From the operating data obtained from the above described test runs, plans for indicated modifications in the apparatus were drawn up, and rebuilding started early in 1950. This work was completed, and further test work started in June.

High-Pressure Gasification

During the fiscal year 1950, a high-pressure-gasification pilot plant was designed for the Morgantown, W. Va., station. Construction of the unit is well under way, and test work will be started in the fall of 1950. The plant is to operate at 450 p.s.i.g. and process 500 pounds of coal, 4,000 cubic feet of oxygen, and 400 pounds of steam per hour to generate 18,000 cubic feet per hour of carbon monoxide and hydrogen.

The pressure vessels have been furnished under a cooperative agreement with the Babcock and Wilcox Co. A novel feature of the pressurized fluidized feeder is a recycle compressor to recycle gas at 600 p.s.i.g. and 5,000 std. cu. ft. per min. This machine was developed in cooperation with the Sawyer-Bailey Corp.

Purification Pilot Plant

Figure 15 is a view of the gas-purification pilot plant. It includes an absorber and reactivator for the removal of hydrogen sulfide, iron oxide towers, activated carbon drums, and a reactor for the catalytic conversion of organic sulfur compounds.

The pilot plant was originally designed for a gas flow of 500 cubic feet per hour at a pressure of 6 p.s.i.g. The hydrogen sulfide removal equipment and the activated carbon drums have been modified, however, to permit operation at 300 p.s.i.g.

The selectivity of triethanolamine for hydrogen sulfide in the presence of carbon dioxide is being studied at present. The gas used in these runs is inert gas containing about 14 percent carbon dioxide to which hydrogen sulfide is added.

Laboratory-Scale Experimentation

Development of the laboratory-scale down-draft type, atmospheric pilot unit to precision with automatic controls allowed the testing of various types of fuels for their utility in making synthesis gas on commercial scale. Gasifying up to 55 pounds of finely powdered coal in down-draft entrainment in oxygen and superheated steam, a high-quality low-CO_2 synthesis gas up to 1,200 cubic feet per hour can be produced, continuously, for any length of time chosen. The process is easily controlled; the gasification is not interrupted by slagging of the ash, and the results, as judged by material and heat balances, are reproducible. More than 60 gasification runs have been carried out to date.

Substitution of a pneumatic coal-feeding system (fig. 16) for the former Syntron feeder permitted the charging of coal into the generator at a more constant rate and a considerably increased throughput. These, and very thorough mixing with oxygen prior to injection into the generator, resulted in substantial improvements in the quality of the synthesis gas produced, in the percent of coal gasified per pass, and in the thermal efficiency of the process.

A self-explanatory flow diagram (fig. 17) shows the silicon-carbide lined 6-inch-diameter generator unit, 7 feet in length, in which practically any type of coal (regardless of its ash or sulfur content) pulverized so that 70, 80, or 90 percent passes a 200-mesh screen may be gasified. The same flow sheet shows also the synthesis-gas-purification train and the accessory units. Two Kemp low-pressure industrial burners installed in the water-cooled generator head, using premixed natural gas and air, are used to preheat the generator prior to each run to temperatures ranging from 2,400° F. on the top to 1,600° F. at the bottom.

Each run is started by shutting off the preheat burners and charging the powdered coal, carried by the oxygen into the generator head at a velocity of about 120 feet per second, with or without steam in addition to that formed from the moisture in the coal. Gasification of the coal takes place in entrainment (suspension) in a turbulent atmosphere, and the extremely fine carbonaceous residue plus fly ash are carried along by the raw synthesis gas into the subsequent dust-recovery units. Figures 18 and 19 show the external appearance of these units located on two floors below each other and the control board on the upper floor.

In spite of the comparatively small size of the generator, the heat losses were reduced to about 6 percent when coal was charged at a rate of 50 pounds per hour. This has permitted thermodynamic calculation of the operating results, such as composition of the gas made, oxygen requirement per 1,000 cubic feet of synthesis gas, etc., under assumed negligible heat-loss conditions as obtaining in gasification on commercial scale. Calculations have also been made of the percent of carbon in coal gasified and other operating results under thermal-balance conditions, upon the assumption of charging superheated steam at various rates or introducing oxygen at various ratios to coal gasified.

Thus, it was found, for example, that if the 5.7 percent heat loss obtained in a given run were eliminated [Run No. 46: Sewickley coal gasified; coal feed-rate: 44.6 pounds per hour; oxygen to coal ratio: 0.624 and steam to coal ratio: 0.023 pound per pound of dry, ash-free coal. This run was made without steam, except that originating from the moisture in coal. All these are fixed, and the percent of carbon in coal gasified (54.9 percent) was assumed to remain constant.], the percent CO_2 in the gas would drop from 7.1 to 2.7, the volume-ratio of H_2/CO would sligtly change from 0.63 to 0.65, the outlet temperature of the make-gas would increase from 1,820° to 2,800° F., the oxygen requirement would decrease slightly from 354 to 325 cubic feet per 1,000 cubic feet of $CO + H_2$, and the yield of synthesis gas would increase from 20.9 to 22.7 cubic feet of $CO + H_2$ per pound of dry, ash-free coal. However, upon increasing the steam to dry, ash-free coal weight-ratio from 0.023 to 1.023 (assuming the addition of 1 pound of steam per pound of dry, ash-free coal, at a temperature of 2,100° F.) under thermal balance conditions, the CO_2 content would go up to 18.0 percent, and the H_2/CO ratio would increase to 1.54. The outlet temperature of the make-gas would drop back to 1,800° F., the oxygen requirement would decrease further to 281 cubic feet per 1,000 cubic feet of $CO + H_2$, the H_2 yield would increase to 26.2 cubic feet per pound of dry, ash-free coal, and 61.7 percent of the carbon in the coal would gasify.

The silicon-carbide lining of the generator was found to have a limited life under the severe conditions to which it is exposed, such as repeated heating and cooling, abrasion, effects of slagging coal ash and strongly oxidizing atmospheres at the top. The upper part of the lining must, therefore, be replaced after a period equivalent to about 100 days of continuous use.

The carbonaceous residue, containing 25 to 30 percent of ash, can be recycled for a second pass through the generator, either alone or in admixture with fresh coal. However, owing to its extremely fine particle size (50 percent less than 7.5 microns) and highly fluffy consistency (bulk density: 2.0 to 2.5 pounds per cubic foot), the residue might find industrial utilization for certain purposes at a lower cost than carbon black. Electron micrographs (fig. 20) revealed a very close similarity to commercial carbon blacks. The carbonaceous residue can also be burned in standard equipment, using powdered coal for underfiring boilers.

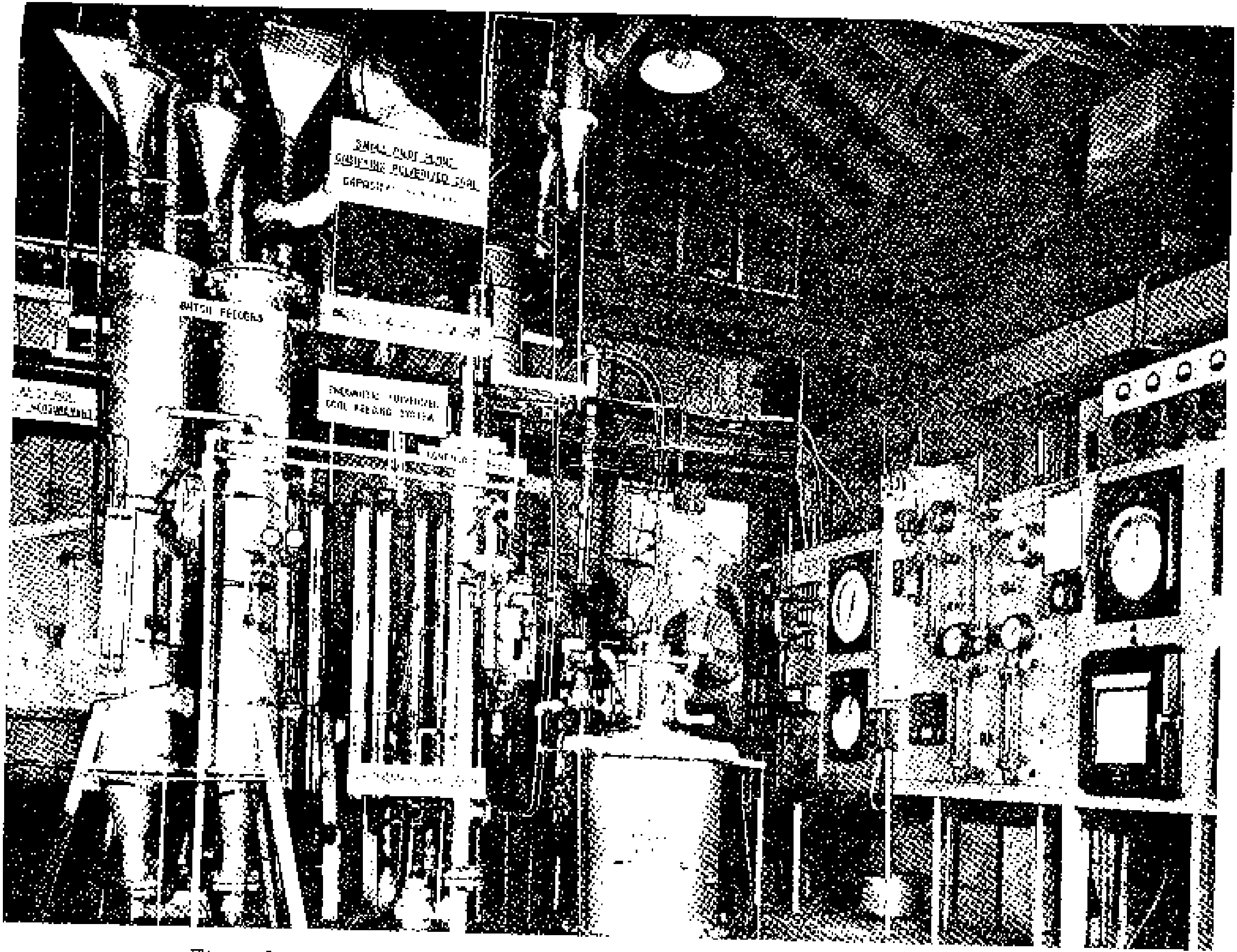

Figure 18. - Laboratory-scale pilot unit (upper floor) for powdered-fuel gasification.

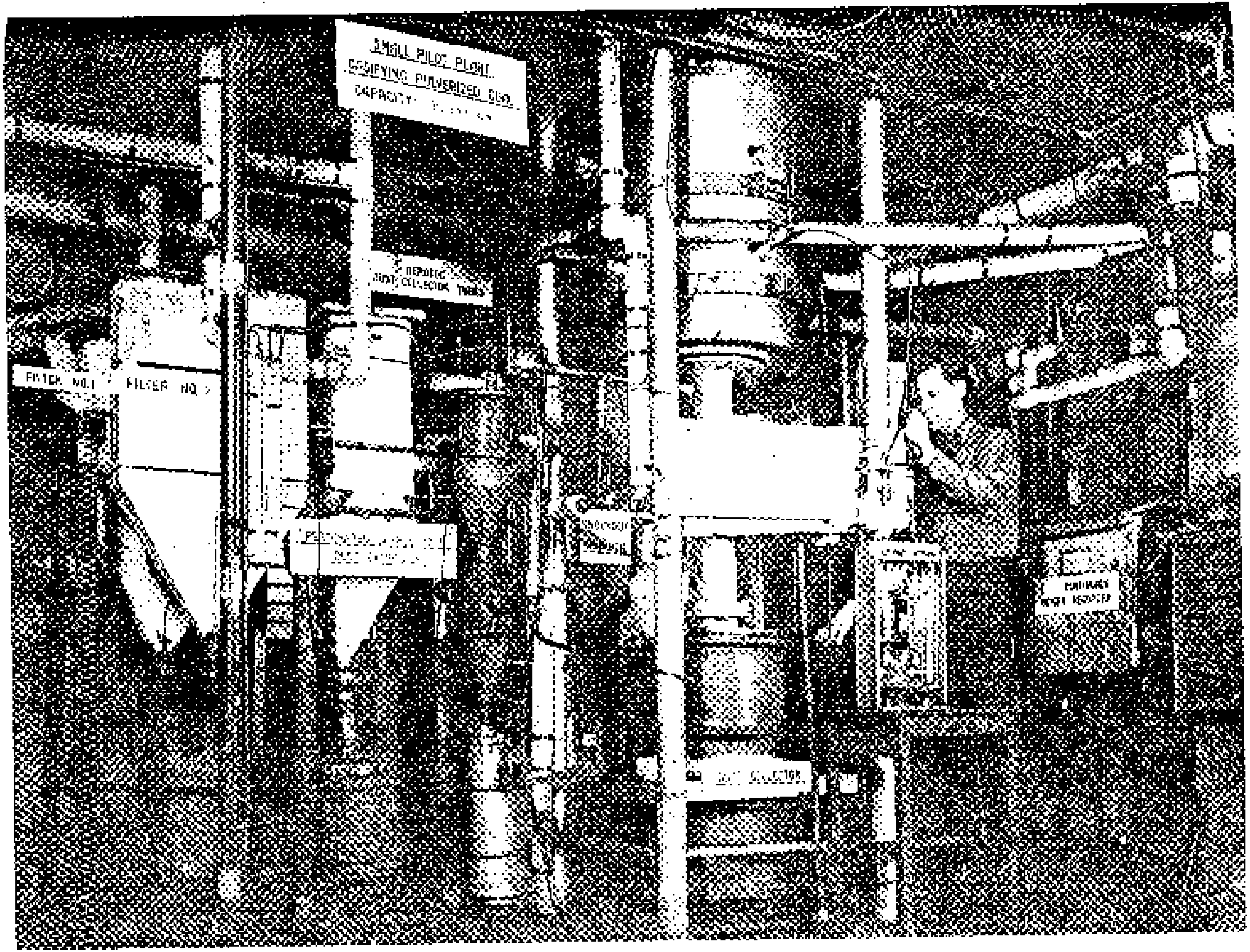

Figure 19. - Laboratory-scale pilot unit (lower floor) for powdered-fuel gasification.

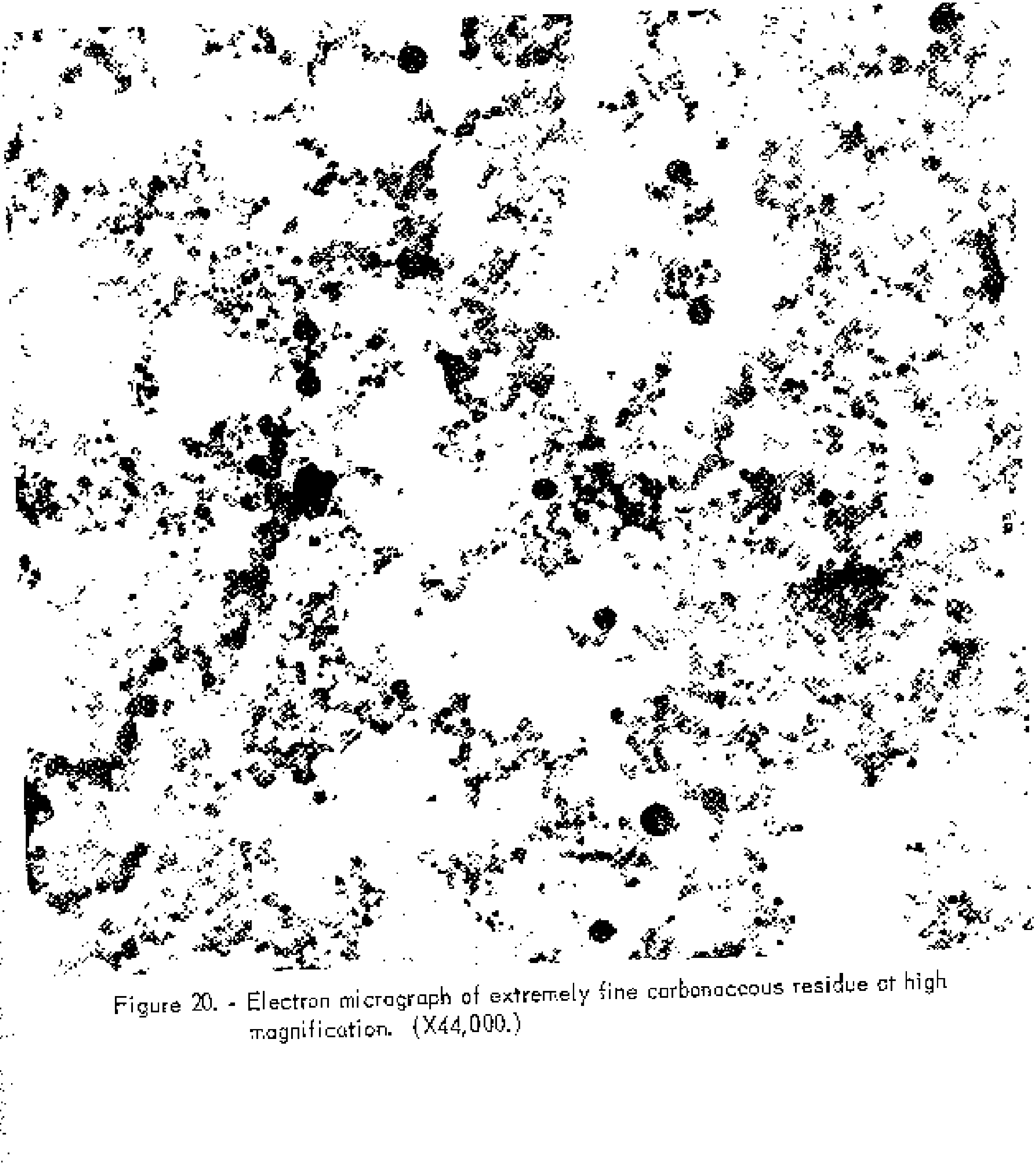

Figure 20. - Electron micrograph of extremely fine carbonaceous residue at high magnification. (X44,000.)

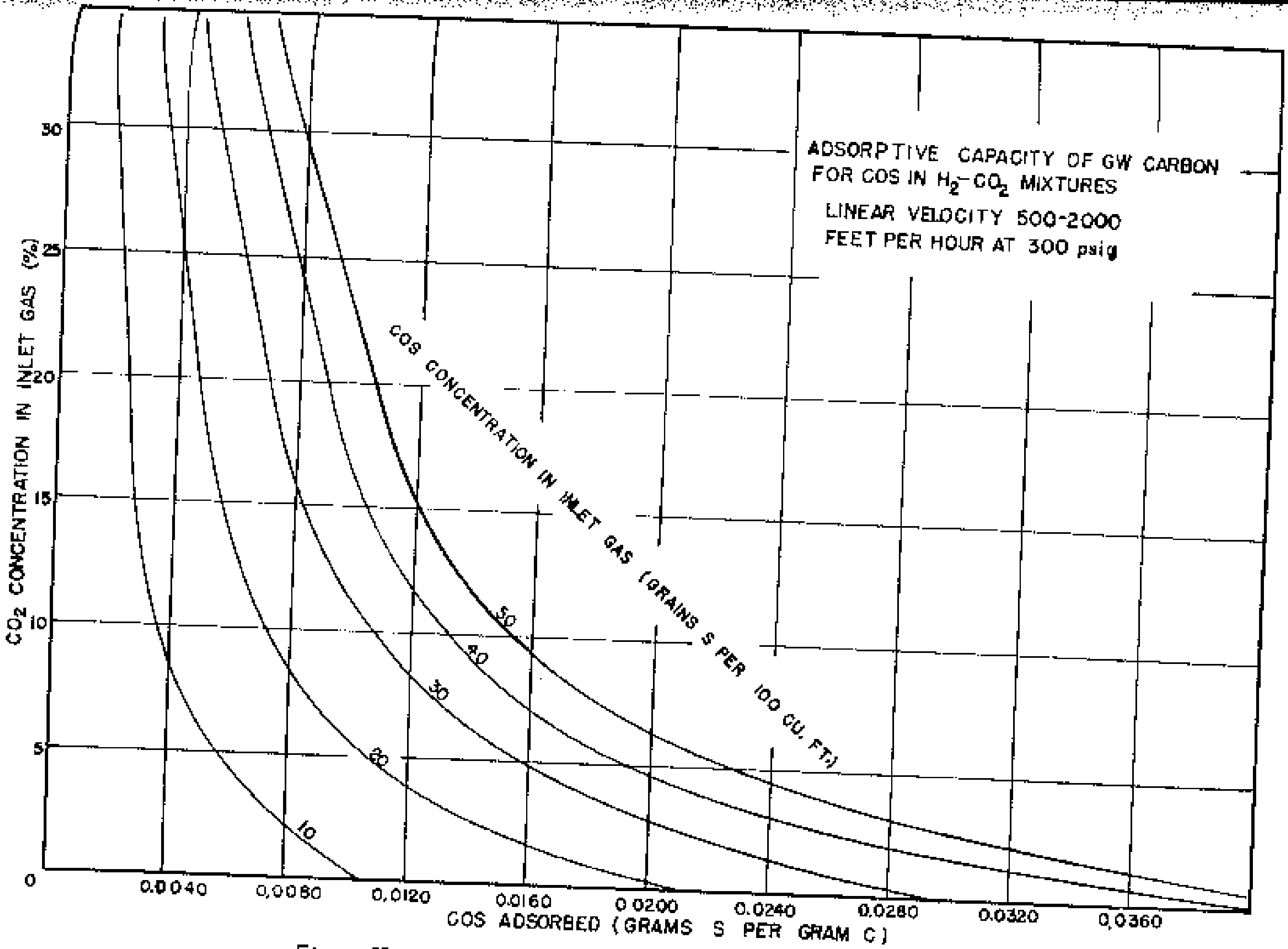

Figure 21. - Adsorptive capacity of GW carbon for COS in H_2-CO_2 mixtures.

Production of Synthesis Gas

Gas Treating and Testing

Sulfur analyses on the gas made in the 50-pound and 500-pound gasifiers indicated that the organic sulfur concentration in the gas is not necessarily proportional to the sulfur content of the coal but is greatly affected by the steam:coal ratio. Other conditions remaining unchanged, increasing the steam:coal ratio greatly decreased the organic sulfur concentration in the gas. Gas made from Sewickley bituminous coal having a sulfur content of 2.4 percent contained approximately 30 grains of sulfur as organic sulfur per 100 cubic feet when steam:coal ratios of about 0.40 were used. Using the same rank of coal having a slightly higher sulfur content of 2.9 percent and steam:coal ratios of 2.0 to 2.7, the organic sulfur content of the make-gas was considerably lower, ranging from 11 to 14 grains of sulfur per 100 cubic feet.

No thiophene sulfur was found in the gas from either gasifier. An experiment in which hydrated lime was added to the coal feed to the small gasifier showed that the addition of 0.038 pound of lime per pound of coal lowered the organic sulfur content of the gas, but had no effect on the hydrogen sulfide. Doubling this ratio of lime to coal further reduced the concentration of organic sulfur and reduced the concentration of hydrogen sulfide in the gas.

Development of analytical methods continued. A turbidimetric method for determining naphthalene in gas using the spectrophotometer and a colorimetric method for nitric oxide were developed. Further investigation of the isatin method for determining thiophene showed that unsaturated hydrocarbons, such as ethylene and propylene, which are known to vitiate the test, do not effect the accuracy of the method if they are present in the gas in amounts less than 3 percent by volume.

An alkalized iron catalyst containing 26 percent sodium carbonate successfully lowered the organic sulfur content of a simulated synthesis gas to less than 0.1 grain of sulfur per 100 cubic feet until 65 percent of the carbonate has been converted to sodium sulfate. Somewhat higher conversion of the carbonate to the sulfate (78 percent) was obtained whenever 100 percent soda ash was used. Experiments with these alkali catalysts were run at 250° to 300° C. and 300 p.s.i.g., employing linear velocities up to 750 feet per hour at 20 atmospheres and space velocities up to 7,000 std. cu. ft. per hr. per cu. ft.

Investigation of a copper-chromium-vanadium catalyst for removing both hydrogen sulfide and organic sulfur from gas was continued. The catalyst, after absorbing about 10 percent of its weight in sulfur, is revivified with air and steam. At a temperature of 450° C. the catalyst reduces the organic sulfur content of the gas to less than 0.01 grain of sulfur per 100 cubic feet while removing 99 percent of the hydrogen sulfide. At a lower temperature of 300° C. the outlet gas contains less than 0.01 grain of sulfur as hydrogen sulfide per 100 cubic feet, but the organic sulfur conversion is somewhat less than that at 450° C., averaging 98.5 percent. Ultrafine purification should be possible by operating two beds in series, the first at a temperature of 450° C. and the second at 300° C.

Numerous tests were made to study the removal of carbon oxysulfide by means of activated carbon at 300 p.s.i.g. Figure 21 graphically presents data obtained from tests using a relatively inexpensive carbon.

The presence of carbon dioxide in the gas has a marked effect on the capacity of the activated carbon for carbon oxysulfide adsorption.

By combining a specially developed colorimetric method for hydrogen sulfide[79] in gas, with a method whereby organic sulfur compounds in gas are converted to hydrogen sulfide, it is possible to determine the organic content of purified gas in 1 hour.

Previous methods, whereby the gas was burned and sulfur oxides scrubbed from the combustion products, with subsequent gravimetric determination of sulfate, required as much as 48 hours. This reduction in time is important, not only in the laboratory, but especially in commercial plants where very expensive liquid fuels catalysts can be ruined in a few hours if sulfur in the gas becomes excessive.

Vortex Combustion Studies for Powdered-Coal Gasification

As the manufacture of synthetic liquid fuels by the Fischer-Tropsch process requires approximately 30,000 standard cubic feet of hydrogen and carbon monoxide for each barrel of product, any commercial application of this process must be predicated on an abundant source material for the production of synthesis gas. The development of a process which would convert any class of coal into a satisfactory synthesis gas mixture is, therefore, of obvious importance.

One of the most promising methods appears to be the gasification of pulverized coal in suspension in a stream of oxygen and steam, the flow diagram for which is shown in figure 22. Favorable characteristics inherent in such a process appear to be (1) relatively high specific rates of gasification due to the high specific surface of the fuel; (2) the advantages of a continuous process in ease of control and the need of a small plant size for large throughputs; and (3) the use of any class of coal. Suspension gasification of pulverized coal may be classified, in general, in two ways, depending upon the path of the coal particle with respect to the gas: (a) The coal may flow with one or both of the reacting gases; (b) the coal may have relative motion with respect to the reacting gases, thereby making use of the fact that the speed of the diffusion-controlled phases of the gasification reactions is increased. It is this latter type of process which is currently being studied in a reactor of the vortex type in Bureau laboratories.

Preliminary experiments in the vortex reactor (fig. 23) have now been completed. In the absence of methane in the product gas, the chemical reactions in a mixture of carbon, oxygen, and steam at elevated temperatures are:

$$C + O_2 \longrightarrow CO_2 \qquad (1)$$

$$C + H_2O \longrightarrow CO + H_2 \qquad (2)$$

$$C + 2H_2O \longrightarrow CO_2 + 2H_2 \qquad (3)$$

$$C + CO_2 \longrightarrow 2CO \qquad (4)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (5)$$

At atmospheric pressure, reaction (1) is assumed to go to completion and the dissociation of steam and carbon dioxide is assumed to be negligible. In the vortex reactor, reaction (4) was found to take place so slowly as not to influence the final product-gas composition. Reaction (5), the water-gas shift reaction, is the only remaining independent equation, since equation (5) equals equation (3) minus equation (2).

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[79] Sands, A. E., Grafius, M. A., Wainwright, H. W., and Wilson, M. W., The Determination of Low Concentrations of Hydrogen Sulfide in Gas by the Methylene Blue Method: Bureau of Mines Rept. of Investigations 4547, 1949, 19 pp.

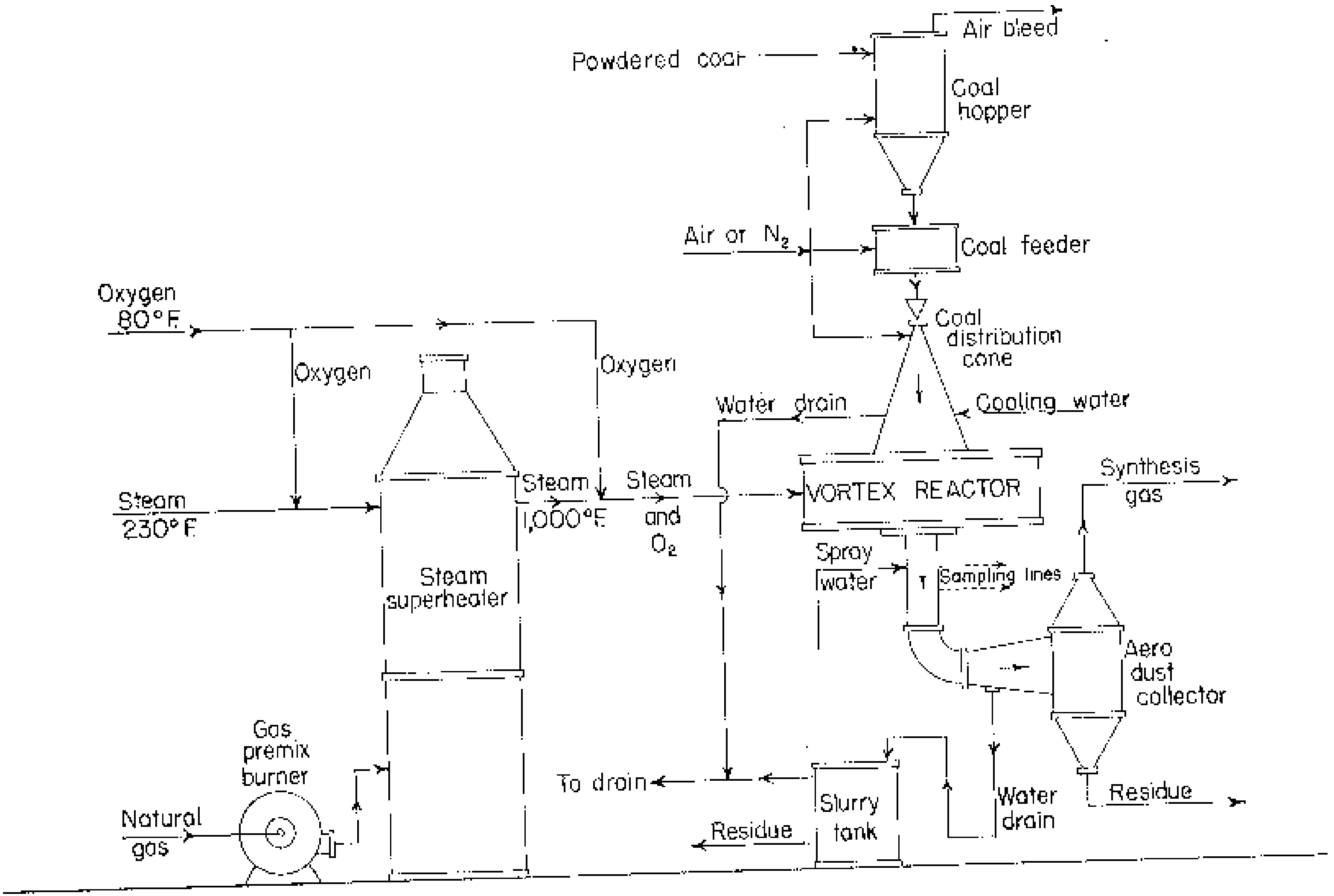

Figure 22. - Flow sheet of vortex gasifier.

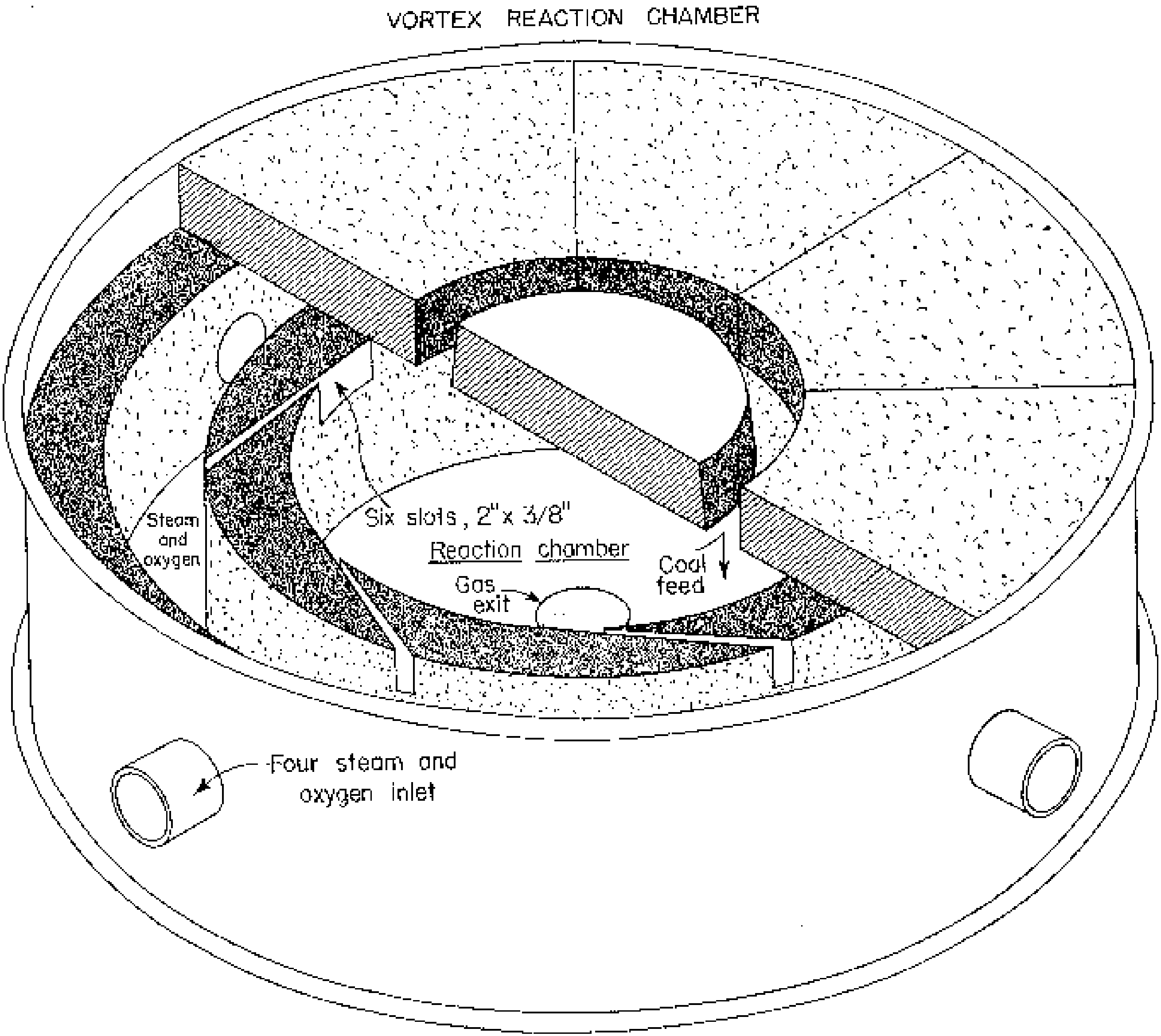

Figure 23. - Vortex reaction chamber.

The percent of carbon dioxide in the dry product gas, the percent steam decomposition, and the ratio of hydrogen to carbon monoxide were calculated as functions of the heat lost by radiation, the preheating of the steam, the oxygen-to-coal ratio, the steam-to-coal ratio, and the percent carbon gasified. These tests confirm the assumption that from the knowledge of the above variables, the approximate composition of the gas produced can be predicted for this reactor. In the preliminary experiments, the carbon conversions were low, and the resulting product gas had a high carbon dioxide content. In order for this reactor to be commercially feasible, the carbon conversion must be increased. For a given set of feed conditions, any means of increasing the carbon conversion will improve the quality of the product gas.

Oxygen Production by Multistage Fractional Permeation

An important factor in the cost of coal gasification is the cost of oxygen used in the process. At present, oxygen is produced commercially almost exclusively by the Linde process. The fact that many organic membranes are appreciably more permeable to oxygen than they are to nitrogen is the basis for experimental work on a possible process for oxygen production.[80]

The permeabilities of a number of thin organic films toward oxygen and nitrogen have been measured.[81] For an ethyl cellulose film, the studies were extended to include CO_2, A, He, and H_2. The enrichment of a binary gas mixture in a single stage of permeation has been calculated for the extreme cases of perfect mixing and no mixing. Application of these results indicates that the use of a fractional permeation process may be of practical importance in effecting the separation of oxygen from air, helium from natural gas, and hydrogen from coke-oven gas, as examples.

Major improvements in the economy of a permeation process could be made by (1) increasing the magnitude of the film permeabilities or (2) increasing the selectivity of the films toward oxygen. Improvements in (1) would permit a decrease in the area of the film required to achieve a given throughput; this might be achieved by finding more permeable films or by making thinner films. Improvements in (2) would not only decrease the size of the plant required but would also decrease the power requirements necessary for a given oxygen production. Such improvements might be achieved by finding films more selective than rubber latex, or by incorporating into films specific oxygen carriers (possibly cobalt chelate complexes).

An apparatus was assembled to investigate the selective permeability of organic films, and eight different commercial materials were studied (table 13). Natural rubber is outstanding for its high permeability and its selectivity; it is, however, subject to oxidation. Ethyl cellulose and polyethylene are promising. Additional work with ethyl cellulose films and with pure gases showed (table 14) that these films had an O_2/N_2 permeability ratio of about 3. Argon is enriched in almost the same proportion as in oxygen, while carbon dioxide becomes enriched to a much greater extent. For any commercial application, it will probably prove desirable to remove carbon dioxide before or just after the first permeation stage. The removal of argon will be impractical, and it will be enriched along with the oxygen.

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[80] Weller, Sol, Thermo-Osmosis of Gases Through a Membrane: Nature (British), vol. 165, Feb. 4, 1950, pp. 199-200.

[81] Weller, S., and Steiner, W. A., Separation of Gases by Fractional Permeation through Membranes: Jour. Appl. Phys., vol. 21, April 1950, pp. 279-283.

TABLE 13. - Film permeabilities to oxygen and nitrogen at 30° C.

Film	Film thickness, mils	Permeability coefficient[1] Q, cm.^{2}min.$^{-1}$ atm.$^{-1}$ x 10^6		Q_{O_2}/Q_{N_2}
		Q_{O_2}	Q_{N_2}	
Ethyl cellulose[2]	0.7	3.25	1.36	2.4
Polyvinyl chloride-acetate	2.0	1.75	1.17	1.5
Vinyl resin + Buna-N rubber	2.0	.70	.58	1.2
Natural rubber latex[3]	7.3	18.1	8.6	2.1
Polyethylene (Plax)	1.5	2.20	.88	2.5
Polyethylene (Bakelite)	.9	2.10	.79	2.7
Polystyrene	1.0	1.31	.44	3.0
Pesproid 1404	4.3	3.01	1.08	2.8

[1] Permeability coefficient = (film permeability) (film thickness).
[2] Average of 3 determinations.
[3] Average of 2 determinations.

TABLE 14. - Permeabilities of gases through film EC-12

Gas	Permeability (P),[1] mole x 10^6 cm.$^{-2}$min.$^{-1}$ atm.$^{-1}$	P_{gas}/P_{N_2}	
		Pure gas studies	Mass spectrometer
N_2	0.075	(1.0)	(1.0)
O_2	.231	3.1	3.2
CO_2	1.07	14.3	[2]32
A	.176	2.3	3.1

[1] Rate of permeation of gas per unit time per unit film area per unit pressure differential.
[2] A blank determination on normal air gave a high CO_2 value.

Synthesis-Gas Production

The synthetic liquid fuels program of the Bureau of Mines at Bruceton, Pa., requires sizeable quantities of hydrogen and mixtures of hydrogen and carbon monoxide. To obtain these gases for operating the pilot plants and experimental units, two plants using Pittsburgh natural gas as a raw material were designed and constructed. One of these plants produces 99-percent pure hydrogen. By the reaction between natural gas and steam over a suitable catalyst, a mixture of hydrogen and carbon oxides is obtained which is passed over a water-gas shift catalyst. The carbon monoxide is thus converted to carbon dioxide, which is removed by monoethanolamine scrubbing. This type of plant has been described in the literature, and a number of installations are in successful operation. The synthesis-gas plant, while using similar equipment, reacts natural gas, steam, and/or carbon dioxide to prepare mixtures of carbon monoxide and hydrogen suitable for use in the Fischer-Tropsch reaction and represents the first plant of this type using industrial-scale equipment to produce synthesis gas of these specifications.

Initial test runs on this plant[82] covered operation at minimum and maximum design rates of $2H_2$:1CO synthesis gas. Studies were also made on production of $1H_2$:1CO synthesis gas. In addition, selected ratios of high carbon monoxide-content gas were

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[82] Clark, E. L., Kallenberger, R. H., Browne, R. Y., and Phillips, J. R., Synthesis Gas Production - Reaction of Light Hydrocarbons, Steam and Carbon Dioxide in Commercial Equipment: Chem. Eng. Progress, vol. 45, November 1949, pp. 651-654.