustment of the relative amounts of steam and O_2 admitted to the generator.

The grate is rotated at a rate adapted to prevent excessive accumulation of ash, the speed being adjusted in accordance with the ash content of the fuel used and the rate of making gas. The usual speed is 1/2 to 2 revolutions per hour. The ash discharged contains 5 to 7 percent of carbon.

Using a fuel such as partly dried brown coal, containing 20 to 25 percent of water, the temperature of the gas leaving the generator is approximately 300° C. The gas contains tar and dust, which in the early stages of development of this process were troublesome. Various scrubbing methods were employed experimentally. The most satisfactory method thus far developed for solving these difficulties is the partial cooling of the gas by direct contact with water immediately after it leaves the generator and simultaneous promotion of rapid change in direction of flow of the gas stream; the means of accomplishing this are shown at F in figure 6.

The tar is discharged from the latter scrubbing device through a separate drain, and the excess water is recirculated through a heat-exchange cooler back to the scrubber. The gas enters the scrubber at about 300° C. under 20 atmospheres pressure and leaves at about 150° C. Subsequently, the gas passes through tubular coolers, wherein it is further cooled to 100° C., and then through baffle-type tar separators. Finally, after further cooling the gas, the condensed light oils are removed and the gas is oil-scrubbed for recovery of benzole.

The treatment of water gas for removal and recovery of tar and oil is not common practice in the United States for two reasons - (1) fuels that evolve tar and oil during the process are not commonly used, and (2) the temperature reached by the gas in the generating equipment is so high that the byproducts produced do not warrant their recovery. This statement does not apply to carbureted water gas or to gas made for special uses when it is necessary to remove certain byproducts.

After condensable products have been removed from the gas, the latter is scrubbed with water under pressure for the removal of CO_2 and H_2S. The total gas from the plant at Böhlen is passed in parallel through four scrubber towers packed with Raschig rings. The water, which is recirculated, is first delivered at high pressure to the scrubbing towers and then, after absorbing CO_2 and H_2S, it is expanded to atmospheric pressure through turbines similar to the Pelton wheels commonly used in this country for the same purpose. Subsequently the water from these scrubber towers is passed down through another series of four towers, which are packed with wooden grids while air is blown upwardly through the latter towers; this treatment removes the remaining H_2S from the water, conditioning it for recirculation. The air from the latter towers, laden with H_2S, is passed to the bottom of the powerhouse chimneys, where the H_2S reacts with SO_2 in the stack gas, forming sulfur, which is carried along in the stack gas and discharged into the atmosphere. After washing, the gas passes to Lux purifiers. These consist of two parallel sets of four boxes each, three of which are used while one is being recharged with oxide. The working life of a charge is approximately 4 weeks. The boxes are cylindrical, approximately 5 feet in diameter and 26 feet high; each contains 5 double trays with layers of oxide 16 to 18 inches deep, whereby the gas flows in parallel through the 10 layers in each box. The three boxes in use on each stream are worked in series. The gas entering the boxes contains 10 to 30 grams of H_2S per 100 cubic meters, which is equivalent to 4.1 to 12.3 grains per 100 cubic feet, and on leaving the boxes it contains 0.1 gram per 100 cubic meters, equivalent to 0.04 grain per 100 cubic feet. The amount of Lux purifying material used per annum was approximately 33 short tons. The total pressure loss in treating and purifying the gas was approximately one atmosphere.

Steam is supplied from the adjacent power station and is superheated to 500° C. by means of waste gas from the charging hopper and from the CO_2-removal plant before it enters the generators.

Oxygen is supplied from a Linde-Frankl plant on the premises. The latter plant comprises four units, two of which have a capacity of 37,000 cubic feet per hour and two 74,000 cubic feet per hour of free-oxygen measured as dry gas at 60° F. and 30 inches mercury pressure. The oxygen used is approximately 95 percent pure O_2 and is supplied to the generators under pressure of 23 atmospheres at 40° C. The power capacity of the oxygen plant is 4,600 kilowatts.

<u>Some operating results making gas in the Lurgi pressure generator at Böhlen, Germany (average for month of January 1945):</u>

Kind of coal used	Broken pieces of partly dried and briquetted braunkohle and partly dried braunkohle.	
Size of coal used	mm.	3 to 10 (about 1/8- to 3/8-inch)
(Not more than 5 percent under 3 mm. and not more than 10 percent above 10 mm.)		
Purity of O_2 used	percent	95
(Results are reported on the basis of quantity of equivalent pure O_2 used.)		
Composition of coal:		
Moisture	percent by weight	18 to 22
Volatile and fixed carbon	do.	70 to 74
Ash	do.	8.0
Total sulfur	do.	2.8
Divided: Sulfur in ash	percent by weight	1.2
Combustible sulfur	do.	1.6

Calorific value of the coal (high value)...B.t.u. per lb.	7,820 to 8,450
Speed of rotation of grate..........revolutions per hour	1/2 to 2
Purified gas made month of January...............cu.ft. (measured at 60° F., 30 inches mercury pressure, dry)	460,015,200
Purified gas made per day........................cu.ft. (measured at 60° F., 20 inches mercury pressure, dry)	14,839,000
Purified gas made per generator, per hour, mean....cu.ft.	89,280
Rated capacity of generator per hour.....cu.ft., dry gas	111,600
Total coal used per month..............U. S. short tons	21,560
Total coal used per day.................................do.	695
Coal used per 1,000 cubic feet of purified gas.........lb.	93.6
Oxygen used per day (measured at 60° F., 30 inches mercury, dry).................................cu.ft.	2,158,700
Oxygen used per 1,000 cubic feet of purified gas made (measured at 60° F., 30 inches mercury, dry).........do. (Oxygen is given as pure O_2; actually, somewhat larger amounts of 95 percent O_2 were used)	146
Steam used, per month....................U. S. short tons	20,001
Steam used, per day......................................do.	645.2
Steam used, per 1,000 cubic feet of purified gas made, to generator..lb.	87
Steam used, total per 1,000 cubic feet of purified gas made...lb.	114.9
Power consumption, per 1,000 cubic feet of purified gas made...kw.-hr.	7.36
Water used, per 1,000 cubic feet of purified gas.U.S. gal.	142

Average gas composition (January 1945):

	Crude gas	Purified gas
CO_2..............................percent by volume	32.1	9.1
H_2S..do.	1.6	0.0
Illuminants...do.	0.7	0.6
O_2..do.	0.2	0.2
CO..do.	12.1	16.7
H_2..do.	37.5	52.3
CH_4..do.	14.5	20.0
N_2..do.	1.3	1.1
	100.0	100.0
Calorific value (high value):		
Basis dry gas at 60° F., 30 inches mercury pressure ....B.t.u. per cu.ft.	331.1	438.0
Basis saturated gas at 60° F., 30 inches mercury pressure...do.	325.3	430.4
Basis calorimeter test (calculated to dry gas at 0° C. and 760 mm.)...................................do.	-	a/432
Specific gravity (air = 1.0)	0.753	0.499

a/ The calorific value of the gas usually made at this plant is said to be about 5 percent higher than the above values, and the reason given was "bombing interfered with plant operations."