(a) Increased production of water gas,

(b) Increased H_2 to CO ratio in the gas made, and

(c) Increased amount of carbon in the ash.

The ash comprised to a large extent pieces of coke cemented into agglomerates with mineral matter that had been partly fused. The actual combustible matter (carbon) in the agglomerates was 50 to 55 percent. The latter were not discarded but were washed to remove fines and dust and were then used as charging stock to the slagging gas producers. With this fuel it was not necessary to introduce additional (recirculated) slag, although at times it was necessary to add some lime to the charge. The gas made in the producer, when operated in this manner, was equally as satisfactory as that made from fresh coke; however, the rate of make, or gas-making capacity, was lowered to 340,000 cubic feet per hour, a decrease of 28.5 to 33 percent from maximum capacity with lump coke.

Remarks

The value of this process of making gas under conditions in the United States depends on a number of factors, including the cost of O_2. The high gas-making capacity relative to that obtained in other processes making the same kind of gas favors the slagging-type process. The fact that the operation is continuous also favors the latter. Against these advantages must be weighed the cost of the required O_2, cost of recirculating slag, and difference in the cost of generator fuel above that of generator fuel used in other processes. The progress made thus far in Germany indicates that screened fuel having a minimum size of 1-1/2 inches is required. The gasification efficiency is high, as indicated by the gas composition and the fuel consumption per 1,000 cubic feet of gas made.

Even though operating costs were not obtained with reference to the production of gas in the slagging-type producer, the data obtained indicate the usefulness and limitations of the latter producer in making synthesis gas. Figure 10 shows the effect of changes in the costs of oxygen and coke upon the total cost of gas-making materials per 1,000 cubic feet of gas made; it also indicates comparatively the changes in the cost of materials used in making water gas with variations in the cost of generator fuel. On the basis of these costs (gas-making materials only), the use of oxygen at a net cost of 20 cents per 1,000 cubic feet, making the producer gas as described, is not economical, compared with the ordinary water-gas process, until the cost of coke reaches $7.50 or more per ton. However, with a net cost of oxygen at 10 cents per 1,000 cubic feet, the cost of gas-making materials is substantially the same for both gases (producer and water gas) when coke costs $3.20 per ton. Thus, the economy in making the producer gas with oxygen is greater, as the net cost of oxygen decreases and the cost of coke increases. Accurate total or operating costs of making producer gas with oxygen are not available to the author, but it seems reasonable to assume that the benefits derived from high gas-making capacities are not entirely neutralized by other costs characteristic of this process; hence, with the prevailing cost of coke, it may be

advantageous to make gas in a slagging-type producer with oxygen instead of by the standard water-gas process when the net cost of oxygen decreases to 10 cents or less per 1,000 cubic feet.

The foregoing comparison was made on the basis of the production of a unit volume of gas without consideration of differences in composition of the gases made or their relative usefulness in producing synthesis gas or hydrogen. The H_2 to CO volumetric ratio in water gas usually is 1.25, whereas in the producer gas this ratio is 0.41. Accordingly the extra cost of conversion to the desired gas must be considered before any advantage in the production of gas by the use of oxygen in a slagging-type producer can be proclaimed. When hydrogen is the end product sought it will be necessary to treat all of the latter gas whereby the 68 percent of carbon monoxide normally present therein is converted by the "shift reaction" to an equivalent amount of hydrogen. This reaction ($CO + H_2O = CO_2 + H_2$) is conducted at $400°$ to $450°$ C. in the presence of an iron-oxide catalyst and requires an excessive amount of steam. If, on the other hand, the gas sought is synthesis gas having a ratio H_2 to CO equal to 2, only a portion of the producer gas need be treated in this manner, namely, about 60 percent when allowance is made for incompleteness of the reaction with such a high initial carbon monoxide content. In each case the carbon dioxide formed is scrubbed out of the resulting gas.

Cost of Oxygen

Of recent years the subject "cost of producing oxygen" has been of increasing interest to gas engineers because the natural belief exists that the cost will progressively decrease with time, which is usual for other products of manufacture when demand warrants their use. The cost of making O_2 has already decreased over the past 10 years, and there is little doubt that it will be produced in the future at a lower cost. Using high-priced fuels, the cost of O_2 may be vitally important, but in gasifying low-cost fuels a greater charge for the required O_2 may not be prohibitive. In other words, when one can substitute a low-cost fuel for an expensive one in making gas, the cost of using O_2 with the former may be more than offset by the savings in the cost of fuel.

The cost of O_2 as made in a large plant in Germany operated in conjunction with another plant that consumes O_2, as given to the author by the head of a large construction company interested in erecting oxygen plants, is 2.3 to 2.5 Pf. per normal cubic meter, which is equivalent to 24.7 to 26.9 cents per thousand cubic feet of dry O_2 measured at $60°$ F., and 30 inches mercury pressure; this equivalence is based upon one Mark being equal to 40 cents. Electric power cost was 0.6- to 0.7-cent per kw.-hr. On this basis, and taking 18 kw.-hr. as the power consumption per 1,000 cubic feet of O_2 produced, the cost of the electric current required was equivalent to 10.8 to 12.6 cents per 1,000 cubic feet of O_2. Obviously, the cost of O_2 would be reduced by about 3.6 cents per 1,000 cubic feet if the cost of power were reduced to 0.4 cent per kw.-hr., making the over-all cost 21.1 cents. To verify this cost estimate, data were obtained from a large chemical plant operating a large Linde-Frankl O_2 plant as a part of the whole works. In this case the cost of O_2 was said to be 1 Pf. per normal cubic meter (19.3 cents per 1,000 cubic feet) when

Cost of the oxygen used per 1,000 cubic feet of gas made, cents

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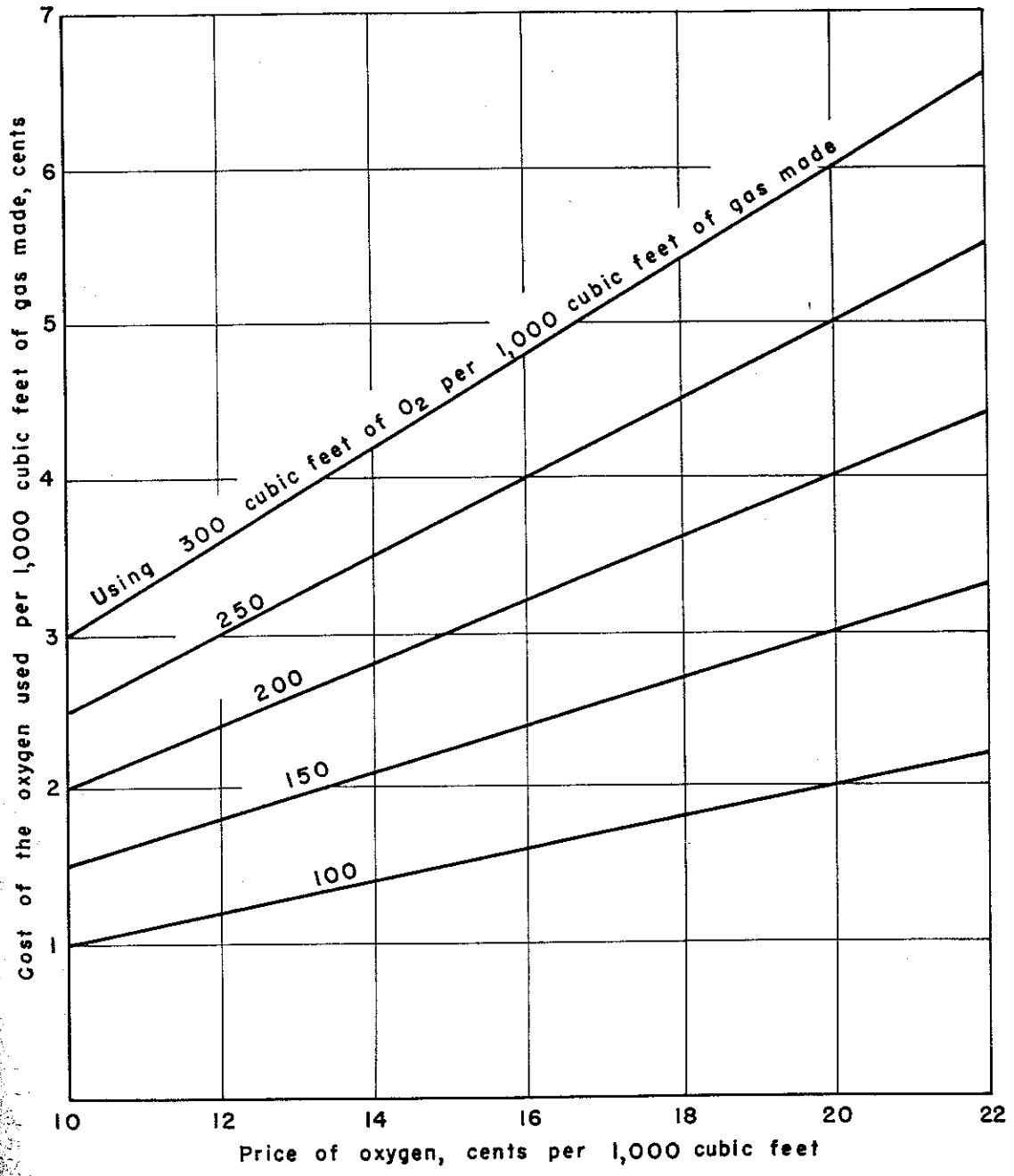ent per
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Figure 11.— Cost of the oxygen used in making gas, with variously priced oxygen, using 100 to 300 cubic feet of it per 1,000 cubic feet of gas made.

electric power cost was 0.4 cent per kw.-hr. Although this is a reasonably accurate estimate, it was stated by an operator at the chemical plant that the cost of O_2 could be divided as follows:

	Percent of total cost
Electric power	60
Amortization	30
Other costs	10
	100

If this "break up" of cost is correct, and O_2 costs 19.3 cents per 1,000 cubic feet, the cost of power would be $\frac{60 \times 19.3}{100}$, or 11.58 cents, and the amount of power used accordingly would be $11.58 \div 0.4 = 28.95$ kw.-hr. per 1,000 cubic feet of O_2 produced. This is at variance with the above estimate. Other checks on the cost of O_2 lead to the conclusion that whereas the cost in previous years in Germany was stated to have been 4 to 5 Pf. per normal cubic meter (43 to 53.6 cents per 1,000 cubic feet), improvements made in the process of recovering O_2 from air have lowered the cost materially, so that in the combination of an oxygen plant with a manufacturing plant consuming O_2 the cost is in the approximate range 19 to 24 cents per 1,000 cubic feet. The prospects are that the cost will be lowered further when application is made to industry in the United States.

In all gas-making processes in which O_2 is substituted for air as a gas-generating fluid, the cost of the O_2 consumed must at least be equaled by economies that might be made by virtue of such substitution. In other words, the cost of the fuel used, labor, or other items contributing to the total cost of gas must decrease when air is replaced by O_2. Figure 11 indicates what this economy must be; the figure shows the cost of O_2 per 1,000 cubic feet of gas made for variously priced O_2 and for varying O_2 requirements. The higher the cost per 1,000 cubic feet of O_2 the greater must be the economies neutralizing this cost.

SUMMARY AND CONCLUSIONS

1. Three gas-making processes have been discussed, each of which employs free oxygen as a gas-making fluid; they differ from those in common use in this country.

2. Two of these, the Winkler and the Lurgi pressure gasification process, are unique, in that they use generator fuel in a finely divided state. They apparently have been developed as a means of gasifying certain solid fuels readily available in parts of Germany where other gas-making fuels were scarce. The conditions for gasification have been discussed. The use of oxygen in these two processes has made practicable the gasification of solid fuel that cannot be utilized in ordinary gas generators. It is believed that the Winkler process as now developed and the Lurgi process with some improvement or in a modified form may be used effectively under certain conditions and with particular fuels in this country; this is especially true when the costs of fuel and oxygen are very low.

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3. The other process referred to above employs the slagging-type gas-producer principles. The gas thus made differs from ordinary producer gas; its calorific value is higher, and its composition is different from that of the latter gas. Mixtures of oxygen and steam are used as gas-making fluids, and they are so proportioned that a temperature suitable for slagging the ash is maintained in the fuel bed. Slag is withdrawn at intervals of 20 minutes. Normally the fuel used was furnace coke freed from fines and sized by screening 1-1/2 inch and larger. Lime was added to the fuel charged, and required amounts of slag were recirculated (the cooled, crushed slag was recirculated). In a particular case, the lime used amounted to 3 percent of the fuel charged, whereas the amount of slag recirculated was about 20 percent of the total fuel charged.

4. Some operating data relative to the three processes are presented and discussed; they are summarized in table 4 for the purpose of comparison, as follows:

TABLE 4. - Operating data for Winkler, Lurgi, and slagging-type gas generators

	Winkler continuous water-gas process	Lurgi (20 atmospheres pressure) water-gas process[a]	"Slagging" producer-gas process
Fuel used............................	Carbonized brown coal	Partly dried brown coal (22% water)	Furnace coke
Size of fuel used............inches	0.12 to 0.40	0.12 to 0.40	1-1/2 and larger
Fuel used in generator, pounds:			
Per M. cu. ft.[b] of raw gas......	47.04	67.8	26.7
Per M. cu. ft.[b] of gas, free of H₂S and CO₂....................	62.15	102.0	27.7
Per 300,000[c] B.t.u. in the gas.	59.36	69.6	25.8
Per M. cu. ft.[b] of purified gas (9.1% CO₂)...................	-	93.6	-
Oxygen supplied to the generator, cu.ft.:			
Per M. cu. ft.[b] of raw gas......	243	106.6	250
Per M. cu. ft.[b] of CO₂-free and H₂S-free gas....................	321	160.8	259
Per 300,000[c] B.t.u. in the gas..	307	100.7	241
Per M. cu. ft.[b] of purified gas (9.1% CO₂)...................	-	147	-
Steam supplied to the generator, pounds:			
Per M. cu. ft.[b] of raw gas......	29.1	63.2	22.4 (470 cu.ft.)
Per M. cu. ft.[b] of gas free of H₂S and CO₂....................	39.5[d]	95.3	23.2
Per 300,000[c] B.t.u. in the gas..	37.7	59.7	21.6
Per M. cu. ft.[b] of purified gas (9.1% CO₂)......................	-	87.2	-

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TABLE 4. - Operating data for Winkler, Lurgi, and slagging-type gas generators-Continued

	Winkler continuous water-gas process	Lurgi (20 atmospheres pressure) water-gas process a/	"Slagging" producer-gas process
Gas made per square foot of generator area (horizontal cross section) per hour, cu. ft.:			
Raw gas b/	10,500	1,990	6,350 c/
Gas free of H_2S and CO_2	7,950	1,320	6,230
Therms (100,000 B.t.u.)	24.96	6.3	19.74
Purified gas (9.1% CO_2) b/	-	1440	-
Composition of raw gas, percent:			
H_2S	1.2	1.6	-
CO_2	23.1	32.1	3.5
Illuminants	-	0.7	-
CO	29.1	12.1	68.0
O_2	0.0	0.2	0.0
H_2	44.2	37.5	28.0
CH_4	0.8	14.5	0.0
N_2	1.6	1.3	0.5
	100.0	100.0	100.0
Specific gravity of dry gas	-	0.753	0.735
Calorific value of dry gas, B.t.u. per cubic foot b/	253	333	311
Composition of purified gas, percent:			
CO_2	0.0	9.1	0.0
Illuminants	0.0	0.6	0.0
CO	38.4	16.7	70.5
O_2	0.0	0.2	0.0
H_2	58.4	52.3	29.0
CH_4	1.1	20.0	0.0
N_2	2.1	1.1	0.5
	100.0	100.0	100.0
Specific gravity of purified dry gas	0.438	0.477	0.707
Calorific value of dry purified gas, B.t.u. per cubic foot b/	314	438	322

a/ The figures in this column are based upon actual operating results over a period of one month in early 1945. It was stated that the amounts of steam and solid fuel used were excessive during this period because of interruptions due to the war. Other reported results indicate that the fuel and steam used might be 75 to 85 pounds of 7,500 to 8,000 B.t.u. coal and about 80 pounds of total steam per 1,000 cubic feet of purified gas made.

b/ Measured at 60° F. and 30 inches Hg.

c/ This unit of comparison is chosen because 300,000 B.t.u. represents the heat of combustion of 1,000 cubic feet of water gas measured at 60° F. and 30 inches Hg.

d/ The amount of steam used will vary with the rank and reactivity of the fuel used; at the Leuna plant an appreciably smaller amount of steam was used.

e/ The internal diameter of the generator at the tuyeres was 9.84 feet.

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5. In the Winkler and Lurgi processes, the reactivity of the fuel employed is an important factor. These processes are adapted for use in gasifying fuels at temperatures below their ash-softening points, and therefore a highly reactive fuel is desired and in some cases may be essential.

6. In the Lurgi process the methane content of the gas increases with pressure; at 20 atmospheres pressure and with a reactive fuel, operating at 1,000° C. in the hot zone, the methane content of the gas is substantially as shown in table 4. Other factors remaining the same, the use of appreciably higher temperatures causes a reduction of the methane content. The methane produced in this process is formed at temperatures below that prevailing in the hot zone and in the upper portion of the fuel bed. The temperature in the hot zone is kept below the ash-softening temperature. Temperatures favorable to the formation of methane have been discussed.

<div align="center">APPENDIX</div>

<div align="center">Manufacture of City Gas in Conjunction With the Production of Synthetic
Liquid Hydrocarbons. (Plant Under Construction at Leipzig.)</div>

At Leipzig, Germany, city gas was manufactured by standard procedures, and both coke-oven gas and water gas were produced. However, during the late stage of World War II, plans were made for producing some synthetic liquid fuel and wax at Leipzig in conjunction with the manufacture of city gas, and the equipment for accomplishing this was about 75 percent constructed by April 1945.

The plan was to pass a portion of each of the gases (water gas and oven gas) through Fischer-Tropsch converters, wherein CO and H_2 would react catalytically to form hydrocarbons, remove the liquid hydrocarbons thus formed, and blend the residue gas from the converters with the remainder of the manufactured gas for city distribution. Although this plant was not in operation at the time of the author's visit, the results that were anticipated, based upon experience in the operation of such converters elsewhere in Germany, are indicated in table 5.

An analysis of the data shown in table 5 indicates that 1,000 cubic feet of synthesis gas (column 3) would produce 500 cubic feet of residue gas (column 4), which later would have a calorific value of substantially 450 B.t.u. per cubic foot, which is an increase of 35.6 percent. In forming this residue, gas hydrocarbons and water also are formed, which do not appear in the gas analysis. Calculations show that for each 1,000 cubic feet of synthesis gas converted as shown in table 5, 4.50 pounds of carbon and 1.63 pounds of hydrogen are removed from the system (from the gas) and presumably form hydrocarbons and water by the Fischer-Tropsch reactions. From these figures, it can be approximated that the amount of motor fuel and some higher molecular-weight hydrocarbons formed would be about 4.85 pounds per 1,000 cubic feet of synthesis gas treated. Thus, a gas plant producing 14,694,000 cubic feet of combined water gas and oven gas (as in columns 1 and 2) per day, with a calorific value of 387 B.t.u. per cubic foot, would yield, according to table 5, 10,602,000 cubic feet of city gas having a calorific value of substantially 426 B.t.u. per cubic foot and hydrocarbon byproducts (chiefly motor fuel and wax) amounting to about 39,700 pounds per day.
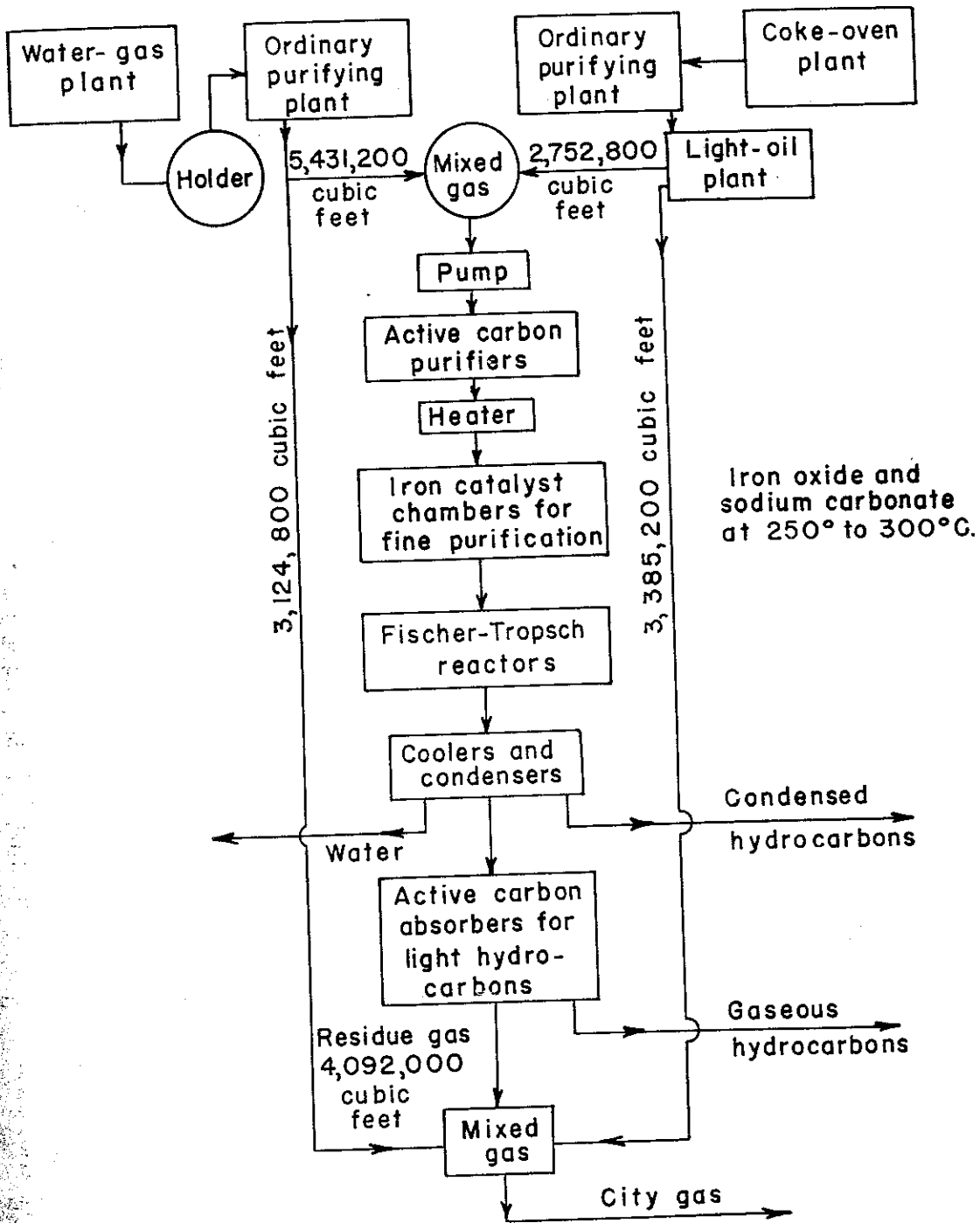
Figure 12.- Diagram of the flow of gases through the conversion and gas-treating units of a Fischer-Tropsch plant making city gas.

TABLE 5. - Data relating to the production of city gas and liquid fuel from oven gas and water gas in Fischer-Tropsch converters

	1	2	3	4	5
			Mixed gas to converters		
	Oven gas	Water gas	(synthesis gas)	Residue gas	City gas
Oven gas............	-	-	2,752,800	-	3,385,200
Water gas..........	-	-	5,431,200	-	3,124,800
Residue gas........	-	-	-	-	4,092,000
Volumes, cu.ft. per day..........	6,138,000	8,556,000	8,184,000	4,092,000	10,602,000
Composition of the gases:					
CO_2............	2.4	5.0	4.1	8.1	5.4
Illuminants....	1.2	-	0.4	1.0	0.8
O_2............	0.4	-	0.1	-	0.1
CO............	5.7	38.0	27.2	21.3	21.2
H_2............	59.0	52.0	54.3	37.5	48.6
CH_4...........	27.8	0.3	9.6	23.6	18.1
N_2............	3.5	4.7	4.3	8.5	5.8
	100.0	100.0	100.0	100.0	100.0
Specific gravity..	-	-	0.4640	0.5805	0.49
Calorific value, B.t.u. per cu.ft. (dry gas)........	516	294	368.7	449.9	425.8
B.t.u. per cu.ft. sat. at 60° F. ...	507	289	361.3	442.1	418.4

It appears that in the combined operations described, not only would the daily output of gas in cubic feet be less than the total water gas and oven gas made, but, also, the heating value of the total city gas produced would be approximately 79.6 percent of that of the latter gases. In other words, in order to produce enriched gas and liquid hydrocarbons on a basis indicated by the data presented in table 5, it would be necessary, for the daily production of a unit number of therms in the city gas, to increase the gas-generating capacity appreciably above that required in making a similar city gas by mixing water gas and oven gas. The cost of this additional gas-making equipment plus that of the Fischer-Tropsch converters will occasion an increase in the cost per therm of city gas. The process can be economical when the increased costs are more than compensated by the value of the wax and the liquid and gaseous hydrocarbons produced. It would be most economical to employ this combination process when the cost of mixed water gas and oven gas is low and the prices of motor fuel, wax, and gas enricher are high.

Description of plant and proposed operating procedure

Figure 12 shows the flow of gases through the conversion and gas-treating units of a Fischer-Tropsch plant used in making city gas. The quantities of raw materials to be used and the conversions expected are those shown in table 5. A water-gas plant supplies water gas, and coke ovens supply the oven gas.

The mixed gas in the quantities indicated is to be compressed to somewhat more than three atmospheres pressure and then passed through activated carbon for removal of remaining traces of H_2S and gum-forming compounds and other impurities. For this purpose, 11,000 pounds of activated carbon will be used, distributed equally in three purifiers, which latter are steel vessels 7 feet in diameter and a little more than 10 feet high. These units are not to be operated in series; when one of them is in use treating the gas, one will be subjected to a steaming operation for revivification of the carbon, and the other will be under treatment for cooling the carbon. In this manner the operation will be conducted in 40-minute cycles; that is, each purifier will be used for treating gas 40 minutes, steamed 40 minutes, and cooled for a like period. Actually only one-third of the 11,000 pounds of carbon will be treating gas at any one time. The optimum temperature of the carbon while "on stream" (treating gas) is said to be 75° to 85° F., whereas the maximum allowable temperature during reactivation is 335° to 355° F., the desired temperature being 300° to 320° F. The cooling operation will be accomplished by circulating water-cooled residual gas through the steamed carbon bed.

Computations from the foregoing show that the total carbon to be used in the purifying boxes amounts to 1,344 pounds per million cubic feet of gas to be treated daily. Furthermore, since only one of three chambers will be "on stream" at any one time, all of the 8,184,000 cubic feet of mixed gas (synthesis gas) will pass daily through a purifier 7 feet in diameter; that is equivalent to a mean linear gas velocity of 0.69 foot per second at 80° F. and 39.5 pounds gage pressure, without allowing for space occupied by the carbon. The true linear velocity will approximate 1.65 feet per second. The carbon has a bulk density of 21.8 to 23.7 pounds per cubic foot and is made from brown coal. The pressure of the gas passing through the carbon bed, it is said, will decrease about 7.75 pounds; this pressure drop seems to be too high for the bed depth.

As shown in figure 12 the gas from the activated-carbon purifiers will pass through iron-oxide catalysts for final purification. It appears that the carbon does not remove all of the organic sulfur from the gas and that, in order to prevent rapid deterioration of the catalyst to be used in the converters, additional purification is necessary. For this purpose, a catalyst comprising iron oxide and sodium carbonate, confined in six steel purifiers, will be used. These purifiers are cylindrical, approximately 8 feet in diameter and 8 feet high, and each one has a capacity for confining 353 cubic feet of the iron catalyst. The gas supply to these purifiers, will be divided into two streams, so that the gas will not pass serially through all six of the boxes. Any box in the system can be shut off for replacement of the catalyst without interrupting operations. Means are provided whereby the gas will be so preheated before entering the purifiers that a "working temperature" in the catalyst mass will be 480° to 570° F. Under these conditions organic sulfur is converted to hydrogen sulfide, which, in turn, is oxidized and forms sodium sulfate by reaction with the sodium carbonate initially present in the catalyst. A small amount of O_2 must be present in the gas for the latter reactions to occur; it is to be added in amounts necessary when not already present. The loss in pressure occasioned by the resistance of the catalyst to passage of gas in traversing this purification system will be approximately 9.67 pounds. The catalyst used is granular.

After the latter purification, frequently designated "fine purification," the gas is to be passed directly to the Fischer-Tropsch converters (reactors) for the synthesis of hydrocarbons. These reactors, of which there are 12, are of the standard variety used in Germany and are 16 feet long, 9 feet high, and 6 feet wide. Each reactor has a capacity for confining 353 cubic feet of catalyst. It was the declared intention to use the "cobalt catalyst" having a density of about 22 pounds per cubic foot. The reactors were to be internally water-cooled by tubes imbedded in the catalyst mass. The 12 reactors were arranged in groups of 3, each group having a common overhead steam accumulator. The connections for the supply of synthesis gas were such that the gas would flow through each of the reactors in parallel, not in series. The water tubes were so connected in the system that the water condensate from the gas works would flow into the lower tubes, and then, by virtue of heat of reaction evolved in the catalyst bed, it would flow upward through the upper tubes to the overhead accumulator.

In operation of the reactors, the purified gas was to be supplied at about 23.2 pounds gage pressure, and the temperature in the catalyst mass was to be maintained at $365°$ to $392°$ F. Temperature in the catalyst bed is controlled by regulating the pressure in the accumulator and cooling system; gage pressures corresponding to $365°$ and $392°$ F. are approximately 149 and 211 pounds per square inch. The gases, upon reaction in the catalyst bed, are expected to yield approximately 550 tons of readily condensable hydrocarbon products per month, divided as follows: One-third benzine (light oil), one-third medium oil, and one-third wax. The anticipated yield was also reported as 100 grams of condensable products boiling at a higher temperature than the C_4 hydrocarbons per normal cubic meter of gas; this is equivalent to 5.92 pounds per 1,000 cubic feet of dry gas measured at $60°$ F. and 30 inches Hg. pressure. On this basis, the daily yield at rated capacity, as indicated in table 5, would be 8,184 x 5.92, or 48,449 pounds, equivalent to 24.2245 x 30, or 726.7 tons per month. The latter figure is higher than that given above (550 tons per month), indicating operations would not be continuously at capacity; but it is also higher than the yield computed by the author and given in the foregoing at approximately 4.85 pounds of total hydrocarbons removed from the system per 1,000 cubic feet of synthesis gas, which amounts to approximately 39,692 pounds per day or 595.38 tons per month. It appears reasonable to expect a yield of hydrocarbons having more than 4 carbon atoms per molecule amounting to about 550 tons per month with continuous operation of the plant.

The drop in pressure in the gas stream, between inlet and outlet of the reactors, will be about 9.67 pounds per square inch.

After the reactions have occurred in the reactors, the hot exit gases will pass into a common header, which leads to a cooling and water-scrubbing system adapted to cool the stream containing the reaction products by direct contact with water. The scrubbing system comprises 2 packed towers 30 feet high and about 4 feet in diameter, each confining 6 separate beds of Raschig rings 2-1/2 feet thick spaced 18 inches apart. The drop in pressure of the gas stream when it passes through the scrubbers will be about 0.97 pound. Separators are so arranged with reference to the scrubbers that the major portion of the readily condensable hydrocarbons will separate from the gas and be collected there.

The cooled gas stream will then be subjected to treatment with activated carbon (absorbent carbon), somewhat as described for purification, for removal and recovery chiefly of ethane, ethylene, propane, propylene, butanes, butylene, and pentanes. The residue gas, stripped of these hydrocarbons, will then be mixed with the excess water gas and oven gas as shown in figure 12.